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A shell garniture from Gujarat, India in the British Museum

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Summary This garniture – or set of paired and single display items – from the collections at the British Museum comprises a pair of candlesticks, a pair of ewers, a large basin and a bottle. It is made from shaped plaques of the marine gastropod *Turbo marmoratus* L. (green turban shell) with small inserts of two other marine shells, the gastropod *Trochus (Tectus) niloticus* L. (button shell) and the bivalve *Pinctada margaritifera* L. (pearl oyster). Garnitures and individual items of this type were made from the late sixteenth century in Gujarat, western India, to Portuguese order for export to Europe and possibly also for the Jesuit missionary market throughout Asia.

The available literature describes the expected method of construction as being, for the larger items, either shell plaques pinned to a wooden substrate, or a double-walled technique of shell plaques alone. The initial simple visual examination had shown transmitted light visible through the walls of the ewers, candlesticks and all but the very centre of the basin. Thin plaques of mother of pearl shell may be translucent, but a wooden core does not permit light to pass through. To identify the method of construction, X-radiography and X-ray fluorescence analysis were employed. A skeleton of brass bands was found between the inner and outer walls of the vessels. A dense material, possibly a metal plate, was seen at the domed centre of the basin. Other than the body of the bottle, it became evident that all pieces are made of a mosaic of precisely shaped and closely associated small mother of pearl shell plaques held together with pins and an adhesive over a sub-structure of metal bands.

Various phases of repair and intervention were observed and noted. Conservation treatment for display was straightforward; a simple method was developed to reveal the particular qualities of the iridescent shell. Recommendations for care of objects made from shell materials on display and in storage are given.

INTRODUCTION

In October 2005 a garniture of items made from green turban shell was placed on public exhibition at the British Museum. It forms part of a display that addresses issues relating to European trade and discoveries in the seventeenth and eighteenth centuries, as illustrated by the Museum's collection. The garniture, first published and illustrated in 2006, comprises a bottle (OA+ 2642), a basin (OA+ 2644), a pair of candlesticks (OA+ 2643,1–2) and a pair of ewers (OA+ 2645,1–2), Figure 1 [1].

At 15 cm, the green turban shell (*Turbo marmoratus* L.) is the largest of the turban shells belonging to the Turbinidae family. *Turbo marmoratus* occurs in warm waters, particularly around coral reefs in the Indo-Pacific region, in conjunction with other *Turbo* species such as *T. argyrostromus* (silver mouth turban) and *T. petholatus* (tapestry turban). It has long been exploited commercially to provide mother of pearl for making buttons, beads, jewellery and decorative inlay on wooden or lacquered furniture. It has been reported that large quantities of these materials were traded, for example the 100–150 tons of *T. marmoratus* and 400–500 tons of *Trochus niloticus* fished annually from around the Andaman and Nicobar Islands [2]. The spire of *T. marmoratus* is small in relation to its widely expanded body whorl that is dull green with brown blotches. The periostracum (a hard outer covering layer) can be rubbed away to reveal the pearly inner layer. It is significant to note that this modification has obviously been carried out on the green turban shell used in the garniture. It is not the only *Turbo* species which can be modified in this way – the South African turban (*Turbo sarmaticus*) is covered with a thick red periostracum which, when rubbed down, also reveals a nacreous inner layer. Most *Turbo* species show a thick

FIGURE 1. The shell garniture with the basin centre back and the bottle centre front, flanked by the pair of candlesticks and the two ewers

pearly aperture; that of *T. marmoratus* often has a golden appearance, although the iridescent qualities of mother of pearl on any shell result in the presence of very variable colours.

Mother of pearl or nacre is the smooth, shiny, iridescent inner layer of the shell present in some marine and freshwater bivalves and gastropods including oysters, mussels, abalone, topshells and nautilus. Around 95% of the material is composed of thin platelets of aragonite – calcium carbonate ($CaCO_3$) crystals – arranged in parallel lamina (see Figure 4 on page 46 of this *Bulletin*), separated by sheets of an organic matrix composed mainly of proteins and polysaccharides that make up the remaining 5% [3]. Nacre exhibits an interlocked layered 'brick-and-mortar' structure where the bricks are the aragonitic calcium carbonate and the mortar is the organic phase [4, 5]. Nacre is secreted by the epithelial cells of the mantle tissue of these molluscs not only to create a smooth surface to the shell but also as a defence against parasites and detrital particles, hence the process of pearl formation.

The history of the manufacture and collecting of such items as this garniture has been well researched in recent years, thanks to three major international exhibitions and their accompanying catalogues, which have dealt with European contact with Asia and European collecting of the exotic [6–9]. The provenance of the Museum's garniture remains unknown, as are the precise details of its acquisition by the Museum: the registration number has as its prefix 'OA+' for 'Oriental Acquisitions' rather than the standard year of registration. Each piece is inscribed on the underside in ink 'FB', possibly for 'Franks Bequest'. If so, it may suggest that the garniture was acquired by Sir Augustus Wollaston Franks (1826–1897), the influential Keeper of British and Medieval Antiquities (1851–1897), a great collector of the exotic and a renowned benefactor of the Museum.

In summary, the establishment of the Portuguese trading empire throughout Asia from the early sixteenth century brought an unprecedented flow of exotic goods to Europe. Transhipped via Lisbon, such rare materials as tortoiseshell, marine shell, seeds and nuts were highly valued, both in their raw state and as manufactured items made expressly for the European market. Exotic and costly garnitures were commissioned by the Portuguese as magnificent display pieces and were dispatched to Europe as well as being used throughout the Portuguese Empire. Jesuit missionaries also played a significant political and artistic role in the Portuguese settlements throughout India and Asia, and the Church commissioned liturgical furnishings from local craftsmen. There is some conjecture that garnitures such as these may have served as altar sets, but it has not been possible to verify this.

The archaic English term 'the great green turban snail' probably refers to the attributes of this species – its large size, its marbled green outer surface and its resemblance to the eastern headdress [6–10]. Gujarat in western India had a long craft tradition in the use of shell as a decorative inlay and in the construction of smaller items such as bowls, cups and boxes. The form and scale of items commissioned by the Portuguese generally followed European metal prototypes, as in the ewers, but the influence of Chinese porcelain forms and Mamluk metalwork of the 'Veneto-Saracenic' type was also significant, and can be seen in the basin and candlesticks respectively.

EXAMINATION AND CONSTRUCTION

Although there are a number of similar garnitures and numerous individual pieces in European public and private collections, the exact method of construction of these pieces remains uncertain. Smaller items, such as containers in the form of boxes, cups and bowls are usually described as being constructed in a double-walled technique whereby an inner and an outer wall of shell plaques are secured together by pins. Larger items such as basins, ewers and candlesticks are generally described as being made of a thin wooden substrate to which shell plaques are attached on both sides by pins [7; Nos 24–32 pp.118–131, 10; pp. 36–43]. One of the catalogues for the 2000 *Exotica* exhibition [7] illustrates a pair of candlesticks (No. 24) a ewer (No. 26) and a basin (No. 30) similar to those examined in this paper. A number of other large pieces have, however, been described as of double-walled construction [8; Nos 68–69 pp. 162–164].

The initial visual examination had shown transmitted light visible through the walls of the ewers, candlesticks and all but the very centre of the basin. Thin plaques of mother of pearl shell may be translucent, but a wooden core would not permit light to pass through. This raised the questions of how these large items were made and to what they owe their robustness if a void exists between the shell walls. To elucidate the construction of the Museum's set, X-radiography and X-ray fluorescence (XRF) analysis were carried out.

To examine the interior structures, X-radiography was carried out at 75 kV, 5 mA for three minutes. The film used was Kodak Industrex AA/MX in cassettes with lead filters back and front, Figures 2 to 8. The X-radiographs were scanned using an Agfa RadView digitizer with a 50 μm pixel size and a 12-bit resolution, to allow digital enhancement of the images. To emphasize edges and discontinuities, the images were subject to greyscale manipulation and enhanced using an 'unsharp mask' filter. The results show real features that are faintly detectable in the images prior to enhancement. Some of the images are presented as positives – that is where dense areas appear pale, as on the original X-radiographic film – and others are presented as negatives, where the dense areas appear dark; it was found that more features could be clarified by using both modes.

X-radiography revealed an unexpected skeleton of metal bands, approximately one centimetre in width and three to six centimetres apart, between the inner and outer walls. The X-radiographs indicate that each of the metal bands has a soldered join, the density of which suggests it to be a soft solder of tin and/or lead. The bands are perforated by small holes into which some of the pins are secured, but the majority of the pins fix the inner and outer walls directly together.

The metal components were analysed qualitatively by non-destructive XRF spectrometry. The majority of the pins are silver (alloyed with a little copper), as are the collars around the top of the candlestick sockets. The liner to the rim of the bottle is brass (an alloy of copper with zinc). The metal bands providing hidden support inside the shell facings were, by definition, inaccessible for analysis, but a small portion of the edge of one band supporting the footring of one of the ewers protrudes far enough for qualitative analysis. The metal of this band was identified as brass, and because its X-radiographic opacity is comparable to the other structural bands, it is reasonable to suppose that they are also made of brass.

Other than the bottle, it became evident that all the pieces are made of a mosaic of precisely shaped and closely associated small mother of pearl shell plaques held together with pins and an adhesive over a sub-structure of metal bands. It did not prove possible to identify the original adhesive as the only easily sampled areas appear to be repairs. The side of each item intended for view is made up of a delicate pattern of shaped shell pieces, whereas the less visible side, for example the underside of the basin, is mainly composed of larger, rectangular plates. Close inspection of all the X-radiographs shows the two sides superimposed. Fine detail can be observed, but nothing that might be interpreted as a wooden sub-structure.

THE COMPONENTS OF THE GARNITURE

Basin

The basin (OA+ 2644; Figures 2 and 3) has a diameter of 440 mm. The central dome is decorated with geometric and lappet-shaped plaques, while the interior of the basin is composed of shaped plaques forming a radiating petal motif. This radiating pattern of shaped plaques continues to the edge of the basin where it curves upward to meet the outer rim. The curved sides and flared outer rim are made up of rectangular plaques, as is the underneath of the basin. The underneath of the basin is composed of rectangular plaques of *T. marmoratus* shell. Around the outer edge of the rim and similarly at the outer surface of the basin where it curves to meet the rim are inserts of *P. margaritifera* (L.) (pearl oyster) and *Trochus (Tectus) niloticus* L. (button shell). It is possible that these are reused plaques or offcuts, employed to edge the rim and in less visible areas.

X-radiography shows five concentric metal bands inside the walls of the basin, Figure 2. The bowl of the basin appears denser than the rim; where the plaques are thinner, light can be seen through both areas. Although of the same overall thickness as the rest of the bowl, the centre of the domed area is noticeably denser (Figure 3) and does not transmit light. The internal textural pattern of the dome, revealed by X-radiography, cannot easily be identified as wood grain, and its density suggests it may be metal. There is a small hole in the centre of the dome, which may suggest that a device such as a compass might have been used to set out the design, or that the basin was assembled on a lathe. This hole may once have been filled with a small circular shell plaque, known from other basins and the interior of the bases of the ewers studied here.

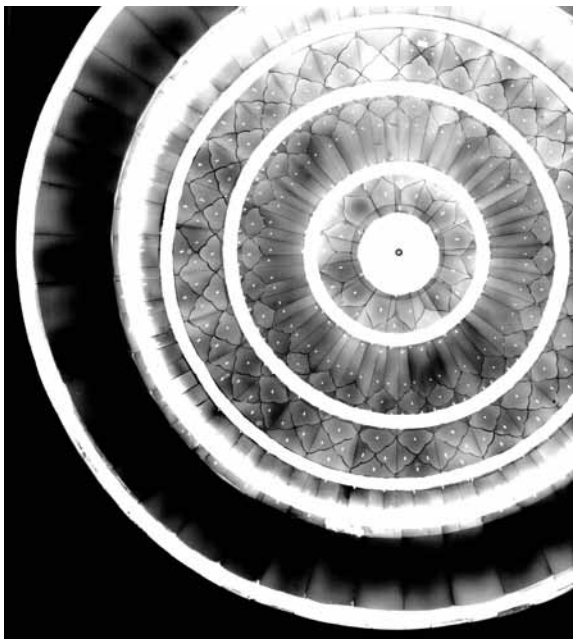

FIGURE 2. X-radiograph (positive image) of the basin, OA+ 2644. The lightest areas are the densest: the concentric rings are metal reinforcing bands and the white spots are silver pins. The shell plaques forming the rim appear darker because they are thinner. The edges of the finely shaped plaques on the front can be seen overlaid on the larger, rectangular plaques on the underside of the bowl

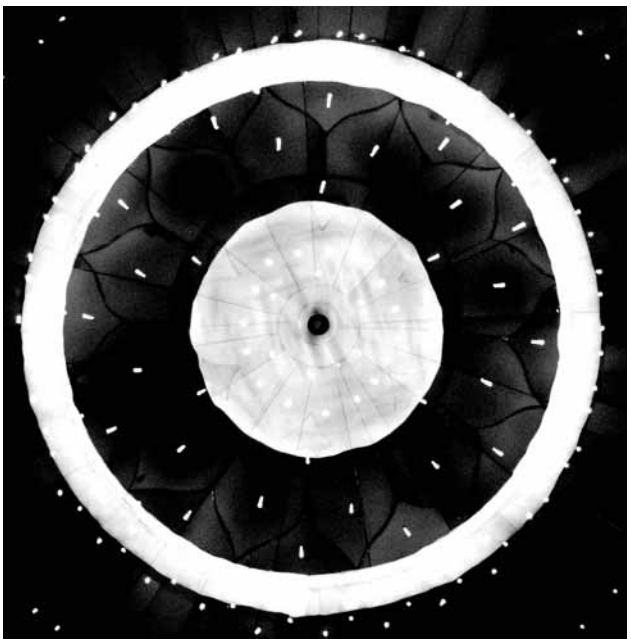

FIGURE 3. Detail of Figure 2, showing the centre of the dome in the middle of the basin framed by the innermost metal band. This dense feature is approximately 4.5 cm in diameter. In this zone, the edges of the plaques appear as grey lines, centreing on the hole (black), and the pins appear as diffuse white dots. There is a smeared texture (light grey) to this area, which gives it a slightly different appearance to the metal band but does not resemble wood grain

FIGURE 4. X-radiograph (negative image) of a ewer. The darkest areas are the densest: note the reinforcing bands. The concave shape just above the rim of the foot is a valve of a *P. margaritifera* shell

There is no evidence of wear on the interior of the basin, although some of the plaques around the outer rim show signs of damage and subsequent repair. There are small rectangular patches to some plaques, perhaps concealing imperfections in the shell. These are very neatly executed and it seems likely they were made before the plaques were built into the basin.

A number of basins were fitted with European mounts of the seventeenth century onwards. These mounts, which are more or less elaborate depending on the patron, tend to be around the rims [7; No. 25 pp. 120–122, 10; No. 13 p. 42]. In the set under examination, an internal brass band is fitted at the junction of the bowl and the rim. This feature would allow the outer rim to be removed from the brass band without compromising or damaging the remainder of the basin. It may perhaps explain how European goldsmiths could remove the outer rim and substitute gold or silver-gilt mounts to the remainder of the basin, or attach mounts over the rim itself.

Ewers

The two ewers (OA+ 2645.1–2; Figure 4) are *c.* 250 mm high; each rises from a pedestal foot and has a curved spout and scrolled handle. The exterior plaques of the body are shaped and arranged in a lozenge pattern above lappets. All the remaining plaques on each ewer are rectangular. One ewer has two parallel lines incised around the bottom rim of the body. The interior plaques of each body are also rectangular, but the plaques forming the bottom of the body are of geometric shape and are arranged in a petal motif around a central disc. The scrolled handles were probably originally fitted with a ball finial, known from other examples. One handle is now fitted with a small replacement piece of shell where a finial may have been, while the other handle has been extensively remodelled with replacement plaques. The body of each ewer has been cut away where the spout has been fitted. Although the ewers are fully functioning pouring vessels, there is no evidence of wear or staining caused by liquid. Underneath the foot of each ewer, a valve of a *P. margaritifera* shell is fitted, which may act as a strengthening device. Each ewer has five metal bands to reinforce the vessel and three further bands inside the foot, Figure 4. The band at the edge of the foot protrudes sufficiently to allow its identification as brass by XRF analysis. Holes in the bands, which are not filled with pins, are noticeable at the rim and base, suggesting later repairs to these vulnerable extremities.

Candlesticks

Each candlestick (OA+ 2643.1–2; Figures 5 and 6) rises to a height of 215 mm from a spreading foot and drum base. The plaques on each drum base are shaped and arranged in a lozenge pattern above lappets, while the remaining plaques are rectangular in form. The bulb-shaped socket is fitted with a silver rim. One particularly fine detail of the candlesticks, which appears original, is the infilling of tiny holes (presumably the result of infestation in the original marine environment) with shell inserts.

FIGURE 5. X-radiograph (negative image) of candlestick OA+ 2643. Note the patchy areas on the base (bottom left) and on the neck just below the candle socket. These appear to be a denser adhesive, perhaps indicative of a repair

FIGURE 6. X-radiograph (negative image) of candlestick OA+ 2644 taken from above showing an area of patchy adhesive on the flared base, similar to that on the other candlestick. The dark circle in the centre is the candle socket, and the dark ring around this is the wall of the base seen from above. Note that the candlestick has been constructed slightly off-centre

The X-radiograph shows the internal brass bands and also reveals a slightly denser uneven feature, perhaps an adhesive layer, in one part of the base of both candlesticks, Figure 5. A similar patchy layer can be seen in Figure 6, just below the candle socket. These patches may indicate repairs.

FIGURE 7. X-radiograph (negative image) of the bottle, OA+ 2642. The pins are very long and the construction appears comparatively crude

FIGURE 8. Detail of the neck from Figure 7, enlarged and enhanced using an 'unsharp mask' filter. The strainer is the not-quite parallel feature across the centre of the neck. There is a decorative brass collar inside the rim of the neck and an internal metal band joining the body of the bottle to the neck concealed beneath a band of shell at the base of the neck

Bottle

The bottle (OA+ 2642; Figures 7 and 8) is 280 mm high and is of a different type of construction to the other elements of the garniture. It is composed of two complete shells of *T. marmoratus* with a funnel-shaped neck and a circular spreading foot of double-walled construction attached by pins, Figure 7. The neck is formed of two sections; the upper, which has a rim of rectangular plaques, fits into the lower, Figure 8. Where the lower section joins the body is a collar comprising bands of petal-shaped plaques, while a strip of rectangular plaques masks the junction between the two shells. The rectangular plaques at the foot rim and where the foot meets the body are incised with two parallel lines. A pierced disc with a foliate pattern, which may act as a strainer, is fixed part way down the neck. This disc blocks any view into the interior of the bottle, but the X-radiograph shows long pins protruding into the cavity. There is an internal metal band at the base of the foot and another where the foot joins the bottle. The same arrangement is seen at the neck, but otherwise the body of the bottle owes its rigidity to the complete shells.

The bottle shows much marine infestation with clusters of bored holes in both the large shells that make up the body of the vessel; mother of pearl plaques shaped in the form of trees, fish or flowers cover some of the worst damage. The bottle is constructed much more crudely than the other pieces of the garniture. The foot and neck elements and the plain joining strips are made from *P. margaritifera* and have relatively few pins.

CONDITION AND TREATMENT

Structurally, all the pieces of the garniture were stable and sound. A layer of dust on the upper surfaces rendered these dull. There were a number of small solid droplets and 'fingerprints' of adhesive/filler on some surfaces, which appeared to result from handling with glue-laden fingers, presumably during an earlier repair campaign. The visible areas of metal were stable, but had tarnished in places to black, grey or brown.

It became clear on examination that the set had undergone at least two phases of repair. This was evident from the different colours of adhesive/cement used; the absence of pins, or unusual pins that do not conform to the general pattern in size and position; and in the use of the bivalve *P. margaritifera*.

It was also apparent that the paired objects did not fully match. For example, the height of the ewers differs slightly and one candlestick shows carved banding that is absent on its pair. Some differences appear original and may be attributed to different hands or practice in a workshop, while other differences probably result from later repair.

The excess 'fingerprint' adhesive was removed using a 50/50 (v/v) mixture of de-ionized water and industrial

methylated spirit, applied to the surface using moistened cotton wool swabs wound on a bamboo stick. Gentle polishing removed the most superficial of the fingerprints. Careful paring down with a small scalpel under magnification reduced the thicker, more resistant, droplets of glue/filler until these too could be polished away.

All the mother of pearl surfaces were cleaned using cotton wool swabs moistened with de-ionized water, polishing lightly to dry with a soft cotton cloth, a process that enhanced the spectacular iridescent colours. The metal mounts and pins were left as found.

FUTURE STORAGE AND DISPLAY

The routine assessment of materials used inside showcases at the British Museum, including fabrics, mounting boards, adhesives, sealants and paints, has been carried out since 1973 [11]. Organic acids have long been known to cause the corrosion of lead, but they can also have an adverse effect on other metals and react with materials such as calcium carbonate. In their presence, shell-based materials may be subject to a damaging efflorescence comprising calcium ethanoate hemihydrate ($Ca(CH_3CO_2)_2 \cdot ½H_2O$), and calcium methanoate ($Ca(HCO_2)_2$), more commonly known as Byne's disease [12]. No evidence of Byne's disease was found on the garniture, and the cleaning method would have reduced any incipient salts. Given the possibility of the objects developing Byne's disease in the future, it is important to avoid storage or display of shell material in conjunction with wood or other materials that may emit volatile acids. Decay is exacerbated by high relative humidity (RH) and elevated temperatures. Conditions that favour the preservation of the shell material would also generally benefit the metal components.

The ambient RH and temperature in the gallery in which the garniture was to be displayed showed some fluctuation in 2006, but the range of conditions noted (30–50% RH and 15–20°C) is adequate, if not ideal, for all the material on display. The nature of the display, focusing on the impact of trade and travel in seventeenth-century Europe, necessitates organic material being shown in the same case as metal and ceramic material; the case will be monitored for any negative interactions.

Recommendations for storage of shell material

Shell material should be stored in archival quality materials that do not emit organic acid vapours. The RH should be kept stable and low, ideally at less than 50% with a daily variation of no more than ±5%, and the temperature reasonably low (16–20°C). It would be advantageous if the gaseous pollutants were removed from the environment, or alternatively scavenger materials placed in the storage boxes. There has been little research undertaken on the effects of light, although it would seem reasonable that high light levels and ultraviolet radiation might eventually constitute a danger to the organic components of the shell.

CONCLUSIONS

This study has discovered that there is a skeleton of brass bands between the inner and outer layers of shell mosaic, providing structural support. There is no evidence for a wooden substrate to the shell mosaic on the ewers, candlesticks and bottle. The central domed part of the basin is dense but is unlikely to be made of wood; the X-radiographic density and the shaped form more closely resemble the metal bands. The vessels were constructed of two layers of shell plaques, joined by silver pins and adhesive, with the hidden metal bands providing strength and stability. It might be envisaged that this structure was built up in stages, with the interior and exterior shell plaques being applied in overlapping rather than in parallel units.

Without further examination of other garnitures, it is impossible to determine whether the Museum's set is unique in its manufacture. Other sets have been described as having brass pins: it may be that the Museum's set is indeed unusual in having silver pins. Individual items and garnitures would have been subject to alteration over the course of time, for example by the addition of mounts for the European market, or by restoration and repair following damage or losses. It seems highly probable, though, that the specialist Gujarati workshops producing these goods had by the late sixteenth century developed the most efficient and stable methods of construction for large-scale production and that at least some of the features seen here, in particular the internal skeleton of metal bands, are characteristic of other sets.

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New visions of a new world: the conservation and analysis of the John White watercolours

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Summary The exhibition *A New World: England's First View of America*, held at the British Museum in 2007, provided an opportunity for conservators and scientists to examine, analyse and treat a unique collection of drawings by the sixteenth-century English artist John White. Before entering the Museum's collection the drawings had suffered fire and water damage, which caused bleeding and offsetting of pigments. They were also fragile at the edges from earlier attachment to and removal from albums, and many had planar distortions. Scientists and conservators studied the drawings to learn more about how they were produced and the changes that have occurred over time. Scientific analysis using X-ray fluorescence and Raman spectrometry showed the palette to be typical of the period, with a heavy dependence on lead white and extensive use of ochres, vermilion, azurite, smalt, indigo and metallic gold and silver. Darkening of the lead white and tarnishing of the silver have altered the appearance of the drawings and digital techniques have been used to attempt to recreate their original appearance. Using microscopic examination conservators were able to confirm that remaining pigment layers in damaged areas were stable. Conservation treatments included repair of skinning and losses using a combination of Japanese and Western papers, flattening of planar distortions and remounting. These aimed to strengthen and stabilize the drawings and ensure their preservation for the future.

INTRODUCTION

The exhibition *A New World: England's First View of America*, held at the British Museum from March to June 2007, provided an ideal opportunity for conservators and scientists to gain new insights into a unique collection of drawings by the sixteenth-century English artist John White. These are some of the earliest English watercolours and are amongst the most iconic images in the Museum's collection of works on paper. Through examination and analysis it has been possible to learn more about how they were produced, the changes that have occurred over time, and also how best to conserve them and ensure their preservation for the future.

HISTORY OF THE DRAWINGS

Very little is known about the life of John White. An Elizabethan 'gentleman artist', he sailed on five voyages to the New World between 1584 and 1590, and was the first Englishman to record what he saw in what was later to be called America [1; pp. 11–38].

The sixteenth century was a period of great exploration and discovery. It was once thought that White had been on an earlier expedition in 1577 with Frobisher in an attempt to find the North West passage as there are several studies of Inuit among his drawings. However, the flora and fauna, coastal maps and plans, and depictions of indigenous people encountered in what is now North Carolina form the main body of extant work. White would have had a brief to record these new discoveries accurately. No work of other artist-explorers of the period survives apart from fragments or in prints made after drawings. Jacques le Moyne de Morgues, a Huguenot who worked in London in the 1580s, is one artist with whom it is known White exchanged ideas. Le Moyne had been to Florida on an earlier French expedition and copies of two of his depictions of Indians (now lost) are amongst White's work.

Seventy-five beautiful watercolours were bound in an album, perhaps intended for presentation to Walter Raleigh who, according to the ink inscription at the beginning of the series, was patron of the voyages. As well as studies from

the New World there are also drawings of Eastern costumes and of imagined Picts, whose tattooed bodies White could be comparing to the similarly decorated native Algonquian Indians 'to showe how that the Inhabitants of the great Bretannie haue bin in times past as sauuage as those of Virginia' [2].

Nothing is known of the history of the drawings before they resurfaced in the 1788 catalogue of the London bookseller Thomas Payne the Elder as an album of '75 drawings coloured in the original binding. Folio – 14 gns' [1; p. 94]. This was bought by the Earl of Charlemont, a great collector and patron of the arts. It remained in Charlemont's library in Dublin until 1865 when it was sent for sale to Sotheby's in London. Unfortunately there was a fire in the warehouse adjacent to the auction rooms, and the spine of the album was scorched. Although the edges of the sheets were only slightly charred by the flames, the volume was saturated with water and lay under the pressure of other books for three weeks. This resulted in pigment transferring to the blank sheets interleaving the drawings, creating remarkably clear offsets, Figures 1a and 1b.

The damaged album was purchased by an American, Henry Stevens, who removed the drawings and trimmed the burnt edges before remounting them into a new volume. He did not retain the old album so it is not possible to say whether this was the original binding referred to in the 1788 sale catalogue or a later binding from the Earl's library. The sequence in which the watercolours were first arranged is unknown.

The new volume, and a second containing the interleaving sheets with the offset images, was acquired by the British Museum in 1866. Placed at first in the Grenville Library, they were transferred to the Department of Prints and Drawings in 1906. The drawings were subsequently removed from the album and housed in archival mounts, which have been stored in Solander boxes in the prints and drawings students' room.

It is worth noting that other versions of the drawings may have been made, perhaps for Elizabeth I or other wealthy patrons. Indeed, the British Museum owns an album that Sir Hans Sloane acquired from the descendants of John White in about 1715 (referred to hereafter as the Sloane album). It contains drawings that have traditionally been considered to be copies. However, the relationship of some of these drawings to John White's work is now being re-examined [1; p. 225]. Yet another set of White's drawings, now lost, are known through the engravings by Theodor de Bry in the 1590 edition of 'A briefe and true report of the new found land of Virginia', written by Thomas Harriott, who had travelled with White to America.

FIGURE 1. The *European roller* 1906,0509.1.64 (160 × 226 mm): (a) the original drawing (b) the offset image, showing how pigments have been transferred during wetting. Smoke damage is visible on both and the charring at the top of the offset image shows how close the drawings came to destruction

TECHNIQUE AND MATERIALS

White's work gives some indication that he had been trained as a 'limner', a term which in his day signified a painter in watercolours. He appears to have started by sketching outlines with 'black lead' (graphite) directly onto the paper, rather than onto a prepared ground, which was the more usual method of miniaturists or illuminators of the period. The outlines are not reinforced by pen and ink but delineated by applying washes of watercolour, building up detail with finer strokes of the brush, Figures 2a and 2b. Sixteenth- and seventeenth-century manuals describe brushes (known as 'pensils' at this time) made from the hair of small mammals

FIGURE 2. White's drawing technique can be clearly seen in this magnified detail of an *Uzbek man* 1906,0509.1.33 (243 × 139 mm), which shows (a) underdrawing in black lead overlaid with (b) fine watercolour brush strokes

FIGURE 3. Transmitted light detail of *Purple-clawed hermit crabs* 1906,0509.1.57 (188 × 155 mm) showing chain and laid lines in the paper and a bunch of grapes watermark

such as stoat or squirrel, bound into a quill. This provided a soft texture combined with the resilience necessary for a good point [3]. White's use of the brush rather than the pen, and his broader freer brush strokes, set him apart from other artists, such as Hilliard, working in the same media.

Drawing with watercolour required a smooth, well-sized paper. At this period there were no specialist artists' papers and it was common practice to use paper produced for writing, which was sized with gelatine to prevent running of ink. White's paper has a watermark of a bunch of grapes (Figure 3), which shows a close resemblance to papers made in France in the 1580s [4]. This is not surprising since imports dominated the English market in fine white paper at this time and it was not until the mid-eighteenth century that English white paper began to rival that of other European countries in quantity, quality or cost [5].

The paints available at the time would have been based on mineral pigments ground to a powder and organic colours such as indigo and sap green [6]. These pigments would be mixed with water and a binding medium such as gum, and the paint held in mussel shells. More opaque body colour (chalk white or lead pigments added to watercolour), which gave a denser effect, would be added last. Gold and silver leaf, traditional decorative elements in mediaeval illuminated manuscripts, are used by White in a more naturalistic way to create highlights and iridescent effects. Many of his drawings also have inscriptions recording names or other details, which are written with a pen and black (carbon) ink; see the later section on the analysis of the watercolours.

EXAMINATION AND CONDITION

The exhibition provided an opportunity to examine the whole body of John White's work and thus gain an overview not only of its current condition but also of how it had been kept during the last hundred years.

Variations in style and mounting materials gave some indication of the age of the mounts. Some drawings may have been mounted in 1906 when the album was transferred from the Grenville Library, but the only precise reference that survives is a pencil note in the empty album, which dates

the removal of several items to 1933. The earliest mounts were made of a thin board with a rather shallow aperture. Many of the drawings were 'guarded' to the backboard, a technique in which a continuous paper hinge (guard) is adhered around the edges of the verso to attach the drawing to the mount. Others were 'traditionally inlaid' – a term given to the attachment of false margins, chamfered at the edges and pasted to the drawing [7; pp. 101–102]. These margins were then adhered to the backboard. A thin cream paper was used for early inlays, while mounting carried out for an American loan exhibition in 1985 [8] probably accounts for work inlaid to a heavier white paper. All of these were solid mounts allowing no access to the verso of the drawings [7; p. 40] and most were dirty and worn from years of handling. A small number of new overthrow mounts had been made for more recent loan exhibitions.

The overall condition of the drawings was very good, with the same type of high quality paper being used throughout.

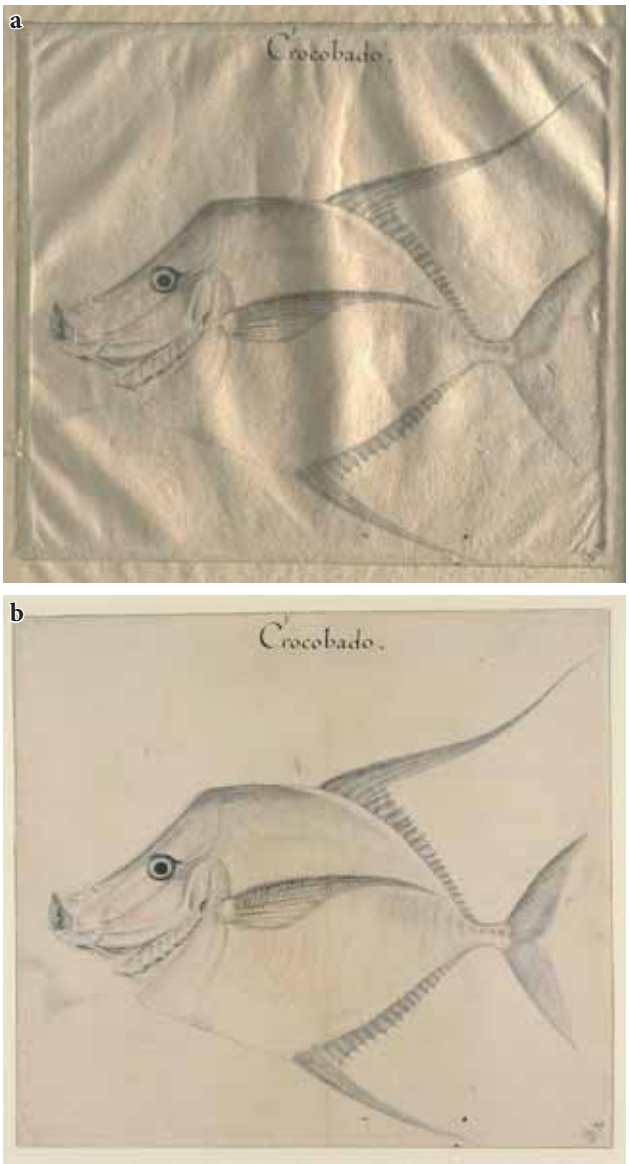

FIGURE 4. *Lookdown fish* 1906,0509.1.49 (191 × 210 mm) showing (a) planar distortions in raking light before treatment and (b) after conservation

It is a fine laid paper, with chain lines about 20 mm apart and approximately 13 laid lines per cm. Transmitted light revealed an even fibre distribution and few impurities. The paper (which at this period would have been made from linen fibres) is still a bright off-white colour, although inevitably there has been some discolouration over time.

Some drawings showed damage resulting from the dramatic effects of the fire and flood – the type and degree of staining depending on where they were positioned in the album. A slight blackening from the smoke can still be seen on some of the edges but, as the drawings are no longer on their original album pages, charring is now evident only on some of the offset sheets, Figure 1b.

Raking light revealed edge ridges and planar distortions in a dramatic way, Figure 4a. In some instances this was directly related to the wetting of the paper and in others to the various methods of attachment to the backboards. There was surface dirt and, on many sheets, a graphite line around the edges, which in some cases extended onto the inlay paper indicating that it dated from previous mounting. Some old repairs were found but many of the drawings had small, unrepaired tears and edge losses (evident in the catalogue photographs which were taken before conservation). When lifted from the mounts many sheets were shown to have quite badly skinned edges on the verso, especially at the top and left. This would seem to have occurred during removal from one of the earlier albums into which they had been directly adhered.

The most obvious damage was to the pigments. Many of the colours would have appeared much more intense before pigment was transferred (offset) to interleaving sheets during the events of 1865. A number of distinct problems were visible. In some areas where the pigment particles were more coarsely ground, or where the paint had been more thickly applied, entire layers of paint had been lost; these could be seen deposited in reverse order on the offset images. When examined under magnification there was no evidence of loose pigment particles or recent cracking, and remaining paint layers were found to be firmly attached to the paper surface. In other areas paints containing pigments of smaller particle size had 'run' into the paper fibres causing indistinct edges, Figure 5. A more soluble light green had bled through many sheets and examination under ultraviolet light revealed the full extent of this staining, Figures 6a and 6b. Some areas containing lead-based pigments (lead white and red lead) had darkened, perhaps due to exposure to sulphur-containing species in the atmosphere, Figures 9a and 9b.

Finally, many of the sheets have a faint horizontal grey line across the centre, indicating that they were once folded. This appears to have occurred before the drawings were executed as no evidence of damage to the pigment layer was observed. Folding into smaller sheets would have made for easier transportation if the work had been carried out on the voyage although, from the condition and uniformity of execution, it is more likely they were drawn on White's return to England from notes and observations made during the voyage.

FIGURE 5. Detail of an *Uzbek man* 1906,0509.1.33. Wetting has caused the blue pigment (smalt) to flake off the paper surface, while the finer particles of red pigment (vermilion) have run into the surrounding paper fibres

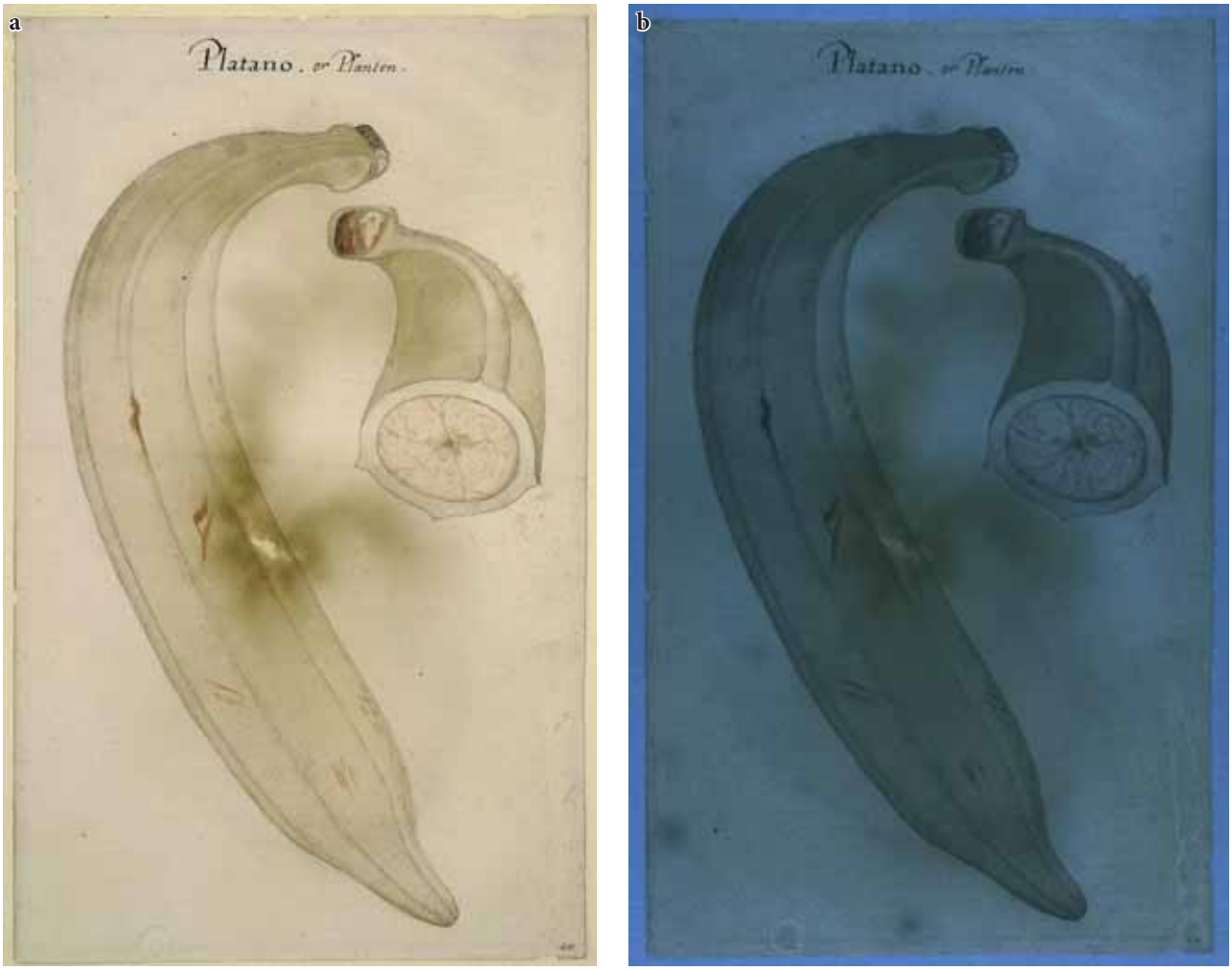

FIGURE 6. *Horn Plantain* 1906,0509.1.40 (294 × 177 mm): (a) an area in the centre stained by green pigment from another drawing; (b) ultraviolet illumination reveals that the affected area is extensive and clearly shows water stains towards the bottom of the drawing

TREATMENT EVALUATION

Although the initial reason for examining the drawings had been their inclusion in the exhibition, the assessment of their overall condition and of appropriate levels of conservation treatment needed to be made in a wider context. The priority for works forming part of a public collection is to ensure they are in a stable condition and preserved for the future while still allowing access for study and enjoyment. Over recent years, public access to prints and drawings in the British Museum collections has increased dramatically, both in the students' room and, in particular, through an extensive loans programme. Due to their unique interest and importance many of the John White drawings have been in considerable demand for exhibitions over the past 50 years and increased interest seemed likely to be generated by the new exhibition. In determining appropriate treatments it was therefore necessary to take into consideration the anticipated future requirements of display, handling, transport and storage.

For display purposes a visual improvement to the edge damage and overall distortions of many of the drawings was desirable. Since the exhibition was subsequently to be shown in the USA, they also needed to be in the best possible physical condition to travel safely. Mounting was an important issue, not only for the immediate display of the drawings, but also for their future handling and storage in a public study collection. The mounting method needed to allow full access to both recto and verso if required, while still providing a good level of protection. Minimizing risk to the skinned edges of the drawings during any future remounting was also a significant consideration.

The most obvious physical problems were the cockling and edge ridges, which were both visually distracting and potentially damaging to the drawings. These posed the risk of surface abrasion with further pigment loss in raised areas and of increased tension and distortion should there be any changes in humidity. Lifting and flattening were therefore considered essential both for aesthetic reasons and to provide better protection, Figure 4b. The processes of lifting and debris removal were delicate, requiring care and skill to avoid further damage to the fragile edges of the drawings. However, once lifted, it was possible to repair and reinforce the edges.

Other factors considered during treatment were the colour changes, pigment losses and staining. Although it might have been possible to treat blackened lead white pigment using ethereal hydrogen peroxide, this is often a time-consuming process and is not always effective. In addition, as this is an irreversible treatment, in which basic lead carbonate ($2PbCO_3 \cdot Pb(OH)_2$) pigment that has become blackened to form lead sulphide is converted to lead sulphate ($PbSO_4$), it is not generally carried out unless considered essential. Since it was possible to create a very good impression of how the colours might have appeared originally using digital images (Figure 12), the treatment was not considered necessary in this instance. Examination under magnification had shown that although areas of pigment loss were quite extensive on some drawings, the remaining paint layers were stable and were not in need of consolidation. The staining affecting many of the drawings would have been extremely difficult to treat without risk of further damage such as movement of discolouration. Although very noticeable in some cases it was not in general considered visually distracting and indeed was now felt, along with the colour changes and losses, to have become an integral part of the history of the drawings.

CONSERVATION TREATMENT

The drawings were lifted from their mounts by slitting the old inlay paper with a scalpel or, for those which were adhered or guarded around the edges, by undercutting. Light surface cleaning was carried out around the edges of the drawings where necessary using Staedtler plastic eraser, grated to a fine powder. Paper debris (primarily the remains of guards and inlay paper) and adhesive residue were then carefully removed from the edges of the verso. In some cases poor quality repairs had been carried out in the past and most of these needed to be removed to ensure the drawings would lie flat after treatment and to minimize the risk of future cockling or distortion, Figures 7a–7c.

The paper was found to be very absorbent around the edges, probably due to deterioration of the gelatine sizing over time, perhaps exacerbated by the nineteenth-century flood. Because of this extreme absorbency, the introduction of moisture to soften adhesive residue needed to be minimized to avoid any risk of staining. Verso debris was therefore first reduced as much as possible using a scalpel. A poultice of methylcellulose (4% in water) could then be applied quite briefly to remove the remainder, followed by swabbing using cotton buds, lightly moistened with water, to remove traces of adhesive residue. During this process the fragile edges of the drawings were gently pressed to prevent curl. Afterwards, where overall flattening was necessary, the drawings were briefly humidified over capillary matting and Gore-Tex® and pressed lightly between blotters and boards.

New repairs were needed to reinforce the edges and improve the visual appearance of the drawings. For this a combination of Japanese and Western papers was used – the former providing support for skinned, weak areas or small tears and the latter being used for infilling edge losses or carrying out repairs where the original paper was particularly thin. The main Japanese paper utilized was a *Mino*, while several old Western papers of slightly differing thicknesses were employed, all chosen for their sympathetic texture and colour as well as a very similar chain and laid line formation. Repairs were adhered using gluten-free wheat starch adhesive with most of the work being carried out on a lightbox to reveal the weakest areas in the support paper clearly and allow accurate positioning. In some of the most severely damaged areas, several layers of both

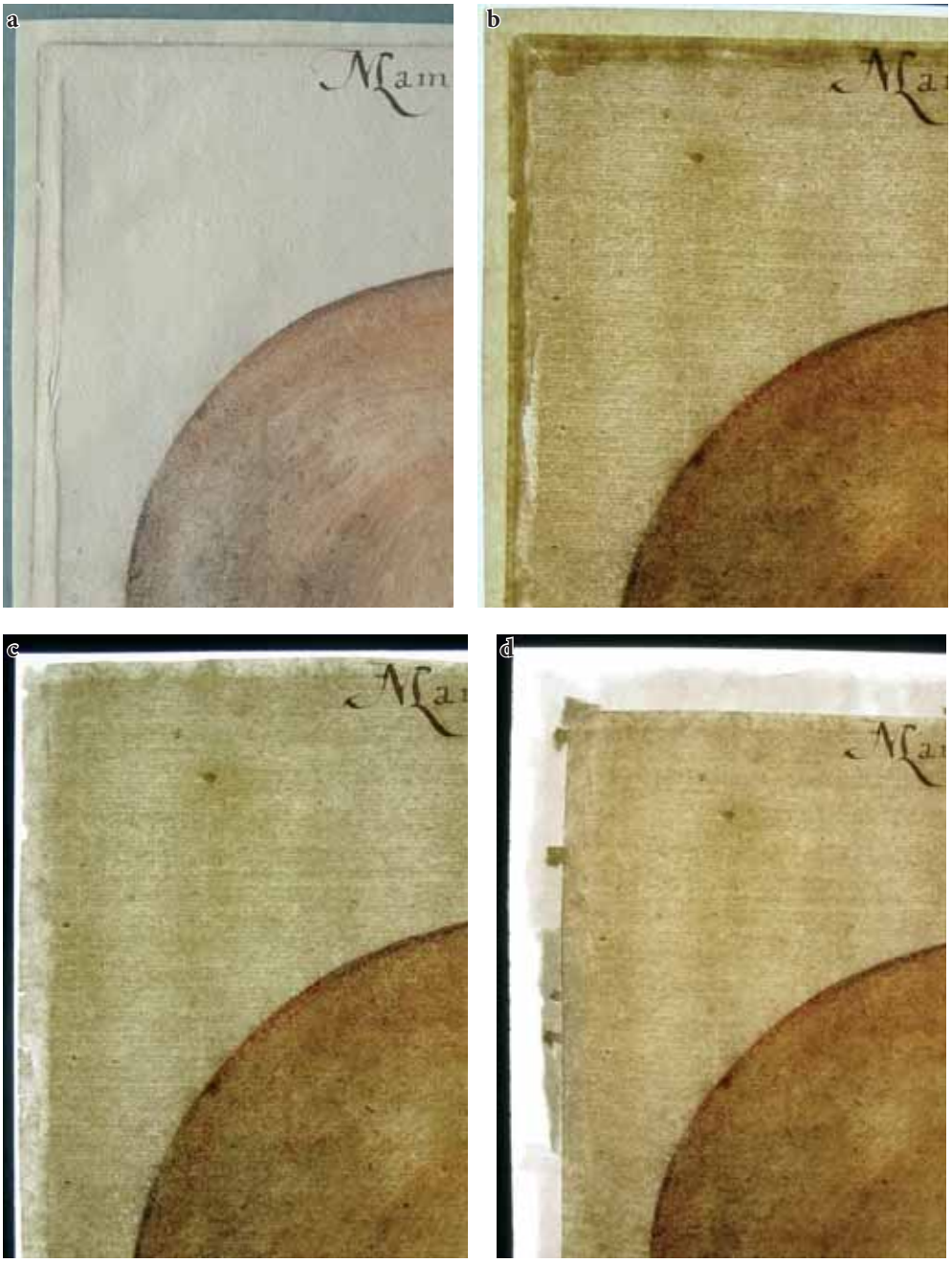

FIGURE 7. Detail of *Mammee apple* 1906,0509.1.40a (210 × 184 mm): (a) after removal from its mount, showing edge ridges caused by the old inlay paper that is still attached to the verso; (b) viewed in transmitted light, showing areas of skinning and loss; (c) in transmitted light after debris removal, revealing the full extent of the damage; (d) layers of Japanese and Western paper have been used to repair and support the fragile edges

Japanese and Western paper needed to be carefully overlaid to match the thickness and opacity of the surrounding original paper. This was an intricate and lengthy process but ensured a result that would not only be strong but would also integrate well when viewed in either reflected or transmitted light, Figure 7d. The completed infills were toned using Winsor and Newton artists' watercolours.

With the edges of the drawings now much stronger and their overall appearance visually improved, it was essential to minimize the risk of further damage occurring in the future. After flattening, the drawings were therefore inlaid into a 100 $g.m^{-2}$ acid-free paper chosen for its sympathetic colour, weight and texture. The false margin provided by inlaying allows safer handling (by reducing the need for direct contact with the object), and safe attachment to a mount, as well as providing protection to the edges. The White drawings were attached to their inlay paper margins using strips of *Tengujo* paper adhered with methylcellulose adhesive [7; p. 103]. This is a more easily reversible method than that used traditionally, and avoids the problem of edge ridges. In future, the drawings can be removed from the inlay paper, if necessary, with only a minimal application of moisture, leaving the

FIGURE 8. Detail of *Greek woman* 1906,0509.1.35 (210 × 94 mm) showing the same severely damaged area at the top edge: (a) in reflected and (b) in transmitted light after lifting and removal of old inlay paper from around the edges; (c) in reflected and (d) in transmitted light after repair and inlaying

edge repairs – adhered with wheat starch paste, which is less soluble – still intact, Figures 8a–8d.

After inlaying, the drawings were hinged to standard royal size (559 × 406 mm) overthrow mounts of cream six-ply acid-free Museum board, which was temporarily overlaid with coloured board for display. For future storage these overlays will be removed and the mounted drawings housed in Solander boxes for protection from light, dust and atmospheric pollutants.

ANALYSIS OF THE WATERCOLOURS

While the John White drawings were undergoing conservation, the opportunity was also taken to investigate the paints used in their production. Time constraints prevented a full investigation of each watercolour, and a subsample was therefore selected for scientific examination, based both on the range of materials and on the practicalities of working around the conservation process. The pictures examined are listed in Tables 1 and 2. Work focused on the drawings accepted as being by White's hand, with only one drawing from the Sloane album (SL 6270.12; Table 2). Visual examination suggests some differences in palette between these two groups, particularly with regard to the greens, and it is hoped that the material from the Sloane album can be examined in more detail at a later date.

Because of the fragile nature of both the paper and the painted surfaces, the methods employed for this study needed to be both non-destructive and non-invasive. For these reasons all analyses were carried out using only optical microscopy, Raman spectroscopy and X-ray fluorescence (XRF) analysis; see the experimental appendix for details. While both these methods have the advantage of posing no danger to the watercolours, there are some drawbacks for this project. First, XRF yields elemental data, giving the elements present on a surface, but does not directly provide identifications specific to a particular compound [9]. In addition, the equipment used cannot detect very light elements (i.e. those below sodium in the periodic table), although with the use of helium gas to flush the region between the X-ray tube, object and detector, the sensitivity for some of the lighter elements can be significantly enhanced. As XRF could not detect carbon it is of limited use in the investigation of organic compounds, especially as identification of these materials relies on additional information about their molecular structure. Raman spectroscopy is a technique that provides compound-specific identifications [10], but when used directly on a painted surface it is also limited when it comes to identifying organic pigments. The Raman equipment available at the British Museum also has some geometric constraints that restricted the areas of the watercolours which it was possible to analyse.

Despite these limitations, these two techniques have served well in answering many of the questions that have arisen about the drawings. However some lacunae are inevitable, with the most obvious omissions being the nature of the media used to bind the pigments. Additionally, with the notable exception of indigo, which is readily detected by Raman spectroscopy, it has not proved possible to identify, or even detect, the organic materials present in the binding medium or pigments.

ANALYTICAL RESULTS

The data collected by XRF analysis for unpainted areas of paper show a wide range of elements, Table 1. The traumatic history of the drawings, particularly the prolonged water damage, makes interpretation of these results difficult. The presence of calcium on all the papers suggests, however, that a calcium compound was used at some point in the preparation of the paper. The Raman results for the unpainted areas offer no further information.

The pigment palette employed seems to be fairly typical for the period [6]. Much use is made of earth pigments (ochres), identified on the basis of the presence of concentrations of iron in the XRF spectrum and/or characteristic peaks for hematite and goethite in the Raman spectra. These ochres provide the main source of the reds, yellows and browns which dominate the drawings of Native American life. Supplementing these ochre colours some use is made of at least two other reds. Vermilion (mercuric sulphide, HgS) is used quite widely, but in far smaller quantities than red ochre (possibly reflecting its higher cost [6]), mainly to emphasize detail and bring out features such as lips. A vivid pink appears on some of the botanical drawings and particularly in the depictions of shellfish. This has not been positively identified, but the absence of metallic elements in the XRF spectrum suggests an organic pigment. Madder is the most common organic red associated with this period and is the most likely candidate for use here. Initial investigations seemed to imply the presence of bromine, perhaps suggesting an organic pigment derived from a shellfish and containing a dibromoindigo-based colourant. However it has not been possible to replicate this finding and careful examination of these areas by Raman has not revealed any indigoid-based pigments in this areas.

The main white used is lead white (basic lead(II) carbonate; $2PbCO_3{\cdot}Pb(OH)_2$), identified by both its Raman spectrum and the presence of substantial quantities of lead in white (or off-white) areas. This reliance on lead white has led to marked changes in appearance of many of the drawings. Lead white is particularly prone to darkening, a phenomenon which has been variously attributed to the formation of oxides (principally PbO_2, plattnerite [11]), or sulphides, mainly PbS [12]. While it has proved difficult to understand the pattern of such darkening on these drawings (perhaps not surprisingly, given their convoluted environmental history) it has certainly occurred. Figures 9a and 9b show an attempt to demonstrate the effects of this colour transformation on one particular drawing using digital imaging. In this case simply correcting the darkening of the pupils of the eyes and reinstating some of the original white highlights on the feathers has a radical effect on how the watercolour is perceived. No other white pigments have been conclusively identified, but calcium has been found in a number of painted areas and may well reflect the use of a calcium-containing white as an extender.

On the basis of Raman results, the blacks used seem to be predominantly carbon-based. In an area where the underdrawing was exposed on a watercolour of a *wife of an Indian werowance or chief and her daughter* (1906,0509.1.13), the black was shown to be graphite.

Three blues were identified. Azurite (copper carbonate; $2CuCO_3{\cdot}Cu(OH)_2$) was identified either by inference, from the presence of copper peaks in the XRF spectra of blue areas, or unequivocally by its Raman spectrum. Smalt, glass coloured by the presence of cobalt, was recognized by the presence in the XRF spectra of cobalt and other elements typically present in glasses, particularly silicon. Indigo, an organic pigment, was readily identified by its clear Raman spectrum [13]. In one particular drawing (1906,0509.1.64; the European roller, *Coracias garrulus*), all three blues were used to give a life-like colour distribution for this spectacular bird, Figure 1a. Even so, when this drawing is compared with modern photographs it can be seen to lack

FIGURE 9. Detail from *An Indian werowance or chief* 1906,0509.1.12 (263 × 150 mm): (a) in its present condition; (b) with the original colour of the lead white digitally reinstated: image Antony Simpson

TABLE 1. Analytical results from the John White drawings

Watercolour	Sample position and colour	XRF results [a]	Raman results	Interpretation
1906,0509.1.6 *Indians fishing*	unpainted surface	(Al, Si, Pb/S, Cl, K, Ca, Ba, Fe, Cu, Sr, Zn, As, Rb)	–	
	fish, blue	(Ca, Ba)	indigo	indigo
	flower, red	[Hg, S]	vermilion, carbon	vermilion + carbon
	body of canoe, brown	not measured	hematite, goethite	hematite + goethite (red and yellow ochres)
	fire in canoe, yellow	[Au]	not accessible	gold
	fire in canoe, red,	[Hg, S]	not accessible	vermilion
	fish, blue	no peaks above paper levels	indigo	indigo
	shore, yellow	no peaks above paper levels	goethite	goethite (yellow ochre)
	plants, green	no peaks above paper levels	goethite, indigo	indigo + goethite (yellow ochre)
1906,0509.1.8 *The town of Pomeiooc*	unpainted surface	(Pb/S, Cl, K, Ca, Fe, Cu, Sr, Zn, As)	–	
	central village area	[Pb]	–	lead white
1906,0509.1.12 *An Indian werowance or chief painted for a great solemn gathering*	unpainted surface	(Pb/S, Cl, Ca, Fe, Cu, Sr, Zn, As, Rb)	–	
	white of eye, black	[Pb]	lead white	lead white
	body paint, red	[Pb, Fe] (Ca)	–	ochre lead white calcium-based pigment/extender?
	kilt, white	[Pb] (Zn, Cu)	–	lead white
	hair	no peaks above paper background	not accessible	carbon
1906,0509.1.13 *A wife of an Indian werowance or chief and her daughter*	unpainted surface	(Pb/S, Cl, K, Ca, Fe, Cu, Sr, Zn, Rb)	–	
	clothing, red/brown	[S, Pb, Fe, Hg] (Ca)	not accessible	vermilion, ochre, lead-based pigment? calcium-based pigment/extender?
	doll, yellow	[Au] (Pb, Ca, Fe, Ag)	not accessible	gold
	doll, red	[Pb, Fe] (Ca)	not accessible	ochre, lead-based pigment, calcium-based pigment/extender
	gourd, red area	[S, Hg]	not accessible	vermilion
	gourd, yellow area	(Hg)	not accessible	organic?
	beads	[Pb]	not accessible	lead white
	tattoo	(Pb, Ca, Fe, Hg)	carbon	carbon ink
	caption	(Pb, Ca, Fe ,Hg)	carbon	carbon
	child's beads, grey	[Pb] (Fe, Ag, Hg)	lead white	lead white
	child's beads, black	[Pb] (Ag, Hg, Ca)	lead white	lead white
	woman's beads, white	[Pb]	lead white	lead white
	woman's beads, mid- grey	[Pb] (Hg)	lead white	lead white
	woman's beads, black background	no peaks above paper background	carbon	carbon ink
	woman's beads, mid- grey	[Pb]	not accessible	lead white
	small cross, black	(Fe, Pb)	carbon	carbon ink
	woman's beads, grey	[Pb] (Zn, Cu)	not measured	lead white
	underdrawing	no peaks above paper background	graphite	graphite
1906,0509.1.38 *Sabatia*	paper	(Pb, K, Ca, Fe, Rb)		
	flower centre, red	[Pb] (Ca)	not accessible	lead pigment calcium-based pigment/extender? organic bromine-containing compound?
	flower centre, white	[Pb]	not accessible	white lead
	petals, purple	[Pb]	not accessible	lead pigment organic bromine-containing compound?
1906,0509.1.33 *Tartar or Uzbek man*	paper	(Cl, K, Ca, Fe)		
	robe, blue stripe	[Si, Pb, Bi, Fe, Co] (Mn, Ni, Cu, Zn, As, K)	no spectrum	smalt
	robe, black stripe	no peaks above paper background	carbon	carbon
	shoes, red	[Hg, S] (Ca)	vermilion	vermilion calcium-based pigment/extender?

Watercolour	Sample position and colour	XRF results [(a)]	Raman results	Interpretation
1906,0509.1.34 *Turkish lady*	paper	(K, Ca, Fe)		
	band, red	[Pb/S, Hg]	vermilion	vermilion
	robe, faint blue stripes	[Pb, Cu] (Ca, Fe)	not accessible	copper blue
	robe, white	[Pb] (Cu)	not accessible	white lead
	veil, black	no peaks above paper background	carbon	carbon
1906,0509.1.50 *Grouper*	paper	(Cl, K, Ca, Mn, Fe, Cu, Zn, Rb, Sr)		
	spot, black	[Au] (K, Cu, As)	not accessible	carbon? plus some gilding?
	body, brown	[Pb/S, Fe, Hg] (Ca, Mn, Cu)	not measured	ochre, vermilion, calcium-based pigment/extender?
	eye, gold	[Au] (Ag, Cu)	not measured	gold
	mouth, red	[Fe] (Hg, Ca)	not measured	red ochre vermilion calcium-based pigment/extender?
	mouth, red (2)	[Fe, Hg] (Ca)	not measured	red ochre vermilion calcium-based pigment/extender?
	belly, grey	[Ag] (Cu, Au, Pb)	not measured	silver
	belly, grey (2)	[Ag] (Cu, Au)	not measured	silver
1906,0509.1.64 *European roller*	paper	(Pb, Cl, K, Ca, Fe)		
	back feathers, bright blue	[Cu, Co] (Si, Cl, Ca, Fe, As, Pb)	azurite	azurite smalt
	tail feathers, dark blue	[Co] (Si, Pb, K, Ca, Fe, Cu, As)	indigo	indigo smalt
	wing, mid blue	[Co, Cu] (Si, Fe, As, Pb)	azurite	azurite small amount of smalt
1906,0509.1.47 *Lookdown fish*	paper	(Cl, K, Ca, Fe, Cu, Zn, Rb)		
	lips	[Hg, Pb/S]	not measured	vermilion
	body	[Ag] (Co, As)	not measured	silver
1906,0509.1 *Flying fish*	paper	(Cl, K, Ca, Fe, Zn)		
	blue body	[Co] (Si, Pb, K, Fe, Ni, As, Bi)	no spectrum	smalt
	fin	[Ag] (Pb)	not measured	silver

Note: (a): For the XRF data, the results in square brackets are present in substantial quantities while results in round brackets are present as traces only. All elements detected are listed for unpainted paper, but for painted areas only elements present in larger quantities than in the paper are given.

TABLE 2. Analytical results from the Sloane album

Watercolour	Sample position and colour	XRF results (a)	Raman results	Interpretation
SL 6270.12 *The skirmish at Bloody Point*	unpainted surface	(Si, Pb/S, Cl, K, Ca, Mn, Fe, Cu, Sr, Zn)		
	flag, cream	no peaks above paper background	no spectrum	organic?
	flag, red	[Pb, S, Hg] (Ca)	red lead, vermilion	red lead plus vermilion
	trousers, European figure, blue	[Fe, Cu] (Pb, Hg)	not accessible	copper blue, ochre
	hills, blue	[Fe, Cu] (Hg)	azurite	azurite (plus some ochre)
	canoe, brown	[Fe] (Hg)	not accessible	ochre
	hills, green	[Fe, Cu] (Pb, K, Hg)	azurite, goethite	azurite plus goethite (yellow ochre)
	Inuit body, brown	[Ca, Fe, Cu] (Mn, Pb, Zn)	not accessible	ochre plus unidentified pigments
	Inuit face, red	[Hg, S]	not accessible	vermilion

Note: (a): For the XRF data, the results in square brackets are present in substantial quantities while results in round brackets are present as traces only. All elements detected are listed for unpainted paper, but for painted areas only elements present in larger quantities than in the paper are given.

the dramatic vividness of the living bird. It is possible that blue pigment has either been extensively lost, or has faded to a duller colour; both azurite and smalt are known to be prone to degradation [14, 15]. The offset page (Figure 1b) certainly shows considerable transfer of blue pigment, but not enough to reach the depth of colour apparent on the living bird. Additionally, no sign of degraded pigment particles can be detected by careful microscopic examination of the original, and none are apparent in blue areas on other drawings from the album. Perhaps a more likely explanation is that the drawing shows a juvenile, as the full colours are not developed until adulthood [16]. Alternatively

White may have used a dead and faded specimen as his subject, although in another drawing of a similar nature, and certainly featuring a dead bird, in the British Museum collections (Gg, 2.220; Hans Hoffmann after Dürer, Figure 10) the blue is considerably brighter.

No evidence has been found on any of the drawings for the use of the most prestigious and expensive blue of the period, natural ultramarine, prepared from the mineral lapis lazuli and employed sometimes as a background to contemporary portrait miniatures [17].

Surprisingly, no inorganic green pigments have been identified on the John White drawings, although in the drawings in the Sloane album there are many areas coated with thick green pigment, which is almost certainly inorganic. Greens are generally rare in the drawings from the main series. Green plants occur at the base of *Indians fishing* (1906, 0509.1.6), coloured with a mixture of indigo and yellow ochre, while the few green areas of foliage found on the botanical drawings give no XRF data or Raman spectra, and must be assumed to be organic in nature. On the basis of what is known of the palette of the time the most likely pigment used here is sap green, normally produced from unripe buckthorn (*Rhamnus* sp.) berries [6]. The possibility that the lack of inorganic greens could be due to alteration of an original pigment has been considered, but there is no sign of the brown staining and damage that normally accompanies degraded verdigris or malachite. Some areas, such as the central village area in *the town of Pomeiooc* (1906,0509.1.8), which might logically be expected to be green, were specifically examined and none showed the presence of any element that might suggest a degraded inorganic green. It remains possible that an organic green was originally more widely used but has now undergone total degradation.

FIGURE 10. *Dead blue roller* (Gg 2.220) Hans Hoffmann after Dürer

The final touches to the rich colours of the drawings are provided by metals. Metallic gold seems to have been present originally on most of the Indian drawings and many of the others, usually applied to small areas to enhance details, although little is now visible. The gold was applied as a final layer, making it very vulnerable to physical damage, and much has been transferred to the offset pages. A good example is provided in the watercolour of a *wife of an Indian werowance or chief and her daughter*, 1906,0509.1.13, Figure 11a. Here the doll and medal/coin worn by the Pomeiooc child (incidentally, the only demonstrably European artefacts shown on any of the Indian drawings) were once richly ornamented with gold. Little, if any, can now be seen on the drawing, but detailed examination of the offset page (Figure 11b) shows where it has been transferred. However, even on the offsets it is not always readily obvious; sometimes transferred pigments from the originally lower layers now rest on top of the gold and obscure it. All the gold surfaces examined in this study had been disrupted in this way. For this reason it has proved impossible to state with certainty if the gold was applied as 'shell gold', small pieces of foil suspended in a transparent medium, or as a foil, although shell gold seems the more likely of the two.

Similarly silver, in this case definitely applied as small metal fragments, featured extensively on the depictions of fish. While little has been lost by transfer (possibly because of the position of the drawings in the album, or possibly because it was applied directly to the paper rather than onto a painted surface) the metal has tarnished to a dull grey, making it difficult to distinguish from the black ink or graphite outlines. When first produced the silver areas would have shimmered, closely replicating the appearance of the living fish. Figure 12 shows an attempt to recreate the original appearance of one of these pictures by digitally reinstating the initial colours of both the lead white and silver.

Overall, the pigments on these drawings are unsurprising for the period. While the possible presence of a shellfish-derived pink may be an indication of the use of a pigment of New World origin, the results of this study do not give a firm indication of where these works were produced or where the pigments were sourced.

CONCLUSIONS

Close examination and scientific analysis of the drawings has allowed conservators and scientists to form a picture of

their condition, the physical changes that have occurred over time and of the techniques and materials used to create them. Information gained about the pigments used and the colour changes suffered during their traumatic history allows us to imagine, and attempt to reconstruct, their original appearance, with the depth of pigment John White intended, with clear whites and with shining areas of silver and gold. Conservation treatment and remounting have not only improved

FIGURE 11. *A wife of an Indian werowance or chief and her daughter* 1906, 0509.1.13 (263 × 149 mm): (a) in its present condition; (b) the offset page; (c) and (d) enlarged details showing the transfer of gold to the offset page

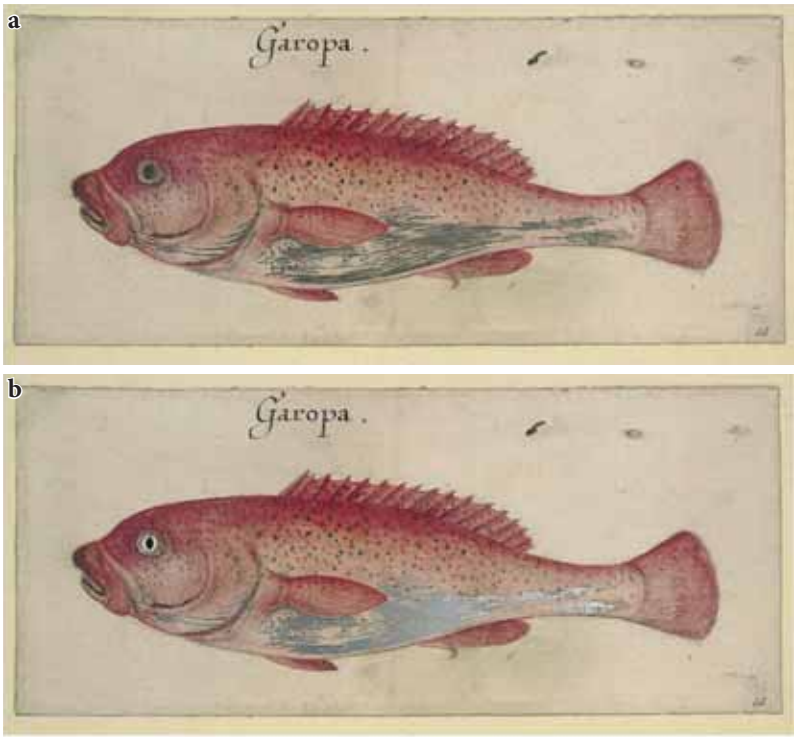

FIGURE 12. *Grouper* 1906.0509.1.48 (93 × 218 mm): (a) in its present condition; (b) with the original colour of the lead white and silver digitally reinstated: image Antony Simpson

the appearance of the drawings but also ensured they are in a more robust and stable condition. The new body of information on their condition, and the records of conservation treatments carried out, will provide an invaluable resource for those responsible for their future care.

EXPERIMENTAL APPENDIX

XRF analyses were carried out using a Brucker Artax spectrometer. The air immediately above the area of analysis was displaced by a gentle stream of helium gas to provide greater sensitivity for lighter elements. The improvement produced is greatest for elements such as aluminium, silicon and phosphorus, while elements such as sodium and magnesium, which are not detectable in air, can just be seen, although their detection limits are poor. While the paint layer on these drawings is thick compared with modern watercolours, it is thin when compared with the depth of penetration of the spectrometer X-ray beam, so that each analysis reflects the elements present in both paper and paint. In all cases, therefore, spectra were also collected for unpainted areas of drawings and these results subtracted from those collected in coloured areas to give results for the pigments alone. The area analysed was *c*. 0.65 mm in diameter. Spectra were collected for between 100 and 300 seconds.

Raman spectroscopy was carried out using a Jobin Yvon LabRam Infinity spectrometer with green (532 nm) and near infrared (785 nm) lasers with maximum powers of 2.4 and 4 mW at the sample respectively, a liquid nitrogen cooled CCD detector, and an Olympus microscope system. This allowed tiny coloured areas to be targeted for analysis, with a sample spot size in the order of a few micrometres, depending on the power of objective lens used. Spectra were collected for between 20 and 100 seconds, with at least five acquisitions used to produce each spectrum. The resultant spectra were identified by comparison with a British Museum in-house database.

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MATERIALS AND SUPPLIERS

- 100% cotton archival inlay paper 100g.m^{-2}, museum board: John Purcell Paper, 15 Rumsey Road, London SW9 0TR, UK. Email: mail@johnpurcell.net
- Culminal MC 2000 methyl cellulose, *Tengujo* Japanese paper 15g.m^{-2}: Conservation by Design, Timecare Works, 5 Singer Way, Woburn Road Industrial Estate, Kempston, Bedford MK42 7AW, UK. Email: info@conservation-by-design,co.uk
- Gore-Tex®, capillary matting: Preservation Equipment Ltd, Vinces Road, Diss, Norfolk IP22 4HQ, UK. Email: info@preservationequipment.com
- Gluten-free wheat starch paste: Masumi Corporation, 4-5-2 Sugamo Toshima-ku, Tokyo 170-0002, Japan. Email: info@masumi-j.com

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The effect of ultraviolet-filtered light on the mechanical strength of fabrics

Capucine Korenberg

Summary As ultraviolet light is known to be detrimental to organic objects, the light entering galleries containing organic objects is filtered in many museums. Conservators have, however, noted that some textiles on permanent display have weakened significantly over time, a phenomenon that has usually been attributed to the deleterious effects of light. This study aimed to investigate the effect of light from which ultraviolet radiation had been filtered on the mechanical strength of cellulose-based textiles. Modern undyed cotton, linen and jute textiles were irradiated for 30 Mlux.hours in two different lightboxes: the first lightbox was fitted with a lamp that mimicked daylight and had a relatively high ultraviolet radiation content, whereas the second lightbox was fitted with the same fluorescent lamps as used in the galleries at the British Museum and from which all the ultraviolet radiation was filtered. The mechanical strength of the jute and linen samples aged in the lightbox with a high ultraviolet content decreased significantly, which was attributed to the high lignin content in jute and to the possible presence of photo-sensitizers in linen. The mechanical strength of the cotton sample was not affected by exposure to ultraviolet radiation. In contrast, none of the samples aged in the lightbox that used light free of ultraviolet radiation showed any signs of mechanical weakening. There was a significant change in colour following light exposure for all the samples, although the change was higher when ultraviolet radiation was included. In particular, the jute samples yellowed, which can be attributed to their higher lignin content compared to cotton and linen. These experiments suggest that visible light does not affect the mechanical strength of modern undyed cellulose-based textiles, although it is responsible for changes in colour. Until the 1980s, light-sensitive objects in museums were often displayed in daylight without ultraviolet filtration on windows and skylights. It is possible that the mechanical weakening of textiles reported by conservators is a result of the exposure to ultraviolet light in the past. Alternatively, in the case of historical fabrics, this could be linked to a treatment applied to the fabric, such as the use of mordants or dyes.

INTRODUCTION

Like many other museums, the galleries of the British Museum contain numerous textiles and objects made with textiles. These include Asian objects decorated with silk banners and tassels, while in the Egyptian galleries, there are mummies, mummy-wrappings and models of boats with linen sails on permanent display, Figure 1. Ultraviolet (UV) radiation is known to be detrimental to organic objects and the light used in galleries at the British Museum that contain such objects is filtered to remove UV. There have, however, been frequent reports from conservators that some textiles on permanent display have weakened significantly with time – an effect that has usually been attributed to the deleterious effect of light. This study aimed to investigate the effect of UV-filtered light on the mechanical strength of cellulose-based textiles.

Very little research has been reported into the photo-ageing of cellulose-based fabrics [1]. Anecdotal evidence suggests that UV radiation affects their mechanical strength, but this has not been demonstrated, and little is known about the effect of UV-filtered light. In contrast, the detrimental effect of light on the properties of paper is well documented [2–7]. It has been shown that lignin plays an important role in the photo-ageing of papers containing lignin, especially in terms of photo-yellowing [2, 3], and there is evidence that lignin affects the photo-induced loss in mechanical strength. For instance, it has been reported that papers with high lignin contents become more brittle on photo-ageing than papers containing less lignin [4]. In addition, Bond et al. observed that lignin-containing papers showed a considerable loss in folding endurance after a 29 month exposure in a north-facing window, while the folding endurance of a lignin-free paper aged similarly did not change significantly

FIGURE 1. Textiles on permanent display in the British Museum: (a) linen sail of a wooden model of a boat (1901,0415.145) in gallery 61; (b) linen mummy-wrapping (1971,0403.1) in gallery 62

[5]. Ultraviolet radiation is responsible for causing lignin to cross-link, leading to the embrittlement of the fibres, but lignin cross-linking has also been observed in papers exposed to UV-filtered light for five years [6]. Lignin has a complex structure, which differs according to the plant species [2]. It is not clear, for example, that bast fibres age in the same way as wood pulp fibres and further research is needed to investigate the effects of light on cellulose-based textiles.

In this study, samples of cotton, linen and jute textiles were photo-aged in two different lightboxes. The first lightbox was fitted with a lamp that mimicked daylight

and had a relatively high UV content, whereas the second lightbox was fitted with fluorescent lamps of a type used extensively in museums and employed widely throughout the galleries at the British Museum; all UV radiation was filtered from the latter source. The aim was to investigate the detrimental effects that UV radiation had on the mechanical strength of fabrics exposed in the first lightbox and compare these with the fabric samples aged in the second lightbox, which simulated current conditions in the galleries. After photo-ageing, the mechanical strengths of the samples were compared to those of the textiles 'as received' and colour changes in the textiles were measured.

EXPERIMENTAL

Fabric samples

Three textiles, 'cotton canvas CC31', 'artist linen L36' and 'jute tarpaulin J65' were purchased commercially. All the textiles were said to be natural, with no dye or finish. The textiles were rinsed at 90°C before use and five strips of each textile were cut with their length parallel to the warp. The strips were 20 mm wide and at least 120 mm long. It should be noted that modern textiles are processed using techniques that differ from those employed historically. Therefore, the results obtained in this study may not be directly applicable to historical fabrics. In addition, mordants or dyes may act as photo-sensitizers and affect the strength of textile fibres and their ageing process; for example, weighted silks deteriorate to a much greater extent than unweighted silks [8]. This study is focused on undyed fabrics and different results may be obtained for dyed fabrics.

The fabrics were tested for lignin using the phloroglucinol test [9]. The test proved positive for jute, but negative for cotton and linen. The detection threshold of the phloroglucinol test is not known, so although none was detected, it is likely that the linen also contains a small amount of lignin. The compositions of cotton, linen and jute, compiled from several literature sources, are given in Table 1.

As acidity has been shown to play a role in the photo-ageing of paper [4], the pH of each fabric was measured using the aqueous extract pH test [9]. All the fabrics were found to have a pH very close to seven.

TABLE 1. Chemical composition of cotton, linen and jute, as found in the literature [10–12]

	Content (%)		
Fibre	Cellulose	Hemi-celluloses	Lignin
Cotton	99 [10]	0 [10]	0 [10]
Linen	71 [10]	18.5 [10]	2 [10]
Jute	65.2 [11]	22.2 [11]	12 [10]
	45–63 [12]	>18 [12]	10.8 [11]
			13.7 [12]

Accelerated light ageing

The samples were aged in the two lightboxes for approximately 30 Mlux.hours; assuming the reciprocity principle holds [13], this dose corresponds to exposure for 10 hours a day at a level of 80 lux for 100 years. The first lightbox was a Microscal LFT1E (model 500) lightfastness tester fitted with a 500 W Philips ML lamp. The Philips ML lamp is a combined tungsten and mercury discharge fluorescent lamp that mimics daylight. The UV content in the Microscal lightbox was approximately 600 μW.lumen^{-1} and the average illuminance at the sample surface was 24000 lux. The second lightbox was purpose-built and fitted with eight Philips 18W/930 TL-D 90 deluxe fluorescent lamps. These lamps are the same as those used in many of the galleries at the British Museum. The UV radiation was filtered using a polycarbonate sheet to give UV levels inside the lightbox that varied between 1 and 2 μW.lumen^{-1} with an average illuminance at the sample surface of 15000 lux. For convenience, the Microscal lightfastness tester is hereafter referred to as 'lightbox I', and the purpose-built lightbox as 'lightbox II'.

It has been reported that humidity has little effect on the photochemical loss of tear strength of paper [13], so no measures were taken to control the relative humidity inside the lightboxes. The relative humidity and temperature inside the two lightboxes were monitored using Hanwell Humbug data loggers; the relative humidity and temperature in lightbox I were 26±6% and 35±3°C during the tests, while the environment in lightbox II was maintained at 28±5% and 22±2°C.

Mechanical tests

The textiles were tested using an Instron testing machine both in the state that they were received from the supplier and after photo-ageing. The gauge length of the samples was 80 mm. The samples were extended at a test rate of 20 mm per minute. The mechanical strength of the fabric was determined as the maximum load before failure.

Colour measurements

The colour of each sample was measured using a Minolta CM-2600d spectrophotometer. The sample area was 8 mm in diameter. For the purposes of colour measurement, UV radiation was not filtered from the illuminant and specular light was included in the measurements. Each measurement was repeated four times and the average value was recorded. The results are expressed as CIE (Commission Internationale de l'Eclairage) L*, a*, b* coordinates using the standard illuminant D65 as reference and the 10° supplementary standard observer [14]. The overall colour change, ΔE_{00}, was calculated using the CIE 2000 formula [15]. To give an idea of the scale of change monitored, a ΔE_{00} of approximately 1.5 corresponds to a visually perceptible change [16].

RESULTS

Mechanical tests

The results of the mechanical tests are shown in Table 2; note that the scatter in the results is relatively large, probably as a result of the inhomogeneous texture of the fabrics.

The linen and jute samples photo-aged in lightbox I became considerably weaker after photo-ageing: the linen textiles lost approximately 25% of their initial strength and the jute textiles 30%. In contrast, the strength of the cotton samples was not affected. In lightbox I, the UV radiation was not filtered. UV irradiation can result in a decrease in the degree of polymerisation of cellulose, but it has been reported that only wavelengths shorter than 310 nm can photolyse pure cellulose [2]. The emission of the Philips ML lamp in this region is very low and it is unlikely that cellulose degraded significantly during the experiment. It is more likely that the loss in mechanical strength in jute and linen is due to the presence of lignin. Given the much lower lignin content of linen compared to jute, it is surprising that the mechanical strength of the linen samples decreased almost as much as the jute samples. The linen fabric possibly contains photo-sensitizers, such as transition metals, which could be responsible for cellulose chain scission [7]. The cotton textile does not contain lignin and this probably accounts for the fact that the mechanical strength of the cotton samples was not affected. These results show that UV radiation can cause mechanical weakening of certain cellulose-based fabrics.

The mechanical strengths of the samples photo-aged in lightbox II were not significantly different from the samples as received. These results suggest that UV-filtered light does not affect the mechanical strength of cellulose-based fabrics under the conditions used in the experiments.

TABLE 2. Mechanical strength before and after photo-ageing in the two lightboxes

	Maximum load at failure (N)		
Textile	As received	Lightbox I	Lightbox II
Cotton	261±52	273±32	269±32
Linen	372±41	280±20	402±72
Jute	705±28	476±24	743±67

Note: figures are ± standard deviation for a set of five samples.

TABLE 3. L*, a*, b* coordinates and ΔE_{00} values for the samples photo-aged in lightbox I, before and after ageing

	As received			Photo-aged			
Textile	L*	a*	b*	L*	a*	b*	ΔE_{00}
Cotton	85.01	2.06	11.22	90.78	0.11	6.26	5.65
Linen	65.18	1.65	10.25	80.14	2.08	11.33	11.25
Jute	58.95	5.80	16.47	65.13	6.63	28.73	8.19

TABLE 4. L*, a*, b* coordinates and ΔE_{00} values for the samples photo-aged in lightbox II, before and after ageing

	As received			Photo-aged			
Textile	L*	a*	b*	L*	a*	b*	ΔE_{00}
Cotton	85.33	2.01	10.91	87.67	0.69	7.73	3.12
Linen	64.82	1.60	10.36	71.44	2.57	10.23	5.39
Jute	58.79	6.42	17.38	66.14	3.60	17.57	7.00

Colour change

The data in Tables 3 and 4 indicate that all the fabrics changed colour after exposure to light and that the colour change was greater when ageing was carried out in lightbox I, in which UV radiation was included. The cotton and linen fabrics became visually much lighter in colour, as reflected by the change in the L* (lightness) values. This was also the case for the jute samples aged in lightbox II. Lightening in these samples is probably due to the destruction of chromophores by light. In contrast, the colour change for the jute samples in lightbox I was mainly yellowing, as can be seen from the large increase in b*. Lignin is known to form yellow-coloured products when exposed to UV radiation and it has been reported that the intensity of yellowing in cellulosic fibres is dependent on the lignin content [17]. As shown in Table 1, jute contains approximately 12% lignin and this would account for photo-yellowing. Unlike jute, linen did not yellow when exposed to UV radiation; linen contains only approximately 2% of lignin and the concentration of chromophores produced during photo-ageing was perhaps too low to affect the colour measurably. Alternatively, the linen textile may have been treated during processing using antioxidants or UV screens to prevent photo-yellowing. These results show that exposure to light can be detrimental to textiles, even when UV radiation is filtered.

CONCLUSIONS

Cotton, linen and jute textiles were exposed to a light dose of 30 Mlux.hours in two lightboxes, one with light with a high UV content and the other with the UV radiation filtered. The mechanical strength of the jute and linen samples aged in the lightbox with a high UV content decreased significantly, which was attributed to the high lignin content in jute and to the possible presence of photo-sensitizers in linen. The mechanical strength of the cotton samples was not affected by UV radiation under the conditions used. In contrast, for the lightbox with UV radiation filtered from the illuminant, the samples did not show any signs of mechanical weakening. There was a significant change in colour for all the samples, although the change was higher when UV radiation was included. The jute samples yellowed, which has been attributed to their higher lignin content compared to cotton and linen. These experiments suggest that visible light does not affect the mechanical strength of modern undyed cellulose-based textiles, although it is responsible for changes in colour. Until the 1980s, light-sensitive objects were often displayed in the British Museum (as in

many other museums) in daylight without UV filtration on windows and skylights. It is possible that the mechanical weakening of fabrics reported by conservators is a post-irradiation effect, following earlier exposure to UV radiation. Post-irradiation degradation is an effect that has been known for more than 60 years; see for example the work of Havermans and Dufour [7]. Alternatively, in the case of historical fabrics, mechanical weakening could be linked to a treatment applied to the fabrics, such as the use of mordants or dyes.

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MATERIALS AND SUPPLIER

- Cotton canvas CC31, artist linen L36 and jute tarpaulin J65: Whaleys Ltd, Harris Court, Great Horton, Bradford BD7 4EQ, UK. Email: info@whaleysltd.co.uk

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An elusive stone: the use of variscite as a semi-precious stone

Andrew Middleton, Susan La Niece, Janet Ambers, Duncan Hook, Richard Hobbs and Guy Seddon

Summary The analysis of the stone beads from one of two gold necklaces found in a Romano-British grave near Gillingham, Kent, using non-invasive Raman microscopy showed that the beads are of garnet and emerald. The second gold necklace is set with seven green beads. These are very similar in appearance to weathered green glass but X-ray fluorescence analysis suggested that the beads are composed essentially of aluminium phosphate, leading to the interpretation that they may be variscite; this was confirmed by X-ray diffraction analysis.

Variscite has been reported only rarely from Romano-British contexts but polished beads and pendants of variscite (often referred to as *callais* or *callainite*) have been reported relatively frequently from Neolithic sites in Brittany and elsewhere in north west Europe. Visual identification of variscite is not straightforward and the ease with which it may be confused with weathered green glass (a material that is relatively common from Roman contexts) suggests that perhaps the striking difference in abundance between Neolithic and Roman contexts is apparent rather than real. The study emphasizes the need for analytical investigation of finds of 'weathered green glass' from Roman contexts, beyond visual examination.

INTRODUCTION

An archaeological investigation was undertaken by Pre-Construct Archaeology on land at Grange Farm, Gillingham, Kent, between October 2005 and May 2006. The site was positioned upon the northern slope of a hill, overlooking the River Medway and was continuously exploited from the Late Iron Age until post-Mediaeval times. Roman occupation of the site seems to have occurred soon after the conquest of Britain. In a tomb, constructed in the third century AD alongside a metalled road, necklace chain fragments were discovered on top of a collapsed tessellated surface.

The tomb contained the lead coffin of a teenage girl and "two gold necklaces were found overlying the grave but no further goods were found with the skeleton" [1; p. 3]. The two necklaces (illustrated in Figures 1 and 2) may have been placed as funerary offerings or be grave goods from another, robbed out, coffin within the same tomb.

In an unpublished report, Hobbs indicated several parallels for the necklaces from continental Europe [2], based in part on suggestions by Sas [3]. One parallel is provided by a child's grave from Bonn [4; No. 99e]; another is a more elaborate necklace from Pouilly-sur-Saône [4; No. 111]. Parallels for the terminals on the fragment of a necklace can be found on items from Archar, Bulgaria and from a third-century tomb in Lyon [5; pp. 212–213; Figure 30j].

The two items were declared under the terms of the Treasure Act and the original purpose of our investigation was to conduct analyses to form the basis of a report to the Coroner. It quickly became apparent however that these finds were of particular interest and, with the agreement of the excavators, a more detailed investigation of the materials used was undertaken. Several techniques were used including optical microscopy, X-ray fluorescence analysis, Raman spectroscopy and X-ray diffraction, as described below.

ANALYSIS AND INTERPRETATION

The gold chains

The metal of the two necklaces was analysed using non-invasive, non-destructive X-ray fluorescence (XRF) analysis.

FIGURE 1. Fragmentary necklace from Grange Farm, Gillingham, Kent. No. KKGF 03 (205). sf234, third century AD

FIGURE 2. Fragmentary necklace from Grange Farm, Gillingham, Kent. No. KKGF 03 (205). sf233, third century AD

A Bruker Artax micro-XRF spectrometer with a molybdenum tube (operated at 50 kV, 0.8 mA) was used. The areas to be analysed were not prepared in any way, so that the analyses may be subject to error due to the effects of surface enrichment of the gold alloy during burial. The long chain was found to contain 85–88% gold with 7–10% silver and 2–4% copper, the shorter chain, 90–93% gold, 3–6% silver and 1–3% copper.

Identification of the gemstones

The gemstones were analysed using Raman spectroscopy. This too was non-invasive and non-destructive and was carried out on unprepared surfaces of the red and green stones. A Dilor LabRam Infinity Raman microscope equipped with two lasers (a green Nd:YAG laser at 532 nm and a near infrared diode laser at 785 nm) was used. Spectra were compared with a British Museum in-house database of standards. Analyses of the red stones on necklace KKGF 03(205).sf234 showed that these are all garnets, probably close in composition to the magnesium-rich garnet, pyrope. Analysis of the bright green stones on the longer necklace fragment showed these to be emeralds. However, it was not possible to obtain useful spectra from the rather dull green stones of the shorter necklace fragment, probably because of surface alteration/contamination during burial.

Examination of these dull green stones using a binocular microscope revealed that they have pitted surfaces, with small cavities containing minute 'globular' (botryoidal) aggregates. The colour of the beads varies both from one bead to another and also within a single bead. Based

upon these microscopical observations, it was thought that the beads might be of weathered green glass. However, the results of XRF analysis did not support this interpretation. Several beads were analysed using the Artax spectrometer: for these analyses helium gas was used to flush the analysis area in order to improve detection of light elements. The spectra obtained indicated that the proportion of silicon was very low, not consistent with the beads being made from glass. Instead, the XRF analyses indicated that the beads contained high proportions of aluminium and phosphorus, together with small amounts of potassium, titanium, chromium and vanadium. Consideration of this rather unexpected composition suggested that the beads might be variscite, a hydrated aluminium phosphate mineral. A very small sample was removed from one of the beads for analysis using a Debye-Scherrer X-ray powder diffraction (XRD) camera. Comparing the resulting diffraction pattern with the ICDD database (International Centre for Diffraction Data, Pattern 25-18) confirmed the identification of the material of the bead as variscite.

Variscite is a member of a group of minerals that includes several arsenates and phosphates with a general chemical formula $AXO_4 \cdot 2H_2O$, where A can be aluminium (Al^{3+}), iron (Fe^{3+}), chromium (Cr^{3+}) or indium (In^{3+}), and X may be arsenic (As) or phosphorus (P). The most commonly occurring minerals of this group are strengite ($FePO_4 \cdot 2H_2O$) and variscite ($AlPO_4 \cdot 2H_2O$); there is a compositional series between the two end-member compositions with varying proportions of iron and aluminium. Frost et al. have demonstrated that it is possible to distinguish between the various minerals of the variscite group on the basis of their Raman spectra [6].

DISCUSSION

Previous reports of variscite in Romano-British jewellery

Necklaces and bracelets of Roman date, comprising gold chains set with emeralds and garnets are relatively well known throughout the Roman Empire, including Britain [7; pp. 96–99]. Emeralds, in particular, were highly regarded by the Romans and Pliny wrote in his *Natural history* "… no colour has a more pleasing appearance. … there is nothing whatsoever that is more intensely green. … engravers of gemstones find that this is the most agreeable means of refreshing their eyes: so soothing to their feeling of fatigue is the mellow green colour of the stone" [8; book 37 XVI]. Sources of emerald are few and it is thought that emeralds used in the Roman world were obtained from the Eastern Desert of Egypt – see, for example, Aston et al. [9; pp. 24–25] or Sidebotham et al. [10]. In her account of these Roman gold necklaces, Johns commented on the use of green glass as a substitute for emerald and also on the use of other coloured glasses to imitate amethyst, sapphire and pearl [7]; see also Murdoch [11; Figures 168 and 169]. Johns [7], however, makes no mention of variscite and the number of published examples of the use of variscite in Roman jewellery from Britain is very low, as discussed below.

Most recently (but now almost 20 years ago!), Hooley reported the recovery of a small bead identified as variscite from excavations at the General Accident Head Office Extension site in York [12; p. 20]. In a fuller, unpublished report (we are grateful to its author for providing this report and for alerting us to previously published reports of variscite beads from Roman contexts), the bead (Find No. 1983/4.32 sf1044) is described as being octagonal in section and is dated to the late second to early third century AD [13]. The material of the bead was identified as variscite by Wilthew using a combination of elemental analysis (by XRF) and XRD. In his report, Hooley also refers to a second variscite bead from York (1981.12 sf35) that was found at the Rougier Street site; this faceted cuboid bead was dated to the mid-fourth century or later. Other reported finds are very few and Hooley commented that, "only half a dozen items of this material are known from Roman Britain". One example, a fragment of a stone finger ring (included amongst 'Miscellaneous objects of bronze') from excavations at Gadebridge Park, Hemel Hempstead was identified as variscite by Bimson [14; Figure 60; p. 138 item 151]. She used a combination of qualitative spectrographic analysis, which showed that the ring consisted mainly of aluminium and phosphorus, and XRD, which produced a diffraction pattern that could be matched with variscite. In Bimson's analytical report, published by Neal [14], it was noted that variscite is a rather rare mineral and that "this is the first time it has been identified [in Britain] in an archaeological artefact". The only other published report of variscite artefacts from Roman Britain that could be located is a record of three beads with octagonal cross-sections that were recovered amongst the small finds from Balkerne Lane, Colchester [15; p. 34 Nos. 1444–1446].

Variscite from Neolithic contexts in Brittany

For some time, pale to bright green beads and pendants (Figure 3) have been reported from many prehistoric sites in western Europe, especially in Brittany [16]. These beads are often described as being of *callais* or *callainite* but now are usually referred to as variscite. The terms *callais* and *callaina* were used by Pliny [8; book 37 LVI and XXXIII], but it is thought that Pliny was referring to turquoise, hydrated copper aluminium phosphate, rather than to variscite [16; pp. 227–229, 17]. Damour made chemical analyses of some *callais* beads from a tomb at Mané-er-Hroek, Locmariaquer and showed that they consisted of a hydrated aluminium phosphate [18]. Later analyses of some Breton beads by Lacroix (referred to by Forde [16; p.228]) confirmed Damour's finding that the Breton beads were made from a hydrated aluminium phosphate, similar to variscite. A further complication is added by analyses of a sample of *callainite* from Montebras, France reported by McConnell;

FIGURE 3. *Callais* beads from Lannec-er-Ro'h (British Museum Reg. No. 1875,0403.552–561) and a triangular pendant from Mané-er-Hroek, Morbihan, Brittany (1875,0403.823), *c.*4700–4300 BC

XRD analysis gave a powder diffraction pattern that could be "satisfactorily accounted for only by assuming a mixture of wavellite [another hydrated aluminium phosphate mineral] and turquois [*sic*; hydrated copper aluminium phosphate]" [19].

The 10 perforated beads and the sub-triangular, perforated pendant shown in Figure 3 were analysed using the Raman microscope. The resulting spectra are consistent with them being made from minerals of the variscite group, based upon comparison with spectra published by Frost et al. [6]. Thus, whilst not all of the green beads from Neolithic contexts that have been described variously as *callais*, *callaina*, *callainite* or variscite may be variscite in the narrow sense, rather than another closely related member of the variscite group of minerals, the term variscite would seem to be a useful way to describe the material that was exploited by Neolithic peoples and later by the Romans. More detailed mineralogical study may permit characterization of different geological sources and provenancing of particular archaeological finds – see below.

Geological occurrence and possible sources of variscite

Variscite is a naturally occurring, hydrated aluminium phosphate mineral. Typically, it is deposited under near-surface conditions in situations where phosphate-bearing waters are available. It occurs usually as nodules or veins of fine-grained material, ranging in colour from very pale green to a bright emerald green; less commonly it may be brown, yellow and (rarely) red [20]. It has been shown that the green colour arises from the presence of Cr^{3+} ions in the structure; small amounts of iron and/or vanadium found in some samples do not contribute to the colour [21]. Variscite is relatively widespread geologically, with several occurrences in Europe (it was named for Variscia, now Voigtland, in Germany); a particularly rich deposit near Fairfield in Utah, USA supplies much of the modern material that is used for jewellery (see, for example, Webster [22; pp. 365–366]).

It was suggested by Jobbins that the variscite used to make the beads found at Balkerne Lane, Colchester may have come from central Europe (see Crummy [15; p. 34]). Harrison and Orozco Kohler record that sources of variscite have been reported in Austria and the Czech Republic [23], quoting the observations of Meireles et al. [24]. A central European source for the variscite used for both the Neolithic and the Roman artefacts cannot be excluded, but the most probable source for the variscite used during the Neolithic is now thought to be northern Spain.

In north east Spain (Catalonia), at Can Tintorer, spectacular mines were dug during the Neolithic to extract variscite, which was worked into beads at a settlement adjacent to the mines (see Harrison and Orozco Kohler [23] and references therein). However, recent analytical work to characterize the various geological sources suggests that variscite for the beads and other ornaments found in Morbihan, Brittany was probably obtained from north western Spain in the provinces of Zamora or Galicia [25, 26].

Is there really so little Roman variscite?

It appears that the use of variscite in early north west Europe was extensive, with many beads and other worked items being recognized from Neolithic contexts. In later periods, however, the use of this material seems to have all but ceased, with very few published reports of its identification from archaeological contexts. Even during the Roman period, when there is evidence from Palazuelo de las Cuevas, Zamora in Spain that variscite was being exploited [23], the number of finds is very low. There are no obvious reasons why variscite should have survived better in Neolithic sites compared to later sites, so the observed difference in abundance may simply indicate that the quantities of material extracted and worked by the Romans (and other post-Neolithic cultures) were very small. However, it may be that the apparent difference in abundances between the Neolithic and later periods reflects a failure to identify

variscite from the later contexts. But why should recognition of variscite from Roman sites be less reliable than from Neolithic contexts?

Underlying any failure to recognize variscite in artefacts from Roman contexts may be the ease with which it may be confused visually with weathered glass – a point made by Hooley [13]. As described above, glass is a material that is known to have been used by the Romans to imitate natural gemstones in jewellery. On Roman sites, glass is perhaps perceived as a more likely material than variscite and it is perhaps significant that in each of the published instances when variscite has been recognized from Roman contexts in Britain, its identification has depended upon a combination of chemical and mineralogical analysis. Thus, critical to the identification of variscite from Romano-British contexts has been a recognition of the need for some analysis beyond visual observation. When considering the nature of such material from Neolithic contexts, however, the choice is more limited and glass is certainly not a contender!

SUMMARY AND CONCLUSIONS

The present study of two items of Roman jewellery from Gillingham in Kent has shown that the chains are of gold alloyed with a small proportion of silver and a trace of copper. One of the necklaces (Figure 1: No. KKGF 03 (205).sf234) is set with emeralds and garnets. The stones from the second item (Figure 2: No. KKGF 03 (205).sf233) have been identified as variscite. The identification of variscite in Roman jewellery – and in post-Neolithic material generally – is unusual, whereas it is well known (though often referred to as *callais* or *callainite*) from Neolithic contexts in north west Europe. A review of previously reported finds of variscite, together with the present observations, suggests that the rarity of variscite in Romano-British contexts may be apparent rather than real and arise from the ease with which it may be confused with weathered green glass, a material that was used widely in the Roman world. This emphasizes the need for careful scrutiny of such finds and the application of techniques for chemical and mineralogical analysis.

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MATERIALS AND SUPPLIERS

- Raman microscope: HORIBA Jobin Yvon Ltd, 2 Dalston Gardens, Stanmore, Middlesex HA7 1BQ, UK. Email: info@jobinyvon.co.uk
- Micro XRF: Bruker AXS Ltd., Banner Lane, Coventry CV4 9GH, UK. Email: info@bruker-axs.co.uk
- XRD database: The International Centre for Diffraction Data, 12 Campus Boulevard, Newtown Square, PA 19073-3273, USA. Email: info@icdd.com

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The emperor's terrapin

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Summary The exceptionally large (48.5 × 32 × 20 cm) and naturalistic stone carving of a terrapin in the collections of the British Museum was found in 1803 in the Mughal fort at Allahābād, northern India, built during the reign of emperor Akbar, 1556–1605. The carving is thought to date from the first half of the seventeenth century, possibly to the reign of emperor Jahāngīr (1605–1627) who was a keen naturalist and a patron of jade carving. The mineralogical composition of the grey-green material of the terrapin was identified by Raman spectroscopy as nephrite jade. Shallow fractures in the material show that a large boulder from an alluvial source was used for the carving. The unusual, banded appearance of the nephrite suggests it was obtained from a small alluvial deposit in central Asia rather than the well-known sources near Khotan, in north western China, or in the region of Lake Baikal, Siberia.

The hardness and exceptional toughness of nephrite render the material difficult to work, and the technology used to carve the terrapin were also investigated. Following an optical survey of the carved features, detailed silicone moulds were made of various features bearing tool marks for examination by scanning electron microscopy. These indicated that the large carving was predominantly worked with non-rotary tools. Diamond, and possibly also corundum, abrasive appears to have been used with various saws and broader files to facilitate the working of the jade. The fine shaping of the terrapin was achieved with diamond-pointed tools. The results demonstrate that an exceptionally large jade boulder was transported from a distant source and carved by skilled lapidaries over a long period of time, suggesting that this terrapin was made for a prestigious person.

INTRODUCTION

The exceptionally large, naturalistic grey-green stone carving of a terrapin in the collections of the British Museum (Figures 1a and 1b) was found during engineering work in 1803 in a cistern within the Mughal fort at Allahābād, northern India, and brought to England by Lieutenant General Alexander Kyd of the Bengal Engineers. The carving has been identified as a female *Kachuga dhongoka*, commonly known as the Indian dhongoka terrapin or three-striped roof turtle, a species native to the tributaries of the River Ganges, including the River Jumna, which joins the Ganges at Allahābād. The fort was built by the third Mughal emperor Akbar (1556–1605) and occupied by crown prince Shāh Selim (1599–1604), who became emperor Jahāngīr (1605–1627). It has been suggested that the terrapin may have decorated a pool in the palace gardens within the fort. On stylistic grounds, the carving is thought to date from the first half of the seventeenth century, possibly to the reign of Jahāngīr who was a patron of jade carving and a keen naturalist.

Museum curators have assumed that the terrapin is jade and, prior to the natural history collections being moved to South Kensington in the late nineteenth century, it was displayed alongside large jade boulders from Siberia in the Mineral Gallery. The first half of the seventeenth century is early for a jade carving as large as the terrapin and the occurrence of such pronounced banding on jade (see Figure 1a) is also unusual. In preparation for a touring exhibition within the 'Museum in Britain' programme, it was desirable to confirm the mineralogical composition and investigate the Mughal techniques of carving. Previous studies undertaken by two of the authors, Sax and Meeks, have shown that the fine detail preserved on the carved features of hard stone artefacts such as jade is ideal for the study of ancient lapidary technology. The use of various tools and techniques can usually be recognized from the characteristic morphology of the 'tool marks'.

FIGURE 1. Seventeenth century, Mughal period, grey-green nephrite jade terrapin (1930,0612.1), 20 cm high, 48.5 cm long, 32 cm wide: (a) front view showing the pronounced grey banding of the material; (b) side view showing shallow fractures around the lower side of the shell that indicate a boulder from an alluvial source was used as raw material

METHODS OF EXAMINATION

The mineralogical composition of the material of the terrapin was identified by Raman spectroscopy (Jobin Yvon LabRam Infinity spectrometer), using a low energy, green (532 nm) laser with a maximum power of 2.4 mW at the sample and an external beam path. The spectra produced were compared with those of standards from a British Museum in-house database. This method of analysis allows totally non-intrusive identification of many minerals and has been widely exploited in the examination of supposed jade objects [1].

The approach adopted to study the carving techniques was based upon experience of an earlier investigation to identify methods of engraving on Mesopotamian quartz cylinder seals dating from the late Chalcolithic period to the early Iron Age, *c.*3000–400 BC, which was subsequently applied to jade carving in China [2, 3]. The large carving of the terrapin was first examined for tool marks using a headband magnifier (×2.3). Features bearing evidence of tool marks were selected for examination by scanning electron microscopy (SEM, a JEOL JSM 840), using secondary electron imaging or a scintillator backscattered electron detector. Detailed impressions were made of six features with silicone moulding material without any risk of damage to the terrapin, enabling the tool marks to be examined in the high vacuum chamber of the SEM. Another advantage of moulding is the ability to examine deeply carved parts of an object that are difficult to view directly and would also have been difficult to shape and polish. Because tool marks are often preserved in recessed surfaces, such areas to the side of the neck under the shell were also moulded. The moulds were mounted on aluminium stubs before coating with gold for examination by SEM.

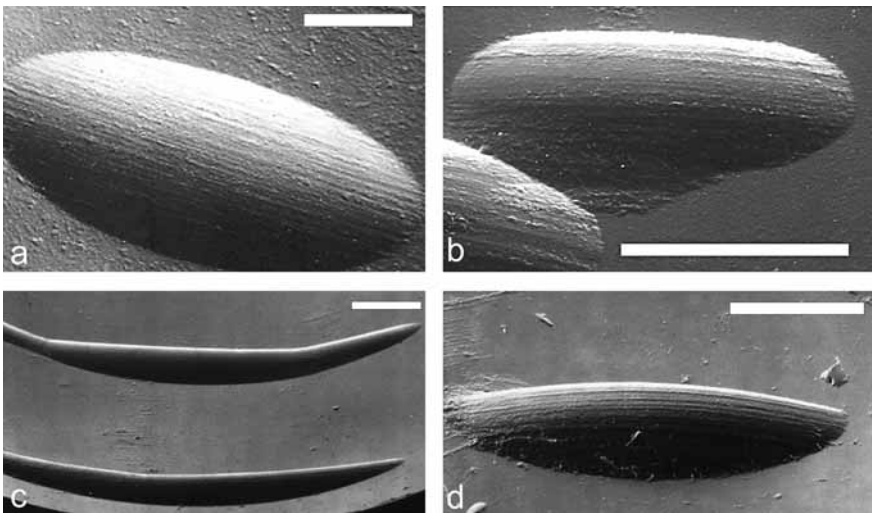

FIGURE 2. SEM images of moulds of features produced experimentally on convex quartz surfaces. The shapes in plan view of (a) sawn and (b) wheel-cut features may be very similar. Profiles of depth, seen from the side of (c) sawn features and (d) wheel-cut features are usually very different, enabling a distinction to be made between the two techniques (scale bars 1 mm)

Following the criteria established by Sax et al., the use of various lapidary tools was recognized by comparing the characteristics of the tool marks on the terrapin with those of standard features produced experimentally on hard stones with a range of techniques, tools and abrasive materials [4]. By considering several characteristics, it is usually possible to distinguish between individual tools, for example, saws and wheels (i.e. disc-shaped tools), Figure 2.

MATERIAL OF THE TERRAPIN

The grey bands and grey-green matrix of the stone were shown by Raman spectroscopy to be nephrite, one of the two main varieties of true jade. Nephrite is an amphibole mineral, the composition of which can vary from the magnesium-containing tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) to the iron-containing ferro-actinolite ($Ca_2Fe_5Si_8O_{22}(OH)_2$).

The exceptionally large size and distinct appearance of the jade suggest the raw material originated from an unusual geological source. Textual evidence discussed by Chandra and Skelton indicated that nephrite was obtained by the early Mughal court from sources in Xinjiang, now the westernmost province of China but then an independent central Asian kingdom [5, 6]. During a hazardous journey, the raw jade would have been carried around the Taklamakan Desert to Kashgar and then over the Karakorum Mountains to Kashmir and northern India. The alluvial pebbles and boulders collected from the banks and beds of the Black Jade River and the White Jade River near Khotan are thought to have been used by the Chinese for carving as early as the tenth century BC [7]. The size of these pieces was however generally limited. Larger blocks, such as the colossal slab of dark green jade used to cover the tomb of the Mongol conqueror, Tīmūr, at Samarkand in 1404, appear to have been obtained occasionally from the primary sources of nephrite in the Kunlun Mountains, south of Khotan. Material was not regularly quarried from these sources until the eighteenth century, in response to increased demand from the Chinese imperial court. Furthermore, the pronounced colour patterning, relatively high opacity and grey-green colouring of the Mughal terrapin contrast with the generally plain colouring and greater translucency of the material from Khotan, which usually ranges from white to dark green or may be yellow-green [8].

Visual examination showed that a large boulder from an alluvial source, rather than a block from a mountain source, was used for the terrapin. Numerous shallow fractures on the side of the shell form wave and mosaic patterns (Figure 1b) that are consistent with damage incurred as the jade was carried and tumbled downstream from a mountain source by torrents of water released by melting snow. It is unlikely that the Mughal material originated from the sources of large boulders in the Sayan Mountains to the west of Lake Baikal, Siberia, as these sources were not discovered until the mid-nineteenth century and do not include banded material [9]. Although grey-green and mottled green nephrite is found at Qaidam, Qinghai province, China [8], a more likely source for the material of the terrapin is central Asia, the homeland of the Mughal ancestors. Several small alluvial deposits have recently been reported and grey banded material is known [10].

CARVING TECHNOLOGY

Traditional methods of carving in India

Nephrite is of moderate hardness, with a Mohs' scale of hardness, H, of 6–6.5. It is therefore harder than iron and

bronze so that it cannot be worked using metal tools alone. The mineral is also exceptionally tough and the methods used to shape and decorate nephrite rely on time-consuming abrasive processes rather than techniques of flaking. The fine abrasive sands and ground stones being used in China in the first half of the twentieth century included quartz (H = 7), garnet (H = 7–7.5) and corundum (H = 9, see below) [11]. All are harder than nephrite. The abrasives were graded from coarse to fine, the finest producing the smoothest surfaces. They were mixed with water and applied to iron or steel tools, some of the grit embedding or 'charging' itself into the surface of the tool while a slurry remained on the surface to be worked against the jade.

Referring to the Mughal methods of carving jade, Chandra quoted Francois Bernier, who visited the Mughal Empire between 1665 and 1668: "it [jade] is so hard as to be wrought only with diamond powder" [5]. Diamonds, the hardest mineral known (H = 10), were available from one or more sources in India, for example, the former kingdom of Golconda, now in the state of Hyderabad [12]. Diamond lapidary tools have a long history in India; quartz beads were perforated with diamond-pointed drills probably as early as the first millennium BC [13], and diamonds may also be crushed for use as an abrasive.

Chandra's account of the traditional methods employed to work jade in northern India during the early twentieth century provides a further insight into likely Mughal lapidary practices [5]. Initially, the raw material was sawn to size using a wire strung between the ends of a bow. The wire was charged with corundum abrasive and worked backwards and forwards by one or two men; water was used as a lubricant, Figure 3. Opaque crystals of corundum (aluminium oxide) occur commonly in India [14]. They may also be ground to provide a high-grade natural abrasive, second only in hardness to diamond (the rarer transparent varieties of corundum – ruby and sapphire – are valued as gems). Once the material had been shaped roughly by sawing, the jade surfaces were finely shaped (then polished) with rotary grinding wheels, which were used with bow-driven lathes. A wheel was attached to the end of an iron spindle/axle, mounted horizontally between wood bearings; the string of the bow was wound around the spindle. Sitting on the ground, a lapidary would steady the lathe with one foot, hold the bow in the right hand and move it backwards and forwards to rotate the wheel; the jade was held in the left hand against the revolving wheel. Rotary wheels were also employed for carving jade in Iran during the twelfth century [15].

Methods of carving the terrapin

Traces of tool marks remain on the Mughal terrapin, particularly on recessed features. SEM observation of the fine detail of moulded tool marks provided evidence for several methods of carving. They involved the predominant use of non-rotary tools: saws and broader files (with long straight working edges), riffler files (with shorter working edges) and pointed tools.

Two straight marks or 'cuts' under the shell above the proper left rear foot appear to be mistakes made during an early stage of carving. The marks are 63 and 38 mm long and *c*.1 mm wide; Figure 4a shows a mould of the longer mark. The depth along an incised tool mark can easily be seen

FIGURE 3. Pencil and ink drawing by John Lockwood Kipling of a lapidary at Agra, India, 1870, using a traditional wire saw to cut a small stone mounted on a post. One end of the bow was hand held whilst the opposite end was balanced with a weight; the wire was charged with an abrasive mix from the bowl. *Drawing (0929/52) is reproduced by kind permission of Victoria and Albert Museum, London*

from the side of a mould, for example, in the SEM micrograph of the shorter cut, Figure 4b. In this oblique view of the mould, the cut protrudes upwards: the straight profile along the feature reflects the linear depth along the cut in the jade. Groups of relatively continuous, parallel linear striations are present along the surfaces of both features, Figure 4b. Straight features with similar characteristics of depth and surface texture to those of the two cuts were produced experimentally on hard stones, using a long straight metal blade or a metal wire held rigidly between the ends of a bow. The experimental tools were charged with an abrasive considerably harder than nephrite, either emery or diamond; they were applied with a lubricant in a backwards and forwards sawing motion, Figure 2a and 2c [2, 4]. The two cuts under the shell of the terrapin show that the jade boulder was initially 'rough' shaped as closely as possible to size using hand-held straight saws or wire saws. The width of the cuts indicates that the Mughal saw was less than 1 mm thick. It may have been iron or steel, similar to the traditional Indian saw illustrated in Figure 3 and those still retained in Hong Kong for the primary shaping of large jade boulders.

Numerous tool marks were seen on the mould of the recessed surface to the side of the neck under the shell. They comprise two principal types: relatively broad marks and fine striations, made during the fine shaping and smoothing of the terrapin. Three broad marks are indicated with arrows on the SEM micrograph in Figure 5a. The features may be straight or curved and as long as 2 to 3 cm. Experiments with diamond points and flint (a variety of quartz) tools showed that both materials are sufficiently tough and hard to score nephrite without an abrasive. The tools produce different surface textures. Features worked with diamond points (Figure 5b) are more sharply defined than those worked with flint tools (Figure 5c) and resemble those on the terrapin, Figure 5a. Following the evidence documented by Bernier (alluded to above) that diamond powder was available in the seventeenth century, it seemed reasonable to infer that the fine shaping of the terrapin was mainly achieved by scoring the surfaces in multiple directions with diamond-pointed tools [5].

Examples of the second type of mark, fine striations, can be seen in the upper left corner of Figure 5a. Elsewhere on this mould, the marks clearly form groups of parallel linear striations, characteristic of hard abrasives. Observation of features produced experimentally on hard stones with metal files separately charged with emery and diamond

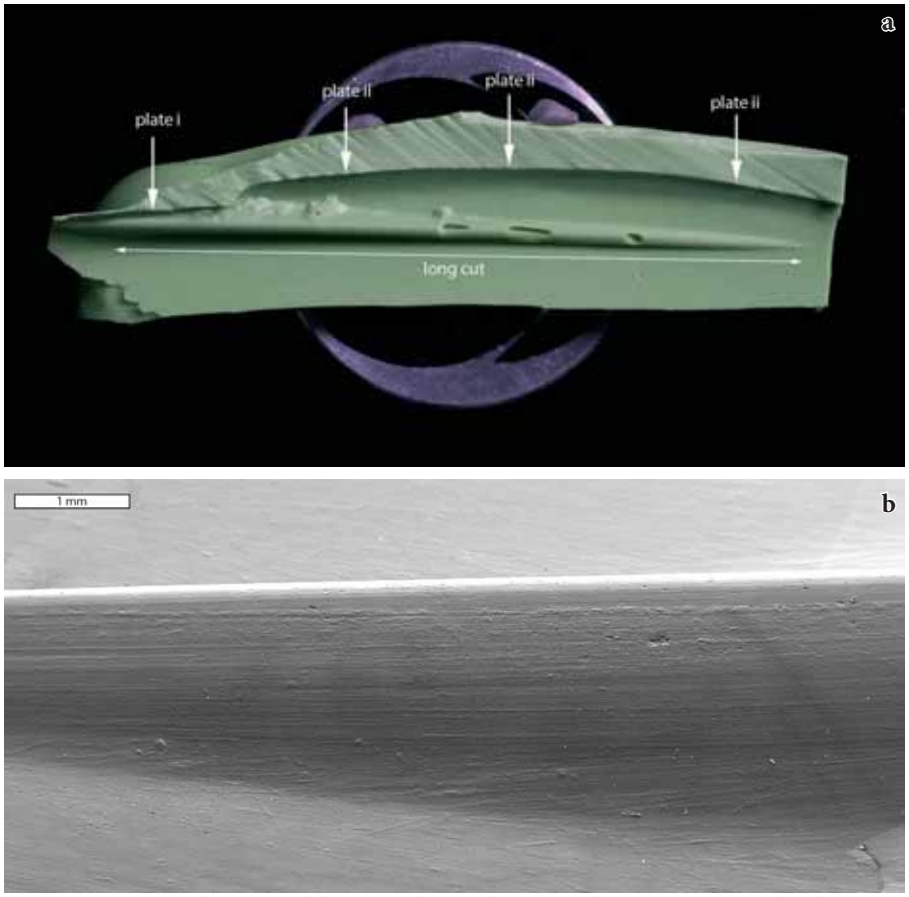

FIGURE 4. (a) Green silicone mould (mounted on an aluminium disc, appearing purple) of a 63 mm long cut in the surface under the shell. Vertical arrows point to the edge of the shell across two adjacent plates (i and ii); (b) SEM image showing the moulded side of a similar cut, 38 mm long. The cut protrudes upwards on the mould, across the image: the profile of depth along it is straight and the groups of parallel linear striations along the sides of the feature demonstrate that a non-rotary saw was used with a hard abrasive (scale bar 1 mm)

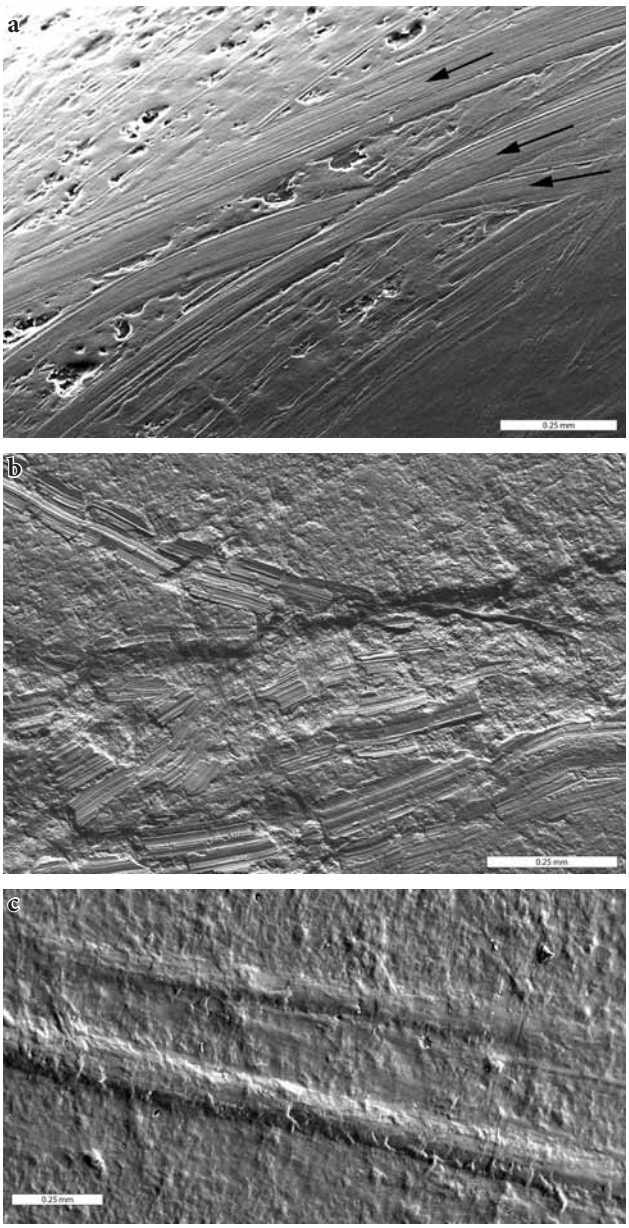

FIGURE 5. SEM images of moulds of: (a) recessed surface to the side of the neck under the shell of the terrapin (cavities in the surface are moulding faults); features produced experimentally on rough nephrite surfaces, using (b) a diamond-pointed tool and (c) a flint tool without an abrasive. The three broad tool marks arrowed across (a) were apparently cut with diamond-pointed tools (scale bars 0.25 mm)

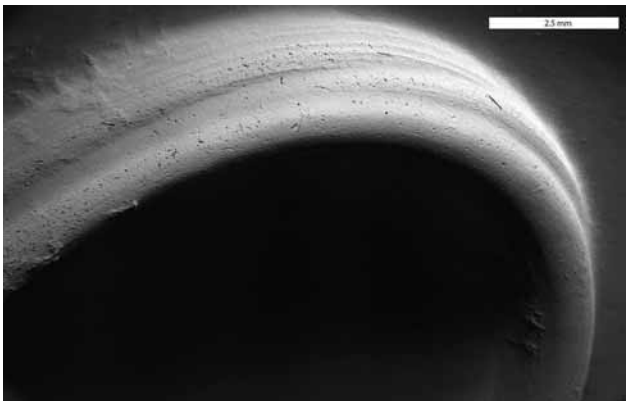

FIGURE 6. SEM image of the moulded details of an eye showing the outer edge was incised with a tubular drill (scale bar 2.5 mm)

abrasive mixes suggested the particularly sharp definition of some striations on the terrapin was achieved using diamond rather than corundum abrasive, as described by Bernier. The widths of the striations moulded from the terrapin vary, reflecting the use of abrasives of different grain sizes; increasingly fine abrasives appear to have been employed to smooth the surfaces of the terrapin prior to polishing. The linear characteristics of the striations indicate that the abrasives were applied with files (broader saws); these were frequently used alternately in perpendicular directions. Although fewer tool marks remain on the shell, these areas appear to have been ground smooth in a similar manner with hand-held tools. Smoothing the largely convex surfaces of the terrapin with the long working surfaces of files would have been straightforward, but smoothing the recessed surfaces that were inaccessible to straight files would have necessitated the use of riffler files, with shorter working surfaces. The rifflers may have been specially shaped with a curved surface or the end of a straight file may have been employed. The folds in the skin of the protruding neck were incised with small hand-held tools using a similar approach.

No evidence, such as curved striations or pronounced concave depths, was found on the terrapin for lathe-mounted rotary wheels. However, drills were employed to work the nostrils and the eyes. Although deposits of dirt/soil in the nostrils precluded moulding, a small wood rule revealed that the circular cavities, which are 3.5 mm in diameter, are remarkably deep at *c.*16 mm. The moulded details of the eye are seen in Figure 6: the annular mark and circumferential striations show that a tubular drill, *c.*17 mm in diameter and *c.*1 mm thick, charged with an abrasive mix, was used to outline the eye. The drills may have been lathe-mounted or hand-held, for example over a capstone, but in either case in the Mughal period the drill would probably have been bow-driven.

Thus, the jade was finely carved to reflect the natural form of a terrapin using predominantly non-rotary tools. The attention to fine detail is exemplified by the plates forming the shell. These were individually shaped with sloping surfaces so that the separation between plates was accentuated by the different heights of adjacent plates. This can be seen on the mould of the surface under the shell shown in Figure 4a, where the vertical arrows point to the profile of the edge of the shell across two adjacent plates (i and ii).

It is interesting to speculate on the time spent carving the terrapin. Hansford observed that it would take three lapidaries several weeks to saw a block of raw jade, estimated to be about 35 cm long and 24 cm high, in two [11]. Although the carving of the terrapin was accomplished with the advantage of diamond-pointed tools and diamond abrasive, both of which were rarely used for working jade in China, its production, achieved almost entirely with hand-held tools, would probably have taken at least a year.

CONCLUSIONS

The composition of the Mughal grey-green stone carving of a terrapin was confirmed to be nephrite jade by Raman spectroscopy. A single large boulder from an alluvial source was used for the carving. On the basis of the size of the boulder necessary and the distinct grey-green colouring, pronounced colour variation and low opacity of the material, it is unlikely that the raw jade originated from the well-known sources of nephrite in the region of Khotan, now in Xingian province, China. It is also unlikely that the boulder was obtained from the sources currently mined near Lake Baikal, Siberia. It seems possible, however, that the material derived from a small alluvial source in central Asia.

Optical and SEM observations of the tool marks remaining on the terrapin enabled the sequence and range of carving methods to be identified. The large piece was roughly shaped using non-rotary saws with long thin working edges, charged with an abrasive mix considerably harder than nephrite. Finer shaping appears to have been achieved mainly by scoring the jade surfaces with diamond-pointed tools. In the final stages of shaping and smoothing prior to polishing, files (or broader saws) and riffler files with shorter working edges were employed. These tools were charged with hard abrasives of successively finer grain size. Diamond abrasive and possibly also corundum abrasive were probably used. The only rotary tools used were drills, which were employed for working the nostrils and outlining the eyes. The examination demonstrated that, firstly, the exceptionally large jade boulder was transported from a distant source and, secondly, the carving was executed by skilled lapidaries over a long period of time. This suggests the terrapin was worked for a prestigious person.

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Aztec conch shell working: high-tech design

Caroline Cartwright and Nigel Meeks

Summary The nine Mexican turquoise mosaics in the British Museum have undergone intensive investigation to study the many natural materials selected for their manufacture. This paper describes the more detailed scientific study of one of these materials – conch shell. Using optical and scanning electron microscopy, it evaluates to what extent both the microstructural and decorative properties of conch shells were well understood by Aztec and Mixtec specialist craftsmen in central Mexico prior to the Spanish conquest in 1519. Sixteenth-century codices have shown the important role played by the form and colour of conches in Aztec cosmology, but this study reveals that these factors were not the only ones crucial to the selection of conch shell for use on the turquoise mosaics. The remarkable strength and toughness exhibited by the characteristic brick-and-mortar-like micro-architecture of conch shell enabled the mosaic craftsmen to fashion durable, three-dimensional components. In this context conch significantly outperforms the other species of shell present, whose use is restricted to small, flat, decorative tesserae (tiles). An interesting slant to this case study has been provided by materials technology scientists who have been publishing details of the remarkable potential of the conch shell structure for load-bearing applications in industry.

INTRODUCTION

For over a decade the nine Mexican turquoise mosaics in the British Museum have been the subject of intensive scientific investigation. This work characterized the variety of natural materials used in their manufacture and resulted in the publication of a popular book on the history, materials and techniques of the mosaics [1]. However, lack of space meant that much of the detailed research could not be included in this book; this contribution describes one such detailed scientific study. Using optical and scanning electron microscopy it evaluates to what extent both the microstructural and decorative properties of conch shells were well understood by Aztec and Mixtec peoples in central Mexico prior to the Spanish conquest in 1519. An interesting slant on this case study has been provided by recent publications from materials technology scientists, who have been highlighting the remarkable strength and toughness exhibited by the micro-architecture of the conch shell and its potential for load-bearing applications in industry.

METHODOLOGY

Optical microscopy, using a Leica stereo microscope, was carried out for the primary stage of examination of the nine turquoise mosaics in the British Museum collections. These comprise two masks (Am, St.400 and Am1987, Q.3), a double-headed serpent (Am 1894,-.634), a knife with flint blade (Am, St.399), a helmet (Am, +.6382), a human skull (Am, St.401), a jaguar (Am, +.165), a shield (Am, St.397.a) and an animal head (Am, St.400.a). This phase identified the raw materials used, which include wood, resin, turquoise, shell, malachite, lignite, pyrite, agave fibre bindings, leather and gold (and later additions such as pearls, glass and gemstones). While turquoise is clearly the predominant material, the use of shell is extremely significant. It is through these shell elements that a greater understanding is reached of the relative importance of three criteria in the Aztec understanding of technological mastery: these criteria are material properties, decorative qualities and symbolic significance within the Aztec cosmology.

To increase our understanding of Aztec shell technology, scanning electron microscopy was carried out. A JEOL 840 scanning electron microscope (SEM) operating under high vacuum conditions was used on prepared (gold-coated) samples of conch shell, to examine the microstructure and also the outer and inner surfaces of the body whorl. This was also used to examine gold-coated samples of *Spondylus* (spiny oyster) shell. A Zeiss EVO variable pressure SEM was used to examine the microstructure of uncoated specimens of *Pinctada* – mother of pearl.

RESULTS AND DISCUSSION

Optical microscopy

The combination of significant colours, raw material and iconography of the turquoise mosaics was intrinsic to their high status and the purposes for which they were made [1]. Optical microscopy revealed a number of interesting observations. Three main species of shell were identified: spiny oyster (*Spondylus princeps*), mother of pearl oyster (*Pinctada mazatlanica*) and conch (*Strombus gigas*). Although the colours of these three shell species played a highly significant part in the decorative designs of the mosaics (Figures 1 and 2), coloured shell was not selected indiscriminately, irrespective of species, simply for its hue. For example, although many red, pink and orange coloured shells, such as *Strombus pugilis* (fighting conch), were available to Aztec shell craftsmen, *Spondylus princeps* and other *Spondylus* species were preferentially selected on account of their symbolic, ritual and cultural importance. This association between *Spondylus*, blood and fertility extended far beyond the confines of the Aztec Empire [2]. Part of the value of *Spondylus* may be attributed to the difficulty of procuring them from the ocean; divers frequently had to recover them from depths of between 25 and 60 metres. This traditional predilection for *Spondylus* also introduced some technological drawbacks. As the common name suggests, these bivalves are covered with spines that have to be removed. The radial bands of each valve have to be ground smooth and polished before tesserae (small tiles) can be cut and shaped for incorporation into the mosaic design. If, for example, the vivid red, pink and orange *Strombus pugilis* had been selected, no spine removal would be needed and the already extremely shiny and flat coloured inner surface would have required cutting and shaping but no grinding and polishing. Furthermore, as described below, the microstructure of *Strombus* outperforms that of *Spondylus* in terms of toughness and strength. In a theoretical scoring system, therefore, *Spondylus* was selected primarily for its symbolic importance, then for its colours and lastly for its working properties.

An even more pronounced example of this process of raw material evaluation is provided by the use of the mother of pearl oyster (*Pinctada mazatlanica*). This bivalve species was also obtained by diving. The use of the silvery, iridescent shell of *Pinctada* on the turquoise mosaics is largely a combination of decorative effect and symbolism. Where used as eye inserts, for example on the mask of Xiuhtecuhtli (Figure 3), its nacreous (pearly) quality is intended to suggest reflective optical properties, giving this mask an arresting presence. On the jaguar figure, *Pinctada* is used freely to simulate the silvery sheen of the animal's pelt, reinforcing the fearful role of the jaguar in Aztec cosmology. However, the structure of *Pinctada* is even less stable than that of *Spondylus* – see below and Figure 4. The fragile *Pinctada* valves needed careful cutting and shaping with sharp-edged obsidian or flint blades to avoid fracturing and delamination. Its theoretical score sheet highlights the decorative and symbolic qualities offered by its silvery iridescence, but its working properties are problematic. On the jaguar figure, incised *Pinctada* tesserae display damage and fracture and, overall, there has been a high loss of tesserae from this figure.

FIGURE 1. Open mouth, right head of the double-headed serpent (Am 1894,-.634) showing the three-dimensionally carved white conch (*Strombus*) shell teeth and fangs set into resin mixed with red pigment

FIGURE 2. Back of a knife (Am, St.399) showing the eagle warrior's costume where geometric inserts of white conch are dramatically set against the green malachite and red spiny oyster (*Spondylus*) shell and incised white conch semicircles containing coloured resin

FIGURE 3. Mask of Xiuhtecuhtli (Am, St.400) with mother of pearl (*Pinctada*) shell eye inserts and white conch shell teeth

Hitherto it has been clear that the selection of *Spondylus* and *Pinctada* by Aztec specialist craftsmen has been less influenced by their working properties as raw materials than by their symbolic value and by their colour or iridescence. However, even at the primary stage of optical microscopic examination, it was apparent that the white conch (*Strombus gigas*) on the turquoise mosaics had to fulfil additional requirements. Figures 1 and 2 display the effective use of the whiteness of the conch juxtaposed against the varied blue and turquoise tesserae, the green of the malachite and the vivid red, pink and orange colours of the *Spondylus*. But there were a considerable number of useful bivalve and gastropod shells with white colours and smooth surfaces that Aztec or Mixtec craftsmen could have selected. Why was none of these chosen? Part of the answer lies in the great status and ritual significance of the conch in ancient Mesoamerican cultures, where it is routinely depicted in association with important people and events of the watery underworld. Such a symbolically charged mollusc would therefore be a natural choice of raw material for the prestigious turquoise mosaics.

The second part of the answer lies in the fact that throughout Mesoamerican and Caribbean prehistory, conch provided the raw material for heavy-duty functional tools such as axes and adzes [3], and was also fashioned into intricate jewellery and figurines. All these items needed to be carefully carved and most importantly, be hard-wearing and durable. Such properties were needed for key elements of the turquoise mosaics, such as the double-headed serpent, Figure 1. Here, far more was required than just the manufacture of small flat white shell tesserae, as the three-dimensional carving of the serpent teeth and fangs necessitated a strong and tough raw material for which conch was the perfect choice.

There are missing teeth on the double-headed serpent, but this is far less likely to be attributable to fracturing of the conch shell than to a failure of the resin to hold them in place, particularly as mixing hematite pigment with the resin to give the red of the serpents' mouths impacted on the latter's adhesive properties [4]. Likewise on the mask of Xiuhtecuhtli (Am, St.400), Figure 3, and on the serpent mask (Am1987, Q.3) where white conch shell was used for the original teeth, there are losses where the resin plus pigment bond has not held, but there is no damage to the extant conch teeth. The toughness of conch allowed the craftsmen to fashion discs with a central hole, which were used as firm surrounds for sockets containing pyrite eyes, as in the human skull mosaic and animal head. On the latter, a conch shell ring hook was carved as a suspension loop inserted into the top of the head. White conch shell forms the circular surround to a polished fragment of dark green, nodular malachite on the helmet. Figure 2 displays more than just the dramatic use of the brilliant white geometric conch shell inserts juxtaposed against the green malachite and red *Spondylus* tesserae on the back of the knife, it reveals the careful incising of semicircles into the conch shell tesserae for infilling with decorative coloured resin. These particular conch tesserae are themselves carefully carved into a subrounded semicircular shape. The point need not be belaboured that any raw material selected needs to be very stable to allow for such careful shaping and incising on such a small scale and conch satisfies these demands. It is noteworthy that the knife's mosaic haft reveals the use of more than just white conch shell. For the miniature details on the eagle warrior's face, the use of reddish *Spondylus* for the lips and eyes has been rejected in favour of the stronger conch shell, an orange-red variety in this instance. This may have been on account of the less reliable nature of *Spondylus* as a durable material for tiny pieces. There is some loss to the mosaic decoration on the eagle warrior's hands, which hold the end of the flint blade, but sufficient survives to show the careful use of pink and orange conch shell to mark out nails at each finger end. There is also striking use of large rectangular pink segments from queen conch (*Strombus gigas*) shell on the underbelly of the haft.

SCANNING ELECTRON MICROSCOPY

The Zeiss EVO variable pressure SEM was used to examine the microstructure of uncoated specimens of *Pinctada mazatlanica* mother of pearl shell. Figure 4 shows its characteristic laminated structure. Although it provides a lustrous, silvery iridescent nacreous surface that is attractive for decorative effects, this shell has little mechanical strength or toughness. The SEM image shows how the prep-

FIGURE 4. Scanning electron microscope (SEM) image of the laminated, friable microstructure of *Pinctada* mother of pearl oyster shell

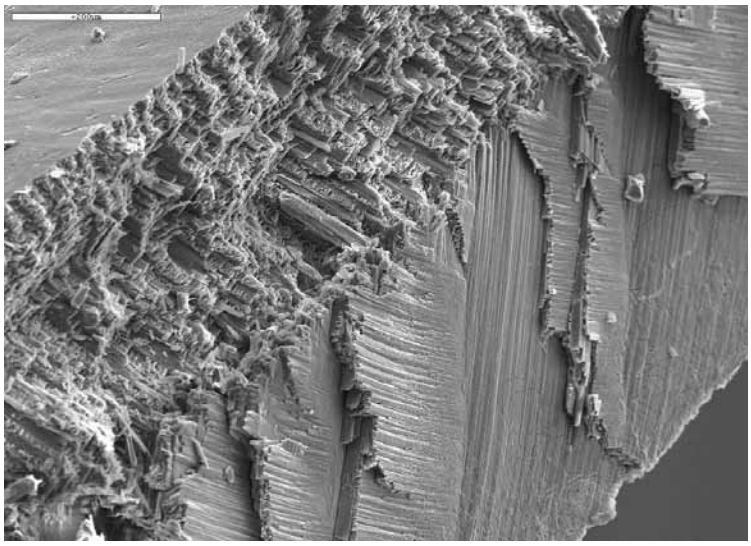

FIGURE 5. SEM image of the characteristic structure of *Strombus* conch shell

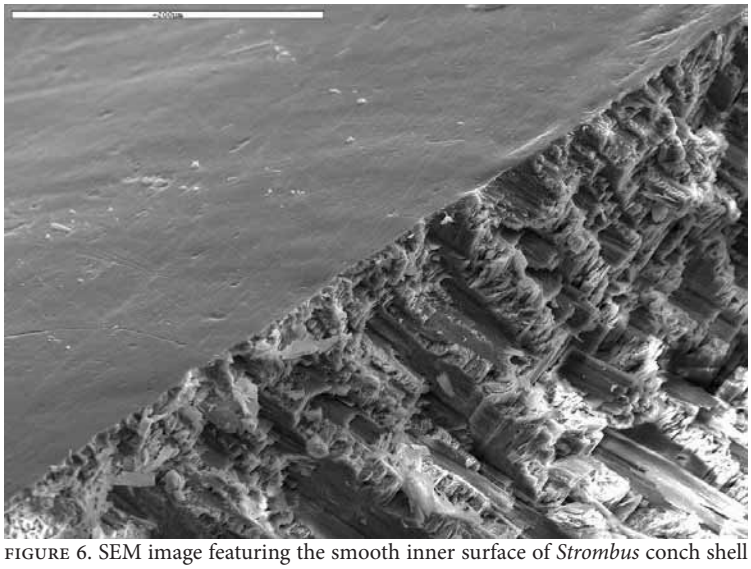

FIGURE 6. SEM image featuring the smooth inner surface of *Strombus* conch shell (showing at the top of the image)

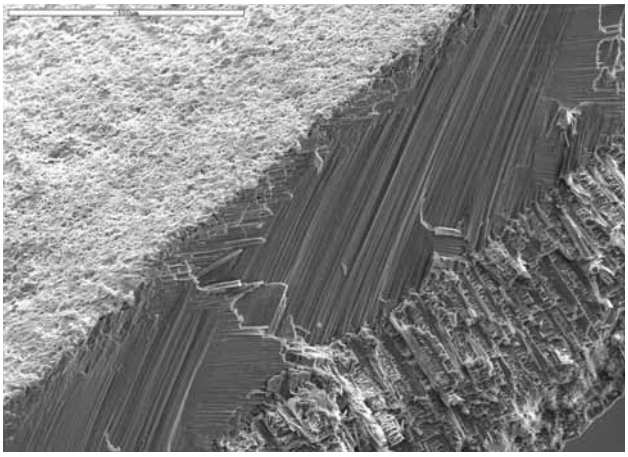

FIGURE 7. SEM image featuring the rough outer surface of *Strombus* conch shell (showing at the top of the image)

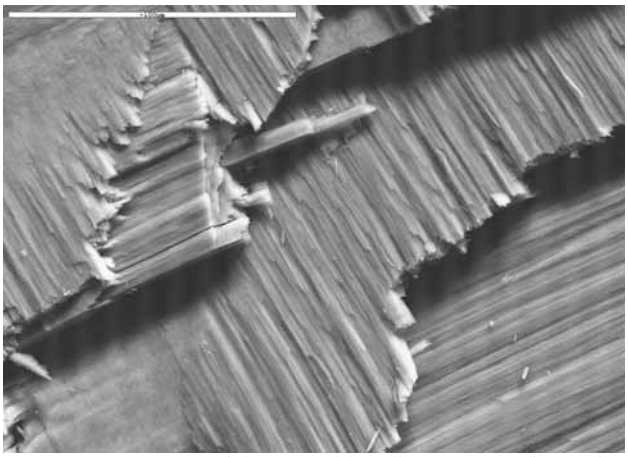

FIGURE 8. SEM image of the crossed-lamellar structure of *Strombus* conch shell

aration of one small sample for microscopy resulted in a series of stress fractures that fragmented the platy structure of the shell.

The JEOL 840 high vacuum SEM was used on gold-coated samples of conch shell to examine the microstructure (Figure 5) and also the outer and inner surfaces of the body whorl. Figure 6 shows the smooth flat inner surface of the conch shell that is in direct contact with the living body of the mollusc. Its relatively few imperfections render it ideal for use as mosaic tesserae; all that would be required is cutting, shaping and affixing to a substrate such as wood or bone. This inner surface contrasts markedly with the rough outer surface, Figure 7.

Materials scientists have recognized that conch shells owe their extraordinary mechanical properties to a hierarchically organized structure, Figure 5. This can be observed at a nanostructural level with single crystals of $CaCO_3$ of 4–5 nm, at a microstructural level with 'bricks' of 0.5–10 μm and, ultimately, with layers of 0.2 mm in the mesostructure [5].

The SEM examination revealed that conch shell has crossed-lamellar structure (Figure 8) and that the angle between two second-order lamellae is 70–90 degrees [6], thus forming a natural high-strength composite material. Studies of modern conch (*Strombus gigas*) shell have recorded that this material is 10 to 30 times stronger, and as much as 1000 times tougher, than its principal constituent aragonite ($CaCO_3$), because it has a brick-and-mortar-like micro-architecture. The proteins surrounding the aragonite crystals that make up 99% of conch shell change the toughness by permitting fractures to be absorbed without shattering the material [7]. Crack deflection, delocalization of damage and viscoplastic deformation of these organic areas are the most important mechanisms contributing to the unique mechanical properties of conch shells [5]. The high fracture resistance is correlated to the extensive microcracking that occurs along the numerous interfaces within the shell microstructure [8, 9]. *Strombus gigas* also has a remarkable capacity to regenerate tissue after the shell is damaged [10].

CONCLUSIONS

Strombus and *Spondylus* shells enjoyed elevated status within the Aztec cosmology and the iridescence of *Pinctada* shell mirrored reflective optical properties when used on objects. All three were selected by Aztec and Mixtec specialist artisans for incorporation into the Mexican turquoise mosaics on account of their ritual significance and decorative allure. However, only *Strombus* can claim to have been selected as much for its extraordinary working properties as for its gleaming whiteness and symbolic resonance. Scanning electron microscopy has revealed the highly ordered structure of conch shell that comprises calcium carbonate and a series of organic binders that underpin its toughness. The use of conch shell on the turquoise mosaics for purposes in which tensile strength and fracture toughness are important indicates that the Aztec and Mixtec craftsmen had an empirical understanding of conch shell's outstanding mechanical properties.

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Writing that cannot be erased: investigations of a box of pigmented inlays from the tomb chapel of an Old Kingdom noble

Janet Ambers, Rebecca Stacey and John H. Taylor

Summary The British Museum holds in its collections a box of pigmented inlays from the tomb of Nefermaat, a senior official of the Egyptian Old Kingdom (early Fourth Dynasty, *c.*2600 BC), collected by Sir Flinders Petrie in the late nineteenth century. The pieces relate to an early, and apparently rapidly abandoned, style of tomb decoration where shapes were cut into limestone slabs and the resultant hollows filled with coloured pastes. This box of inlays thus represents some of the earliest evidence for tomb decoration available for study and reflects a very different form of decoration from the tempera painting generally found in Egyptian tombs. In terms of the pigment component, the most unusual feature was the definite presence of malachite and the apparent absence of either Egyptian blue or green frit, the two frit colours which so dominate the conventional Egyptian palette. The findings for the organic fractions were even more unexpected. Analysis of solvent extracts by gas chromatography-mass spectrometry (GC-MS) showed the presence of fatty acids and diacids that are typical of degraded oils. Subsequent analysis by pyrolysis-GC-MS yielded mostly straight-chain (alkane/alkene) pyrolysis products, which are consistent with a polymerized lipid; this apparently extensive polymerization implies the use of a drying oil. Linseed is the only source of drying oil known to have been available in ancient Egypt, although a number of semi-drying types, such as safflower or poppy oil, may also have been available. The presence of such a medium is potentially extremely significant, as the use of oil binders in dynastic Egyptian painting is virtually unknown. The use of an oil binder is unprecedented for such ancient material and may demonstrate a previously unsuspected technology.

INTRODUCTION

One of the most immediate images brought to mind by the mention of ancient Egypt is of vividly coloured tomb paintings, depicting scenes from life in both this world and the anticipated next. These paintings are among the glories of the ancient world and the source of much information on all aspects of Egyptian life and belief. However, in our current state of knowledge, the methods used in their production seem to emerge almost fully developed at the beginning of the Old Kingdom, the first period in which the distinctive material culture of dynastic Egypt was fully established. Artistic styles and conventions are known to have changed over time, but the technical aspects of both the painting method (tempera on stone or dry plaster), and the (very limited) palette seem to have been established early and to have undergone remarkably few changes until the influence of the Greek/Roman world grew during the Late Period and succeeding eras [1]. This apparently sudden development is almost certainly illusory, resulting from the destruction of earlier examples of the evolving decoration of tombs [2; p. 55]. This study presents the results of examination for the earliest wall painting held in the collections of the British Museum, conducted in an attempt to establish any precursors of these fixed conventions.

THE TOMB CHAPELS OF NEFERMAAT AND ITET AT MEIDUM

Nefermaat and his wife Itet lived during the reign of Sneferu (*c.*2613–2589 BC), the first king of the Fourth Dynasty. Nefermaat was the son of an unnamed king, perhaps Sneferu himself, and held the titles Vizier and Overseer of all the King's Works. The large tomb shared by him and his wife consisted of two undecorated subterranean burial chambers with a common mudbrick superstructure above

in the form known as a *mastaba* (a rectangular, flat-topped building with sides inclined at a slight angle). Structures of this type had first appeared in the early dynastic period (First and Second Dynasties, *c.*3100–2686 BC), and it was the preferred form for elite tombs during the Old Kingdom. A cult place for the dead gradually came to be incorporated into the *mastaba*, evolving from a shallow niche cut in the eastern face. At the beginning of the Old Kingdom, the niche began to be extended into the mass of the superstructure to create a narrow chamber which served as the chapel for the cult. Later, the number of chambers multiplied until, by around 2300 BC, they sometimes occupied the entire superstructure. The eastern face of the *mastaba* of Nefermaat and Itet contained two separate chapels, the southern for the husband and the northern for the wife. Both are among the earliest surviving examples of tomb chapels containing internal decoration, here executed on the limestone slabs that lined the mudbrick walls.

In each chapel (as in those of another high-ranking pair, Rahotep and Nofret, at the same site) the western wall contained the false door, the portal through which the deceased could enter the chapel in spirit to partake of offerings which priests or relatives would present there to sustain the person in the afterlife. A stela with a figure of the deceased seated before a table of offerings was incorporated into this wall. The other walls of the chapels and their façades were covered with images belonging to the genre now known as 'scenes of everyday life'. They represent chiefly the procuring of foodstuffs – hunting desert animals, catching birds and fish, butchering cattle, ploughing – and also depictions of the deceased with family members and rows of servants representing estates from which they were entitled to profit. These scenes reflected the earthly life that Nefermaat and Itet would have known, confirming their high status as master and mistress of productive land and servants, while also magically providing them with an eternal supply of sustenance, a safeguard against the possible failure of the offering cult. These scenes were repeated and amplified in thousands of elite tombs throughout the next two millennia. The chapels of Nefermaat and Itet are historically important as they contain the earliest surviving examples of such scenes found in their original context [2; p. 55]. They were, however, accessible only for a short time, as the tomb underwent several phases of construction, and before its final completion the decorated chapels had been sealed and hidden as the *mastaba* was extended, while new cult places were constructed against the external façade [2; pp. 38–41; pp. 43–44].

Several different methods were employed at Meidum to create the images on the tomb-chapel walls. In the chapels of Rahotep and Nofret the scenes were carved in relief and painted. In Itet's chapel some surfaces were decorated in paint alone; two fragments of this decoration from her chapel are held by the British Museum (EA 69014 and 69015) and have been the subject of a previous article [3]. But in other parts of the chapel of Itet, and in that of Nefermaat, the craftsmen took the unusual step of creating images by applying coloured pastes into cells cut into the limestone. Fine details were then added either by painting onto the surface of the paste, or by inlaying a second layer of differently coloured pastes into the first. Unusually, an inscription in the chapel of Itet makes a direct reference to Nefermaat's paste-inlays, stating: 'He is one who fashions his representations in writing that cannot be erased' [2; p. 84; p. 167]. This suggests that the paste-inlay technique was an innovation at the time, and that it had perhaps been selected at Nefermaat's personal instigation. No other examples of this technique have ever been identified in an ancient Egyptian tomb, and for this reason it is often supposed that it was abandoned at an early date, having been found to be unsuccessful. However, the paste-inlays were largely intact at the time of the tomb's investigation by Auguste Mariette in 1872, and their subsequent deterioration may be attributed to poor handling after excavation rather than to a fundamental technical weakness [2; p. 165]. Since the tomb chapels of Nefermaat and Itet were sealed shortly after their completion, there would have been little opportunity for craftsmen to assess the effectiveness of the technique, and it appears more likely that the practice was discontinued because it was, in evolutionary terms, a retrograde step, a labour-intensive and time-consuming process that yielded a result inferior to that of relief carving or flat painting [2; p. 38; p. 165].

THE INLAY BOX

This contribution discusses a box of pigmented inlays (EA 69384, Figure 1) from Nefermaat's tomb chapel. The tomb was originally excavated by Auguste Mariette in 1872 and later re-examined by Flinders Petrie in 1890–1891 [2; pp. 10–16, 4]. When first excavated, the inlays seem to have been in good condition, but by the time of Petrie's examination, the chapel of Nefermaat had suffered considerable damage and many of the inlays had been lost, perhaps due to the effects of temperature changes or to chemical deterioration of the inlays themselves. Petrie collected a number of samples of the remaining inlays. Although these can now be found scattered across museums worldwide, we know of no attempts to use modern analysis to examine the inlays themselves, some work having been carried out on the plasters between 1986 and 1988 by the Polish-Egyptian Restoration Mission [5]. The pigmented inlays in the British Museum box (EA 69384) discussed below were purchased from Petrie by the Victoria and Albert Museum in 1891, before being transferred to the collections of the British Museum in 1982. There was considerable interest in the nature of the pigments used in ancient Egypt even at the time of Petrie's investigations, and the paints in both the wall paintings and the inlays from this tomb were chemically analysed by Petrie's associate, Flaxman Spurrell [4; p. 29; p. 50], with notable success, as will be discussed below. The results of Spurrell's examinations are included in the descriptions of the inlays written inside the British Museum box, Figure 1.

FIGURE 1. The British Museum box of inlays from the *mastaba* of Nefermaat (EA 69384)

INVESTIGATION OF THE INLAYS

Macroscopic examination

The box contains 12 pieces of coloured inlay mounted in six compartments divided by colour, Figure 1. Hand written inscriptions describe these as 'yellow', 'olive-yellow', 'green', 'red' and 'black', 'red-brown' and 'red', although in some cases, two colour layers are present (see the discussion of the pigments below). The sizes of the pieces vary considerably from around 60 × 70 mm to 5 mm square. There are two basic thicknesses (*c.*5 and *c.*10 mm). No blue is present in this box, and Petrie found no blue inlays, although he did record the presence of blue in the conventional paintings of Itet's tomb. Unfortunately, no blue is present on the painted fragments from Itet's chapel held by the British Museum, so it has not yet been possible to undertake direct analysis, although it is hoped to source such material in the future.

Microscopic examination

Small samples taken from the blocks and subjected to microscopic examination show the inlays to be brittle masses of coloured crystals. All are mixed with a high proportion of small (0.1–1.0 mm) brownish, translucent globules, apparently of an organic material; Figure 2 shows a section through the 'green' block. Spurrell had a number of theories to account for the globular nature of the binder, including the accumulation of organic 'polish' into air bubble spaces at the surface of the inlay and segregation of binder when mixed with the paste. By whatever means it was incorporated into the mass, this organic matter seems to be the principal binder holding the pastes together. In some of the blocks, crystals of calcium sulphate are clearly visible and probably aid in consolidation, but others (such as the 'brick red' block) seem to consist almost entirely of pigment grains, which would have little inherent integrity. The further analysis carried out on the various constituents of the blocks is described below.

Pigment content

The pigment content of the pieces was investigated using Raman spectroscopy, X-ray fluorescence (XRF) analysis and optical microscopy; experimental details are given in the experimental appendix.

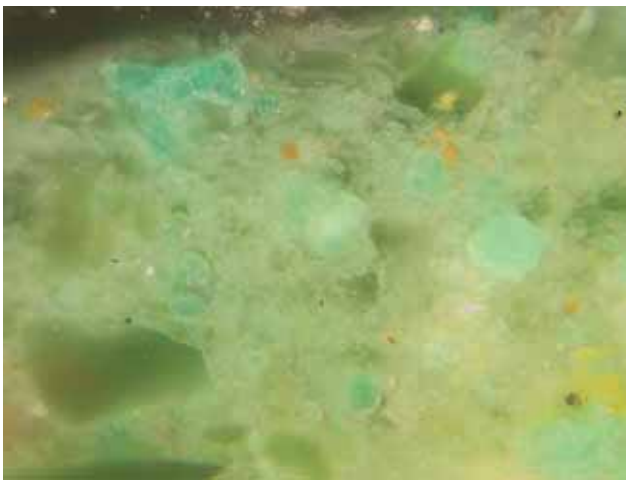

FIGURE 2. Cross-section of a sample from the 'green' block, clearly showing the mixture of organic and inorganic materials

The inorganic fraction of the 'yellow' block was found to consist of reasonably pure 'jarosite' (strictly a mixture of jarosite and natrojarosite). Virtually no calcium sulphate was found to be present and the coherence of the block was presumably maintained by its organic component. The jarosite group consists of naturally occurring minerals formed by the alteration of iron oxides or pyrites. The group includes jarosite itself (hydrated potassium iron(III) sulphate $KFe_3(SO_4)_2(OH)_6$), natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) and a number of other variants, although only jarosite and natrojarosite seem to have been recorded in ancient Egyptian contexts. Jarosite was first recorded as an Egyptian pigment on decorated pottery of the Eleventh Dynasty from El Tarif, but it was later suggested that the jarosite found in Egypt was not used as a pigment in its own right, but was instead a degradation product, present as the result of the chemical decomposition of an iron-rich frit pigment, originally red-brown or green in colour [6]. However, jarosite has since been found in a large number of other contexts from the Old Kingdom onwards (including on the conventional wall paintings from Itet's tomb chapel [3]) and strong arguments have been made against this interpretation based on chemical, historic and stylistic grounds [3, 7, 8]. On this basis jarosite can now be accepted as one of the three yellows which form part of the known Egyptian palette (these are yellow ochre, the most common, jarosite and orpiment (As_2S_3), the last apparently being a late addition, first appearing in the Middle Kingdom period). The 'olive-yellow' block is similar to the 'yellow' but contains a mixture of jarosite, calcium sulphate (present largely as anhydrite) and black carbon particles, presumably added to the mix to temper the colour. The carbon particles were sufficiently large and well separated that at high magnification some cellular structure could be observed, confirming the source to be crushed charcoal, rather than lamp black (soot). These yellows are the only material where Spurrell's early identifications can be questioned; he defines them as 'ochreous clays', but misses the potassium/sodium and sulphur substitutions, something for which he can hardly be faulted given the methods available to him.

The 'green' pigment block is bicoloured, with a malachite-containing layer overlying one of jarosite similar to the material in the 'yellow' block. This layering may relate to construction methods – Petrie refers to the production of complex features, such as feathers, by cutting into a base inlay and refilling with a different colour [4; p. 25] – or to economy; as discussed below it is likely that malachite was an expensive pigment. This use of malachite is the one point where this set of pigments differs from the conventional Egyptian palette. The nature of the greens used in ancient Egyptian art has long been a subject of debate. It now seems clear that green frit (Egyptian green, a glassy pigment consisting chiefly of copper wollastonite) was the main, perhaps only, green pigment in use from the First Intermediate period onwards [9], but prior to this the picture is less clear. It is certain that, with the exception of this sample, there are very few reliable identifications of malachite used as a true paint, although it can occur as a degradation product of the two frit colours, Egyptian blue and green frit. In addition, the most comprehensive survey of Egyptian pigments undertaken in modern times (by the Max Planck Institute) found no malachite [10]. In contrast, it is known that malachite was widely used as a cosmetic throughout the dynastic period. One possible explanation for this differentiation is that malachite was too expensive for widespread use as a pigment, as may be suggested by its use only as the top coating in this block. Its appearance in this very early context may well relate to the lack of availability of alternatives; the earliest known appearance of frit colours is the use of Egyptian blue in the Fourth Dynasty. Green also occurs in the conventional paintings of Itet's tomb chapel but this has so far proved impossible to identify, given the constraints of permissible sample size [3], but it is hoped that this will be revisited in future work.

The 'black' block (more a dull grey) consists mainly of carbon combined with a mixture of calcite and anhydrite. The preponderance of black material made it difficult to distinguish individual particles, and it was not possible to determine if any came from crushed charcoal as in the 'olive-yellow' material. Again carbon is by far the most common black pigment of the Egyptian palette, although a few instances of the use of manganese blacks have been recorded [11].

Finally, three blocks of red material are included in the box, probably reflecting the predilection for the use of red that occurs in tomb paintings throughout the dynastic period. Of these, the one termed 'red-brown' consists largely of hematite (α-Fe_2O_3) of varying degrees of crystallinity, with a small proportion of quartz, and is clearly a block of virtually pure red ochre. The use of red ochre is in keeping with the other evidence from other Egyptian contexts, where it is by far the most commonly reported red pigment [1]. In the other two blocks the red colour is lighter due to hematite crystals sparsely distributed in a white calcium sulphate (mixed gypsum and anhydrite)

matrix. While one of the blocks is of pure red, the other is supported on a white block of gypsum/anhydrite. As with the green material discussed above, this may relate either to production methods or to economy, but given the ready availability of red ochre throughout Egypt, technique seems to be the most likely explanation in this case.

Organic content

The inlays are bound, at least in part, with an organic medium visible as yellow/brown translucent globules described above and seen in Figure 2. Spurrell's investigations of these inclusions (solubility tests and burning) concluded that they were a resinous material, closest to 'mastick' [4; p. 29; p. 50]. Spurrell also attributed apparent hardness, darkening and, in some cases, lamination at the surface of the inlays to the application of an organic 'polish', such as oil or turpentine, or to the addition of an animal matter, possibly gelatine. However, apart from these physical observations it is unclear on what evidence these identifications were based.

The composition of the organic components is now being reinvestigated using gas chromatography-mass spectrometry (GC-MS) and pyrolysis-GC-MS (py-GC-MS). Preliminary results from the globular inclusions indicate that they are composed of plant-derived oil rather than resin. Analysis of solvent extracts by GC-MS has shown the presence of fatty acids and diacids that are typical of degraded oils [12, 13], although a substantial fraction of the globular organic inclusions proved to be insoluble. Subsequent analysis by py-GC-MS yielded mostly straight-chain (alkane/alkene) pyrolysis products, which are consistent with a polymerized lipid [14]; this apparently extensive polymerization implies the use of a drying oil. Linseed is the only source of drying oil known to have been available in ancient Egypt although a number of semi-drying types, such as safflower or poppy oil, may also have been available [15]. The presence of such a medium is potentially extremely significant as the use of oil binders in dynastic Egyptian painting is virtually unknown.

CONCLUSIONS

This box of inlays represents a very different form of decoration from the tempera painting generally found in Egyptian tombs. In terms of the pigment component, the most unusual feature is the definite presence of malachite. It is also noticeable that no blues were recorded in any of the inlayed blocks found in the tomb, and features, such as hieroglyphs, which would be expected to be shown in blue in later convention are here filled with green. The blue that occurs in the conventional paintings in Itet's tomb was described by Spurrell as a "blue verditer tint, apparently derived from an impure earthy blue carbonate of copper"; this is presumably azurite – he uses the term chessylite, an early synonym. Spurrell also clearly states that "no traces of green or blue frits have been found" in either of the tombs. Admittedly he had only limited testing facilities available to him, but the analytical work described here has confirmed the remarkable accuracy of his work, and this comment shows that he was specifically searching for evidence of frit colours. It could be that these two tomb chapels reflect decoration produced before the frits that so dominate the conventional Egyptian palette became available, thus enforcing the use of natural carbonates. Given the extravagant use made of pigments in the coloured blocks – the amount of raw material used in any one of the blocks in this box would have covered a substantial area of wall if used as a simple paint – it is unlikely that cost was a factor.

The findings for the organic fractions are even more unexpected and further work on this material and on other pieces from the tomb is now underway in an attempt to establish the type of oil and to explore the method of incorporation into the inlays. It is hoped that the globular nature of the particles may prove a useful clue as to the processes involved. The use of such an oil binder is unprecedented for such ancient material and may demonstrate a previously unsuspected technology.

EXPERIMENTAL APPENDIX

Analysis of the inorganic materials was carried out mainly by Raman spectroscopy, using a Jobin Yvon Infinity spectrometer with green (532 nm) and near infrared (785 nm) lasers, with maximum powers of 2.4 and 4 mW at the sample respectively. The spectra were identified by comparison with the British Museum in-house reference database and with published data. These results were confirmed by the elemental data produced using a Brucker Artax XRF

TABLE 1. Analytical results for the inorganic fractions of the blocks

Description	Visual appearance	Microscopic appearance	Identification
Yellow	pale yellow	yellow crystals	jarosite
Olive-yellow	darker yellow	yellow crystals with sparse white and black crystals	jarosite anhydrite carbon (charcoal)
Green	bright green mass on yellow support	green crystals yellow crystals	malachite jarosite
Black	dark grey	black particles in yellow and white mass	carbon calcite anhydrite
Red-brown	red	fine red crystals	hematite
Red 1	red on white support	sparse red crystals in white mass white crystals	hematite gypsum/anhydrite gypsum/anhydrite
Red 2	red	sparse red crystals in white mass	hematite gypsum/anhydrite

spectrometer [16]. All the analyses were carried out directly on the surface of the samples without any preparatory cleaning. The two sets of results were in full accord, and the resultant identifications are given in Table 1.

Individual organic binder inclusions were removed with tweezers from the broken edges of the inlays and crushed to fine powder in conical microvials. These were solvent extracted with 100 µL of dichloromethane, transferred to fresh vials, then dried under nitrogen and, prior to analysis, derivatized using bis(trimethylsilyl)trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS) to form trimethylsilyl derivatives. Additional unextracted samples were taken for direct analysis by py-GC-MS. The samples were analysed using an Agilent 6890N gas chromatograph coupled to an Agilent 5973N mass spectrometer. Solvent-extracted samples were injected in on-column mode with the inlet temperature programmed to follow the oven cycle. Pyrolysis of unextracted samples was undertaken using a CDS Pyroprobe 1000 with a probe temperature of 750°C (15 seconds) and interface temperature of 280°C. These were introduced to the GC in split (10:1) mode at 280°C. All the analyses used an Agilent HP5-MS, 30 m × 0.25 mm column with a film thickness of 0.25 µm, fitted with 1 m × 0.53 mm retention gap. The carrier gas was helium in constant flow mode at 1.5 mL per minute. After a one minute isothermal hold at 50°C, the oven was temperature programmed to 330°C at 10°C per minute with the final temperature held for 15 minutes. The MS interface temperature was 280°C. Acquisition was in scan mode (50–600 amu per second) after a solvent delay of five minutes. Mass spectral data were interpreted manually with the aid of the NIST/EPA/NIH Mass Spectral Library version 2.0 and comparison with published data.

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The black bronzes of Burma

Maickel van Bellegem, Philip Fletcher, Paul Craddock, Susan La Niece and Richard Blurton

Summary Following the donation of 25 Burmese lime boxes to the British Museum in 2005, selected boxes were treated and a technical study was carried out. The boxes are made of silver, copper, brass, cupro-nickel and black-patinated copper alloy, or combinations of these materials. Three types of different alloy compositions (copper with 1.8% silver and 1.2% gold, copper with 10% silver or copper with 0.9% arsenic) were found for parts that are suggested to have been patinated originally. The use of black-patinated copper alloys and details of the construction of the boxes are described. The techniques encountered on these boxes include engraving, chasing and the use of niello; silver braze and copper alloy wires used as inlays were also found. The analyses of the alloy compositions indicate that some areas which now have a copper colour were originally intended to be patinated. The condition of the boxes, and conservation treatments that removed surface dirt, corrosion and lime deposits, encourage reconsideration of the original appearance of the objects and form a basis for discussing the desired appearance of the objects for future display. The ethical issues surrounding restoration of the patina on some of the objects are discussed.

INTRODUCTION

Although the patina on ancient bronzes is now a much admired aspect of their appearance, it seems that originally metals were usually kept in a polished metallic state [1]. An exception to this is the family of black-patinated and inlaid copper alloys containing small quantities of gold, silver and sometimes arsenic. The term 'family' is used advisedly, for it seems likely that the manufacture and appreciation of this most sophisticated of materials has been linked through the millennia and across the continents from the Mediterranean world of the third millennium BC to present-day Japan [2].

As Japanese *shakudo* alloys are still in production, there is a much greater knowledge of their methods of treatment and the nature of the patina; these are taken as representative of other black patinas on copper alloys [3, 4]. The copper is alloyed with small quantities of gold and/or silver, typically between about 0.25 and 2%. Although rarely mentioned in the recipes, small amounts of arsenic are often present in quantities significantly above those found in contemporary alloys. The metal can be cast or forged to shape before being inlaid with precious metals; alternatively the alloy itself can form the inlay. The finished piece is then carefully cleaned and polished. As with all surface treatments, the physical condition of the surface is critical to the appearance following the subsequent chemical treatment. After polishing, the surface is first treated with certain fruit or vegetable juices before the piece is placed in boiling water containing small quantities of buffered copper salts including blue vitriol (copper sulphate), verdigris (copper ethanoate) and saltpetre (potassium nitrate) or alum (aluminium potassium sulphate). Dense purple-black patinas are formed that contrast well with the adjacent metals. The principal mineral present in the patina, as detected by X-ray diffraction, is copper(I) oxide [3].

The first studies on the use of these alloys outside Japan concentrated on the earlier, occidental occurrences, exemplified by the *hympty km* of the Egyptians, the *kyanos* of the Greeks and, most famously, the *Corinthium aes* of the Romans [2, 5]. Scholars across several disciplines have known about these ancient black bronzes, or bronze alloyed with small quantities of gold and silver, but links have not been established between the descriptions from these different places and periods, nor with traditional patinated Japanese *irogane* alloys, especially *shakudo*. The British Museum is extremely well placed to examine these interconnections, as not only are objects from each of these cultures present in the collections, but also there are in-house facilities to undertake scientific examination and experimental replication of the alloys [6], allowing factual information to replace speculation as to the nature of these materials.

FIGURE 1. Map showing some of the locations where the black-patinated alloys have been produced in south east Asia

Japanese *irogane* metals have been appreciated for over a century in the west, but more recent work has shown that similar patinated alloys were being made in many centres in east and south east Asia, Figure 1 [7, 8], and that some, notably the *sawasa* wares, seem to have been made in the seventeenth and eighteenth centuries especially for sale to the west [9]. The number of regional varieties and centres of production now known to have been in operation, mainly in the post-Mediaeval period, is steadily increasing.

A recent donation to the British Museum of a collection of highly decorated polychrome metal boxes has significantly contributed to this increased knowledge. This contribution describes the manufacture of these boxes, together with an account of their conservation and some discussion as to whether those that have lost their original decorative surfaces should be repatinated.

MYLAR AND THE BURMESE LIME BOXES

In 2005 the British Museum received a collection of 25 metal lime containers (*hton bu*) used in the preparation of the betel quid [10], presented by Ralph and Ruth Isaacs, who collected them in Burma in the early 1990s. Stylistically, the boxes (registration numbers 2005,0115.1–25; Figure 2) are purely local and were certainly made in Burma, probably mainly in the Shan States in the north east, bordering the province of Yunnan in China. Several of the pieces are dated, usually to the first part of the twentieth century and bear the owner's name; one box is dated to 1959, but this need not necessarily be the date of manufacture. The production of patinated boxes had long ceased by the time the Isaacs made their collection and Fraser-Lu made her study of Burmese crafts in 1994 [11].

The collection comprises boxes manufactured using a range of techniques and materials, including silver, various copper alloys, either embossed or engraved with inlays of niello or lacquer. Thirteen boxes in the collection use a black-patinated alloy, locally known as *mylar* [12]. From the outward appearance of the boxes, it was immediately

FIGURE 2. Selection of lime boxes with *mylar* from Burma that are part of the Ralph and Ruth Isaacs gift to the British Museum. Top left to bottom right, respectively registration numbers: 2005,0115.10, 12, 14–17

FIGURE 3. Selection of ink boxes formerly in the Collier collection, made of *wu tong* with silver braze alloy inlays, dating to the nineteenth or early twentieth century: 1992,1109.1– 6

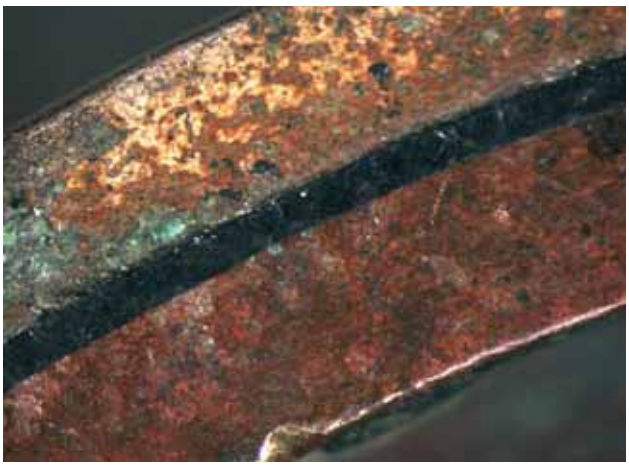

FIGURE 4. Detail of the rim of the bottom of lime box 2005,0115.12 showing the laminated construction; untreated. From the top downwards the metals are white metal (raised strip) but with some corrosion, *mylar* and copper: image size 6 × 4.5 mm

apparent that there were parallels with the *wu tong* boxes produced in the province of Yunnan in China and this has been confirmed by scientific study, Figure 3. All these boxes were made with the black-patinated copper alloy and some had inlays of silver brazing alloy. A number of the lime boxes show a greater range of techniques and materials in their construction and many are polychromic, with reds and yellows of copper and brass inlays used together with the black-patinated alloy and silvery metals.

The boxes have been built up from sheet components brazed together to form outer and inner jackets, Figure 4. The outer sheets are usually of the black-patinated alloy with an inner jacket of copper. Raised strips of silver or cupro-nickel were added at the edges as decoration and to conceal the brazed joins on the outside; a construction that is very similar to the use of silver strips on *wu tong* boxes. The decorative channels on two boxes in the collection were engraved (Figure 5) or chased (Figure 6) and inlaid with molten silver brazing alloy, again similar to *wu tong* boxes, Figure 7; note the sharp points typical of engraved lines in Figures 5 and 7. Additionally, on one box sheets of silver and copper were brazed into recesses made by chasing, Figure 5. The colour difference between both the copper and silver sheets and the silver braze surrounding them is noticeable. Other boxes were built up from outer sheets of cupro-nickel or copper and flat lids with complex annular polychrome decorative schemes have been built up linearly, Figure 8. On these lids there is no underlying metal base plate into which the elements were set – the components were simply brazed to each other. The chevron patterns were made by twisting

FIGURE 5. Detail of the lid of lime box 2005,0115.12 after treatment. The inset to the upper left shows a detail of the inside where the shape of the chased decoration and remnants of lime can be seen. The inset to the bottom right shows a detail of the triangular shape of the engraved lines filled with silver braze: main image size 12 × 9 mm

FIGURE 6. Detail of the lid of lime box 2005,0115.13, made of black alloy, silver braze alloy inlay and silver strips, after treatment. The inset is a detail of the inside where the shape of the chased decoration and remnants of lime can be seen: main image size: 30 × 22 mm

FIGURE 7. Detail of a lid of *wu tong* ink box 1992,1109.4 before treatment: image size: 30 × 22 mm

FIGURE 8. Lid of lime box 2005,0115.16, decorated with concentric bands of red and white, chevrons of red, white and black, brown-red and white bands and 16 circles of white and brown-red; untreated

FIGURE 9. Detail of the lid shown in Figure 8. The chevrons comprise *mylar* (black), copper (red) and cupro-nickel alloy (white). The parallel bands of copper-arsenic alloy and cupro-nickel alloy are brown-black and white in colour respectively: image size: 15 × 11 mm

FIGURE 10. Detail of the chevron pattern on lime box 2005,0115.14; untreated. The left shows the outer surface of the twisted wire, at the right the wires were filed down to the middle causing a change in the pattern to rectangles: image size 30 × 22 mm

together combinations of wires of different metals, such as silver, copper, black-patinated alloy or a copper-arsenic alloy (Figure 9), to make a cable with a helical seam. In one instance it is clear that the inlaid twisted wire was filed down to the centre of the twisted wires revealing changes in pattern, Figure 10. The use of the different alloys – copper, cupro-nickel, *mylar* and copper-arsenic alloy – in and next to the chevron patterns creates an attractive colour scheme and the minor differences in alloy composition are clearly intentional.

CONDITION AND CONSERVATION

The condition of the collection was assessed upon its arrival at the British Museum. Although the general condition was considered stable, 10 of the boxes were judged to require surface cleaning and, to improve the fit of the lids, the removal of corrosion and lime deposits from the rims of both the boxes and the lids.

Little information was available on the methods employed for the maintenance of the patina during use in Burma, although it is clear that the boxes were used and would have been handled frequently. The suggested method of patination for the *wu tong* boxes is through handling, which initiates reactions between perspiration and the metal to promote the formation of the patina [8, 13]. In the case of Japanese *shakudo*, application of a wax after the chemical patination process is often suggested [14].

The following information was provided by Mr Isaacs regarding maintenance of the collection of boxes while they were in his ownership:

> No wax or other coating was used after cleaning. Many of the boxes were really dirty. They were not washed, because I wanted to keep the lime inside them. But water and soap or detergent were used. Boxes of silver were cleaned and polished with a domestic silver cleaner or at least an impregnated cloth. Copper boxes were polished with a brass cleaner, which might well have contained an abrasive. 'Black' boxes were wiped, the silver keel(s) cleaned with silver polish. The black surfaces may have had a wipe with a metal cleaning cloth. And I think it possible that some light mineral oil was used as well. The processes employed were used in order to **see** the decoration patterns and various inlays.

Tarnish and remnants of old cleaning compounds were removed from two silver boxes using successive swabs of white spirits, Silvo® silver polish in white spirits, industrial methylated spirit and distilled water on cotton swabs. A steam cleaner was used to remove traces of chalk or clay when possible. Finally the surface was given a general polish with cotton wool. The rims of the boxes and lids were mechanically cleaned with a scalpel to remove excess lime, providing a better fit.

The surface cleaning of the other boxes was carried out with white spirits on cotton wool swabs. Some corrosion on the silver-braze inlays was removed mechanically with a scalpel (Figure 11), and with Silvo® in white spirits on cotton wool swabs while working under a stereomicroscope at ×20 magnification. On some black surfaces it was found that the sheen was slightly altered. This was thought to result

FIGURE 11. Detail of the lid from lime box 2005,0115.13, showing the removal of a corrosion layer on the surface of the silver alloy decoration: image size: 6 × 4.5 mm

from partial removal of surface dirt or possibly a wax layer; these would saturate the patination layer and thus deepen the colour and sheen. This layer was analysed by Fourier transform infrared (FTIR) spectroscopy, but gave inconclusive results. The necessity of either further cleaning of the grime or wax layer (possibly not without risk to the patina) or applying a microcrystalline wax to the surface to create a more uniform appearance of the surface was considered. It was decided not to undertake any further treatment, since the appearance of the surface was variable, depending on the light under which the surface was viewed.

During analytical investigation of the boxes, it became evident that some that now appear to be made of copper may originally have been patinated. The surface has a copper colour and it is impossible to differentiate visually between pure copper and alloys with small amounts of other metals that were intended to be patinated. Chemical analysis is essential to establish the composition of the alloy and subsequent original appearance. These analyses have also been used to inform a series of experiments that has been carried out to investigate patination methods and possible conservation or restoration methods for patinated materials; the results of these experiments are presented elsewhere [6].

COMPOSITION

Some of the colonial period accounts of Burmese metal crafts suggest that various metals were imported by the European maritime trade [15]. This may have been true in the late nineteenth and early twentieth century, but other sources were also available [16]. The Bawdwin mines in the Shan States of north east Burma, for example, were a major source of silver when worked by the Chinese up to the mid-nineteenth century and were an equally important source of zinc when worked by the British in the twentieth century; these mines also produced significant quantities of lead and copper [17]. So-called *baw* silver from those mines, with a purity of at least 95%, was favoured by some silversmiths [11]. In the province of Yunnan in China (adjacent to Burma), major deposits of copper, tin, gold, silver, zinc and

TABLE 1. XRF results for alloy compositions on a selection of lime boxes

Box	Ag	Au	Cu	Pb	As	Zn	Sn	Fe	Co	Ni	Cr
2005,0115.1											
Side of box	98.8	0.2	1.0								
2005,0115.5											
Lid of box	88.6	0.3	11.0	0.2							
Interior of lid	85.7	0.3	14.0	0.1							
Niello	present		present	present							
2005,0115.12											
Silver	99.2	–	0.8	–	–	–	–	–		–	
Silver braze	80.1	0.3	13.4	0.6	–	5.7	–	–		–	
CuAgAu	1.6	1.4	96.1	–	0.2	0.5	–	0.2		–	trace
Copper	–	–	99.4	0.1	0.1	0.3	–	0.1		–	trace
White metal	–	–	74.2	0.4	0.1	9.7	–	0.2		15.4	–
CuAgAu – underside of lid	1.7	3.6	94.0	–	–	0.5	–	0.2		–	–
Copper interior	–	–	99.5	0.2	0.2	–	–	0.1		–	–
2005,0115.13											
Silver braze	62.3	0.1	28.5	1.1	–	8.2					–
CuAg 1	9.2	–	87.0	0.2	0.4	2.9					–
Silver edge	94.2	0.3	5.0	0.3	–	0.2					–
2005,0115.16											
Copper	0.05	–	99.3	0.24	0.12	0.31	0.15	0.05	–	0.04	–
CuAgAu	3.90	0.83	94.5	0.04	0.10	0.34	0.30	0.04	–	–	–
CuAs	0.05	–	98.8	0.02	0.65	0.31	0.06	0.04	0.02	0.08	–
White metal	0.06	–	59.6	0.56	0.04	24.6	0.56	0.45	0.1	14.4	–
Copper	0.05	–	99.3	0.24	0.12	0.31	0.15	0.05	–	0.04	–
2005,0115.17											
Brass	0.43	–	69.5	1.34	0.29	23.5	4.24	0.10	0.02	0.46	–
Copper	0.06	–	98.9	0.34	0.185	0.31	–	0.04	0.02	0.12	trace
CuAg	1.74	0.12	96.2	0.18	0.3	0.615	0.73	0.08	0.02	0.26	trace
CuAgAu	0.58	0.47	98.1	0.18	0.19	0.25	0.45	0.10	–	0.16	trace
White metal	0.12	–	61.6	0.53	0.12	26.8	0.30	1.27	0.23	9.1	trace

Note: '–' indicates that the concentration was below the detection limit.

nickel have been worked since antiquity [18]. Therefore, all the metals found in the *mylar* and *wu tong* alloys could be obtained locally.

Analysis was carried out on the unprepared surfaces using X-ray fluorescence, see Table 1 and the experimental appendix. The *mylar* components are usually of copper with between about 1.7 and 2.2% (average 1.8%) silver and 0.8–1.8% (average 1.2%) gold, with only traces of other metals, including arsenic. Some of the box components were of copper with about 10% silver and 0.4% arsenic but no gold, reminiscent of some Roman *Corinthium aes* alloys [2]. A third alloy that appeared to be patinated intentionally is the brown-black alloy of copper with 0.9% arsenic. This appears to resemble the Japanese alloy *Kuromi-do*, which comprises copper with 1% arsenic [19]. The inlays of silver brazing alloy that had been melted into place contained approximately 60% silver, 30% copper and 10% zinc.

The cupro-nickel components are copper with very variable quantities of nickel and zinc, but both average about 10%. The alloy also contains between about 0.5 and 1% iron, significantly higher than in the other copper-based components. The production of cupro-nickel may well have started in Yunnan and certainly its production formed a major commodity for trade with Europe in the eighteenth century [20, 21]. It was known as *paktong* and usually contained variable quantities of nickel, typically about 10%, and considerable quantities of zinc, typically between 20 and 40%. *Paktong* was made by co-smelting the iron-nickel sulphide ore pentlandite, $(Fe,Ni)_9S_8$, with copper ores to produce an impure copper-nickel *matte*. This had to be further purified and zinc added, but even so the resulting *paktong* almost invariably contained 1% or more of iron. Cupro-nickel was produced in Europe from the 1820s, but by mixing metallic copper, nickel and zinc, the resulting alloys containing only traces of iron. The cupro-nickel components of the lime boxes have approximately the same nickel content as *paktong* but much less zinc. This could be because this material was intended to be worked as sheet metal and too much zinc might embrittle the alloy and make it unworkable. The average iron content is somewhat less than the average for *paktong*, but still much higher than in European cupro-nickel, suggesting that the source of the metal was Yunnan.

Little is known of the history of *mylar* production. Scott and Hardiman recorded the production of lime boxes, including those with black patination, at the beginning of the twentieth century [15]. They noted that the production of the inlaid lime boxes was a speciality of the brass workers of the town of Pokokku in the Pakokku district of Burma, Figure 1. They clearly had some inkling of the patination process and stated that the finished boxes were placed in a clay pot, heated and then buried for some time. Presumably this is a half-understood reference to the patinating solutions being heated in a pot, to which the authors added the idea of burial. Patinas were popularly believed to have been created by burial, although there is no real evidence for this anywhere. Maryon, for example, included burial as a patination technique in the first edition of his well-known book on metalwork, but it is omitted in subsequent editions [22]. Tilly, in an article on Burmese silverware, refers to this type of material, though his understanding of the process is less profound; he relates it to damascening and claims that the blackening is produced by melting the copper with 5% gold and a little sulphur [23]. The latter part of this is almost certainly incorrect. The patina contains no sulphides, though similar erroneous assumptions were made by others [2].

DISCUSSION AND CONCLUDING REMARKS

The boxes have now been examined, analysed, conserved and cleaned and the intricate designs can be better appreciated. Mr Isaacs very properly chose not to clean the boxes comprehensively when they were in his care. However, before they came to him, some of the boxes had obviously been vigorously cleaned, removing the *mylar* patina along with the dirt in some instances, so that now a coppery inlay is set in a copper background, instead of a black patina contrasting with red metal.

During their examination and treatment the question arose of whether the *mylar* should be repatinated. It is certain that the distinctive *mylar* alloy would originally have been patinated and the knowledge gained from recent experiments would enable the patina to be restored [6]. On the other hand, the present state of the boxes, still containing some of their original contents of lime, worn and missing some of their patina, is a record of their history and should be preserved. This is a dilemma that occurs with many museum artefacts; should they be restored to reflect how it is believed they would originally have appeared, or should they be conserved and cleaned only to the extent that this preserves all visible evidence of their history? It could be argued that the original patina was removed in ignorance, a mistake that should now be rectified, while others would argue that this very ignorance of the deliberate patination of these boxes is a poignant comment on the rapid loss of appreciation of the technique and should, therefore, be preserved.

How ought this dilemma be resolved? There are models available that can be used to guide decisions about conservation and restoration decisions [24]. A similar problem was addressed by a team at the Victoria and Albert Museum, London when considering the watered pattern of *wootz* steel used to make an Indian axe head dating from 1739 to 1753. The distinctive pattern had been inadvertently removed by over-polishing before it entered the Museum's collections. After lengthy consideration, the decision was taken to restore the *wootz* pattern by re-etching using swabs bearing dilute nitric acid [25]. What is the ideal balance between established ethics of conservation, like reversibility and preservation, and the desire to restore the intended original appearance? This dilemma has not yet been resolved in the case of these boxes, but the present work provides a greater

understanding of black-patinated alloys and the protection of the valued patina from inappropriate cleaning.

It comes as something of a surprise to discover that so many metalworking traditions around the world have survived into the recent past only to pass away without adequate record. If this is true for the descriptions of the objects and the style of their decoration, it is even more the case for the techniques used to make them.

At the time of completing (as was thought in the early 1990s) the work on the history of the black-patinated bronzes, south and east Asia were investigated for traditions that could provide a link between classical antiquity and Mediaeval Japan, and the discovery of the Chinese *wu tong* was regarded as highly significant. Since then, no less than four more varieties have come to light and almost certainly there remain still more to be discovered and recorded. It is very likely that there were contacts and technical interrelationships in the production of such a distinctive and sophisticated material, and it is hoped that further research will uncover these.

EXPERIMENTAL APPENDIX

The alloy compositions were analysed using a Bruker AXS ARTAX micro X-ray spectrometer (X-ray tube settings: 50 kV, 800 μA, collimator 0.2 mm with a collection time of 300s). Detection limits for the technique are of the order of 0.01% for Cr, Fe, Co, Ni, Cu, Zn, Pb, Sb, of the order of 0.02% for Ag, Sn and 0.05% for As. Precision for copper is ~1–2% and decreasing down to ~50% for elements at or near the detection limit. The analyses were performed on uncleaned patinated surfaces.

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MATERIALS AND SUPPLIERS

- Cotton wool, industrial methylated spirit, white spirits: VWR International Ltd, Magna Park, Hunter Boulevard, Lutterworth, Leicestershire LE17 4XN, UK. Email: info@uk.vwr.com
- Silvo® Duraglit metal polish wadding: Reckitt Benckiser plc, 103–105 Bath Road, Slough, Berkshire SL1 3UH, UK

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Effects of relative humidity on the corrosion of iron: an experimental view

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Summary The storage of archaeological iron is a problem for museum collections, but a relative humidity (RH) of 12% has been reported to be the critical level to keep iron stable. However, it requires significant effort and expense to achieve and maintain storage conditions with such low RH levels.

Experimental tests on the effects of RH on the corrosion of iron were carried out and the results are reported. Powdered iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) and iron foils with powdered $FeCl_2 \cdot 4H_2O$ applied to the surface were exposed at different RH levels, including 75, 54, 44, 33 and 23%, at room temperature for over a year. Changes in these tested materials were identified using microscopy, Raman spectroscopy, X-ray diffraction and ion chromatography.

The iron(II) chloride powder liquefied and the formation of akaganéite (ß-FeOOH, a symptom of the deterioration of iron) occurred within hours at 75% RH and within a month at 54% RH. Deliquescence did not occur in the powder exposed at 44% RH and below over the period of a year, although akaganéite was detected in these samples. Pitting was observed on the tested foils after one week at 75% RH. It was observed under the microscope within a month and was visible without magnification after six months at 54% RH. Pitting was hardly observed on the foils exposed at 33% RH or below after exposure for one year.

Akaganéite also formed on the control foils indicating that akaganéite found on archaeological iron could be formed with little chloride present in the objects. The morphology and composition of the corrosion depends mainly on the RH levels, although the surface condition of the objects also has an effect. The elongated crystalline akaganéite often found on archaeological iron was probably formed at RH levels of 50–60%, while at higher RH levels akaganéite was formed as 'bubbles'. These findings indicate that keeping iron at RH levels below 35% can slow deterioration significantly.

INTRODUCTION

In the British Museum, the collection of archaeological iron covers all periods from the Iron Age to the post-Mediaeval. A small proportion of unstable metalwork including archaeological iron is, at present, kept in two dedicated dehumidified stores, while the majority of iron objects are in storage areas with no environmental control; in these latter locations some deterioration of some objects has been evident.

The formation of akagenéite (ß-FeOOH) has been recognized as a major symptom of post-excavation deterioration for archaeological iron, although other corrosion products such as goethite (α-FeOOH) and lepidocrocite (γ-FeOOH) may also form after excavation.

Investigation of deterioration of archaeological iron in the Museum collection indicated that no single method of conservation treatment, including desalination using alkaline sulphite solutions, has prevented corrosion for every object [1]. Objects stored in sealed boxes with silica gel desiccant are, in general, in better condition than those located in storage cupboards without silica gel, suggesting that humidity is a major contributor to corrosion. Some objects kept in uncontrolled environments have deteriorated badly and disintegrated, Figure 1.

Removing chloride from iron objects and keeping them in dry storage are currently the two predominant approaches in the conservation and preservation of archaeological iron [2–8]. Keeping iron in controlled environmental conditions is considered a better practice because complete desalination is difficult to achieve and the procedure can result in the uncontrolled removal of evidence preserved in corrosion products [9].

Experiments have been carried out to establish a critical RH level for long-term preservation of archaeological iron.

Experiments by Turgoose revealed that in three months at RH levels below 55% no reaction occurred to $FeCl_2 \cdot 4H_2O$ alone, and that the formation of akaganéite occurred in

FIGURE 1. Anglo-Saxon sword GR93/1066 excavated at Broadstairs, Kent in 1974 stored in an uncontrolled environment, showing disintegration

two months in the mixtures of powdered iron and iron(II) chloride at a RH as low as 20% [10]. A similar, but more detailed study by Thickett, using mixtures of powdered iron with iron(II) chloride and other corrosion products such as copper(I) chloride or goethite, determined that 18% was the critical RH level [11]. A recent study by Watkinson and Lewis, again using powdered $FeCl_2{\cdot}4H_2O$ and iron, recommended 12% as the allowable RH for long-term storage of archaeological iron with chloride present [8]. However, in reality, keeping iron in storage at such a low level of RH can be an expensive option and presents considerable practical challenges.

The corrosion of an iron object comprises one or more reactions between its surface and the corrosive materials in the environment; as such it differs from the reaction between the powdered materials used in the experiments mentioned above. In the research reported here, experimental tests on the effects of RH on the corrosion of iron were carried out using two types of iron foils: modern industrial rolled iron and wrought iron produced by a modern smith. These were tested in contact with powdered $FeCl_2{\cdot}4H_2O$ as a source of chloride to simulate corrosion of archaeological iron more closely. The reason for using $FeCl_2{\cdot}4H_2O$ in these experiments, rather than an alternative source of chloride ions, was that $FeCl_2{\cdot}4H_2O$ is often found on excavated iron objects [12–14]. All the experiments reported here were carried out at room temperature in order to establish a realistic RH level for storage of archaeological iron.

EXPERIMENTAL

The five levels of RH used in the experiments were 23, 33, 44, 54 and 75%; these were achieved by using saturated aqueous salt solutions in sealed chambers [15]. The RH was monitored using Testo thermohygrometers, which showed a variation of RH at each level of about ± 5%, although this could be greater when the chamber was opened on a very humid or dry day. Two combinations of materials, powdered iron(II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) alone, and iron foils with powdered $FeCl_2{\cdot}4H_2O$ applied to the surface, were tested in the experiments.

Powdered iron(II) chloride

The powdered $FeCl_2{\cdot}4H_2O$ was spread in a weighing boat and placed in a humidity chamber. It was weighed after one, two and seven days, after one month and then at monthly intervals. The powder was examined using Raman spectroscopy when visible changes were observed. Three samples at each RH level were tested to improve the consistency of the results. The experiments were conducted over a year at 75 and 54% RH and over two years at the lower RH levels.

Iron foils covered with iron(II) chloride

Two types of iron foil – industrial iron and wrought iron – were used in the experiment. The industrial iron foil was 'as-rolled', with a smooth surface, a purity of 99.5% and traces of manganese, silicon, carbon, phosphorus and sulphur. The wrought iron was produced from modern recycled iron, which was forge welded and finally rolled; it had a rough surface and a heterogeneous composition. The samples of both foil types used in the experiments were 25 × 25 mm and 1 mm thick.

The experimental procedure for both types of iron foils, each covered with $FeCl_2{\cdot}4H_2O$, was as follows. The foils were degreased with propanone and then placed in a desiccator for one day before the experiments started. The foil was put on a piece of microscope slide for easy handling and weighed. Powdered $FeCl_2{\cdot}4H_2O$ (0.0625 g) was spread on the surface of the foil as evenly as possible, covering approximately half of the surface area, giving a 'concentration' of the chloride of approximately 0.02 $g.cm^{-2}$. The foils covered with powder were placed on a tray in each RH chamber and samples of both types of foil without chloride powder were included in each chamber as controls. Prior to use in the experiments, the wrought iron foils were cleaned in 20% sodium hydroxide containing 200 $g.L^{-1}$ of zinc dust to remove the corrosion products [16].

After each exposure period was complete, all the foils were weighed and examined, and any change in appearance of the chloride powder or metal was analysed by Raman spectroscopy. The corrosion products were then removed with sodium hydroxide solution containing zinc dust and the

remaining metal was re-weighed and the iron substrate was investigated. The experiments with the foils lasted six months at 75 and 54% RH and one year at lower RH levels.

The corrosion products were examined by stereomicroscopy, Raman spectroscopy and X-ray diffraction (XRD). The chloride ion content in the corrosion products formed on the control samples was determined using ion chromatography; the experimental details for each technique are described elsewhere [1].

RESULTS AND DISCUSSIONS

Powdered iron(II) chloride

At 75% RH, the formation of akaganéite bubbles occurred within hours, and the $FeCl_2{\cdot}4H_2O$ powder had completely liquefied within three days, Figure 2. The mass of the samples increased rapidly over the first seven days of exposure but decreased thereafter. After five months the samples seemed to have reached equilibrium, and little further change in mass was recorded, Figure 3. This was due to the formation of a film on the surface which prevented the liquid underneath from absorbing more moisture and oxygen.

At 54% RH, some of the chloride powder turned yellow and a droplet of akaganéite formed after three weeks of exposure. Formation of akaganéite was quite apparent after a month and almost complete within three months. The mass of the samples increased sharply between one and two months and more slowly until the fifth month, after which the mass began to fall, Figure 3.

At 44% RH, the chloride powder became yellow after six months of exposure. Raman analysis showed that some of the powder had changed to akaganéite. The formation of akaganéite, identified by Raman spectroscopy, occurred after ten months at 33 and 23% RH. At RH levels of 44% and below, the chloride stayed as a powder throughout the experiment and little change in mass occurred. Table 1 provides a summary of the experimental results for the samples containing iron(II) chloride powder.

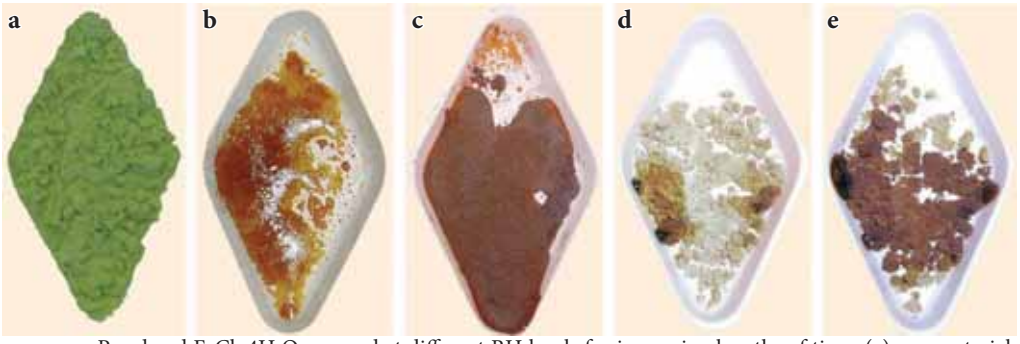

FIGURE 2. Powdered $FeCl_2{\cdot}4H_2O$ exposed at different RH levels for increasing lengths of time: (a) raw material; (b) exposed at 75% RH for three days; (c) exposed at 75% RH for one year; (d) exposed at 54% RH for one month; (e) exposed at 54% RH for three months

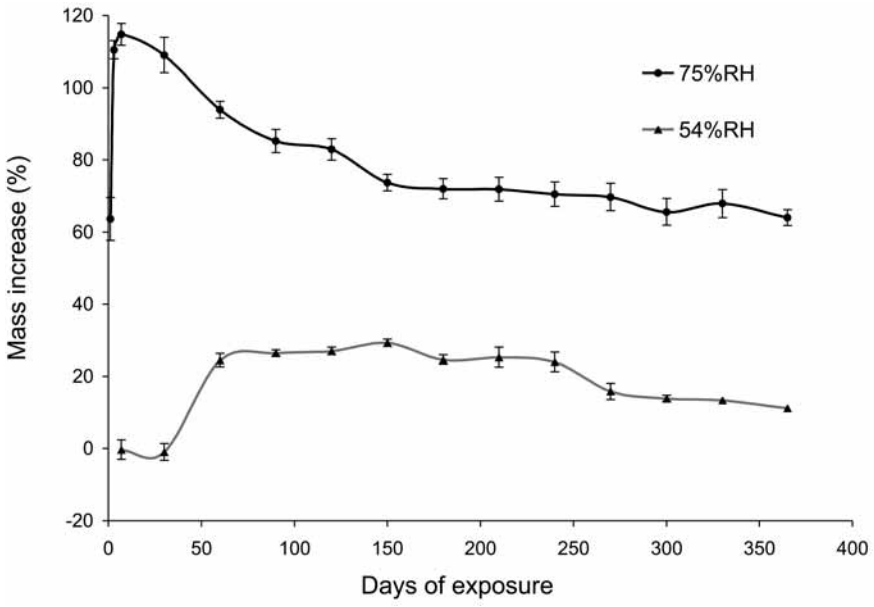

FIGURE 3. Mass increase in $FeCl_2{\cdot}4H_2O$ with time at 75 or 54% RH

TABLE 1. Time after which akaganéite formed in $FeCl_2 \cdot 4H_2O$ powder (formation indicated by an '×')

RH (%)	1 week	3 weeks	6 months	10 months
75	×	×	×	×
54		×	×	×
44			×	×
33				×
23				×

Iron foils covered with iron(II) chloride

At 75% RH, corrosion was apparent on both types of foils within three days. After one week, the control samples were largely covered with brown rust. The chloride powder on the foil liquefied and brown corrosion, a black film and yellow bubbles formed on the foil surface, Figure 4. The brown corrosion and the yellow bubbles were identified as akaganéite by Raman spectroscopy and, although it was not identified by Raman spectroscopy, the black film was identified as a mixture of FeOCl and $FeCl_2 \cdot 2H_2O$ by XRD. The Raman spectrum of the dark brown rust on the control showed a broad peak at 710 cm^{-1}.

After three months at 75% RH, the foil covered with iron(II) chloride was fully covered with corrosion (Figure 4) and the corrosion even spread onto the back of the foil. The black material on the industrial iron was identified as magnetite by XRD and the black film on the wrought iron was identified by Raman spectroscopy as a mixture of akaganéite and magnetite. The rust on the industrial foil control sample contained a mixture of goethite, akaganéite and lepidocrocite, while the rust on the wrought iron control sample was denser and the main component was identified as lepidocrocite by Raman spectroscopy.

After six months, the morphology of the corrosion at 75% RH, as well as at other RH levels, was similar to that seen after three months of exposure. The black film on the industrial iron was identified as akaganéite by Raman spectroscopy and XRD, as was the brown patch. The corrosion on the wrought iron control was more homogeneous and denser than that on the industrial iron control.

Once the corrosion had been cleaned off, pitting was visible on the area of foil covered by the chloride powder in the sample exposed for one week. Pitting increased with time of exposure and was so severe after three months that both the industrial and the wrought iron were corroded through their entire depth, Figure 5. The appearance of the surfaces of the metal foils exposed at each RH is summarised in Table 2.

At 54% RH, brown rust was noted on both control foils after three days and covered the entire foil within one

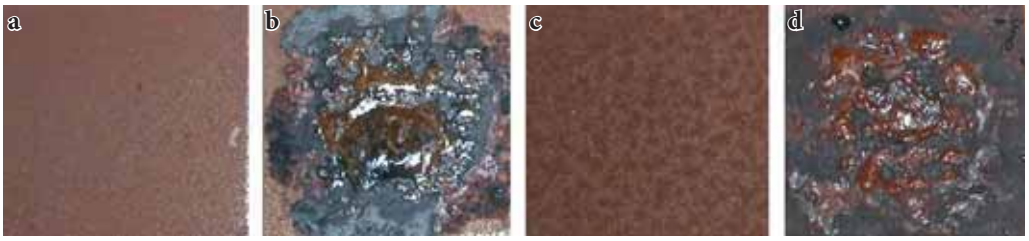

FIGURE 4. Samples exposed at 75% RH for one week: (a) control (industrial foil); (b) industrial iron foil covered with $FeCl_2 \cdot 4H_2O$. Samples exposed at 75% RH for three months: (c) control; (d) foil covered with $FeCl_2 \cdot 4H_2O$

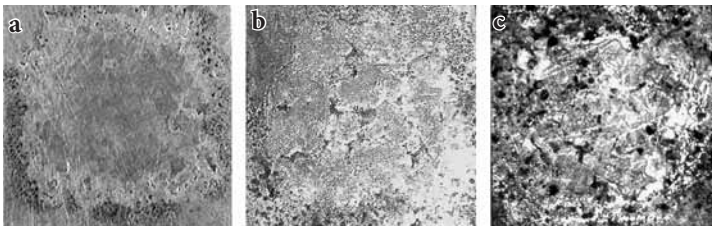

FIGURE 5. Industrial iron foils covered with $FeCl_2 \cdot 4H_2O$ showing pitting after exposure at 75% RH for (a) one week; (b) four weeks; (c) three months

TABLE 2. Summary of pitting corrosion on the iron foils covered with iron(II) chloride powder, exposed to variable RH levels; after cleaning

RH (%)	1 week		4 weeks		3 months		6 months	
	Industrial iron	Wrought iron	Industrial iron	Wrought iron	Industrial iron	Wrought iron	Industrial iron	Wrought iron
75	visible	visible	visible fracture	visible loss of metal	penetration	penetration	deep pitting	penetration
54	macroscopic	macroscopic	macroscopic	macroscopic	macroscopic extensive pitting	worse than industrial iron	severe pitting	severe pitting
44	–	–	–	–	macroscopic	macroscopic	macroscopic	macroscopic
33	–	–	–	–	–	–	pitting was hardly seen	pitting was hardly seen
23	–	–	–	–	–	–	–	–

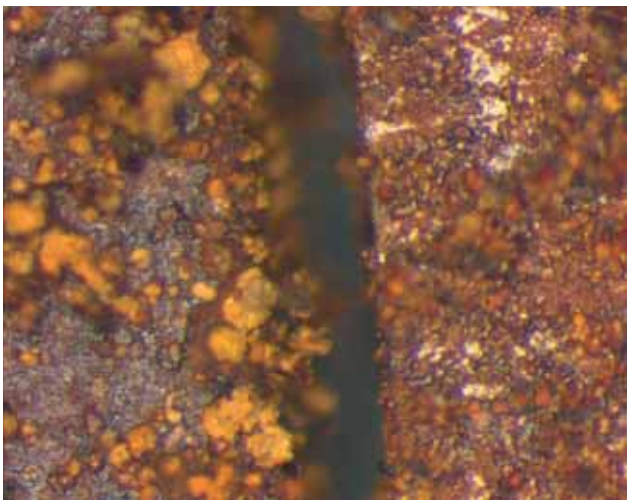

FIGURE 6. Stereo microphotograph of the control industrial foils at 75% RH (right) and 54% RH (left) after four weeks of exposure, showing different corrosion morphology at these two RH levels. Image width: 1.75 mm

week. The Raman spectrum of the brown rust formed on the control showed a broad peak at 710 cm^{-1}, consistent with the spectra for the material on the foils exposed at 75% RH. After four weeks, the control sample was completely tarnished and the number of yellow particles increased. The yellow particles were identified as akaganéite by both Raman spectroscopy and XRD. It is interesting that after a given period the control samples exposed at 54% RH were more highly corroded than those exposed at 75% RH. This was confirmed by stereomicroscopy, Figure 6; the yellow particles were identified as akaganéite. The source of chloride was probably from both the ambient environment and the chloride powder used in the experiment. Pitting of the foils was observed under the microscope within a week but was not apparent to the naked eye until after six months.

At 44, 33, and 23% RH, the iron(II) chloride powder had changed colour after four weeks. It partially converted to akaganéite (identified by Raman spectroscopy) even at 23% RH and the yellow film underneath the powder was also identified as akaganéite. However, the metal itself did not show pitting, which suggests that the akaganéite formed as the result of reaction of the iron(II) chloride with oxygen and moisture rather than a reaction of the iron substrate, although the iron could have acted as a catalyst. After three months, slight pitting was observed under the microscope on the foils exposed at 44% RH (Table 2), although it was not visible to the naked eye.

ATMOSPHERIC CORROSION OF IRON

The rust formed on the control foils contained yellow particles and dark corrosion matrix. The yellow corrosion particles were identified as akaganéite by Raman spectroscopy. The compact dark corrosion again has a broad peak at 710 cm^{-1} in its Raman spectrum. This species is probably one of the ferrihydrates, which are not particularly crystalline and for which the general formula is not yet known [17].

To investigate the significance of atmospheric corrosion of iron, iron foils alone were tested in two humidity chambers held at 54% RH; one was well sealed to limit access to oxygen and the other had two small 5 mm diameter holes at the top. The results showed that the foil in the well-sealed chamber was less corroded than that in the chamber with two holes, Figure 7. This suggests that atmospheric corrosion can play an important part in the deterioration of iron. The formation of akaganéite on the control foils was difficult to understand because no source of chloride ions was deliberately placed in the chamber. This suggests that the ambient environment can be the source of chloride ions.

The corrosion products formed on the control foils of industrial and wrought iron were collected for chloride analysis using ion chromatography. The foils were cleaned and examined, and the results are shown in Table 3. The chloride ion contents in the corrosion formed on the foils exposed at 54% RH were higher than those from the material that formed on the foils exposed at 75% RH. This agrees with the microscopic observations and the identification of the corrosion products by Raman spectroscopy and XRD, i.e. the corrosion on the foils exposed at 54% RH was mainly akaganéite, and the corrosion on the foils exposed at 75% RH comprised a mixture of goethite, akaganéite and lepidocrocite.

The formation of akaganéite on the control foils suggested that some akaganéite found on archaeological iron in the

FIGURE 7. Stereo microphotograph of three control foils after four weeks exposure at 54% RH: (a) industrial iron in a sealed chamber; (b) wrought iron in a sealed chamber; (c) industrial iron in a chamber with two holes. Width of each image: 3.5 mm

TABLE 3. Appearance of the control foils and the Cl^- ion contents in the corrosion products formed on the foils after six months of exposure at 75 and 54% RH

Foils	RH (%)	Appearance after cleaning	Cl^- (Wt%)	RSD%
Wrought iron	75	no obvious pitting	0.231	2.722
Industrial iron	75	patterned pitting due to microstructure	0.177	0.696
Wrought iron	54	macroscopic extensive pitting	3.839	0.371
Industrial iron	54	pitting without a pattern	2.580	0.071

RSD: relative standard deviation

Museum collection might not be due to chloride present in the objects; it could be a result of atmospheric oxidation. Furthermore, the elongated crystals of akaganéite formed on the control foils at 54% RH are very similar to those normally found on archaeological iron in the collection, suggesting that the latter were likely to have formed at RH levels between 50 and 60%. The akaganéite bubbles found on archaeological iron were more likely to be formed at higher RH levels. It has been reported that the critical RH for $FeCl_2 \cdot 4H_2O$ is 55.9% at 25°C, the RH at which the water in contact with $FeCl_2 \cdot 4H_2O$ is saturated with iron(II) chloride [18]. Tests using untreated archaeological nails also confirmed that at 54% RH elongated akaganéite crystals dominated, while at 75% RH akaganéite bubbles dominated in the freshly formed corrosion products, but this influence of RH level on the corrosion morphology needs further study.

Influence of surface condition on iron corrosion

A difference in the appearance of the rust was observed on the wrought iron and industrial iron control samples exposed at 54% RH, Figures 7 and 8; the wrought iron was more corroded than the industrial iron. Akaganéite was detected in the iron(II) chloride powder on the wrought iron exposed for a week, while it was not detected on the industrial iron exposed under the same conditions and for the same period. After three months of exposure, it became more apparent that the corrosion morphology was different on the industrial iron control from that on the wrought iron control when both were exposed at 54% RH. The same difference was also observed for the control foils exposed at 75% RH. This is probably due to the uneven surface of the wrought iron on a microscopic scale. Corrosion of iron is an electrochemical process, and corrosion rate is determined by diffusion of the reactant ions, which can be affected by the surface condition of the metal [19]. The rust that developed on the control samples of both types of iron at 54% RH was identified by Raman spectroscopy as akaganéite. However, the crystals of akaganéite were more developed on the wrought iron than on the industrial iron foil. After six months of exposure, the akaganéite on the wrought iron control sample was further developed and in the typical elongated crystalline form that is often seen on archaeological iron, Figure 8. The influence of surface condition was also proven by the mass loss of the foils, discussed below.

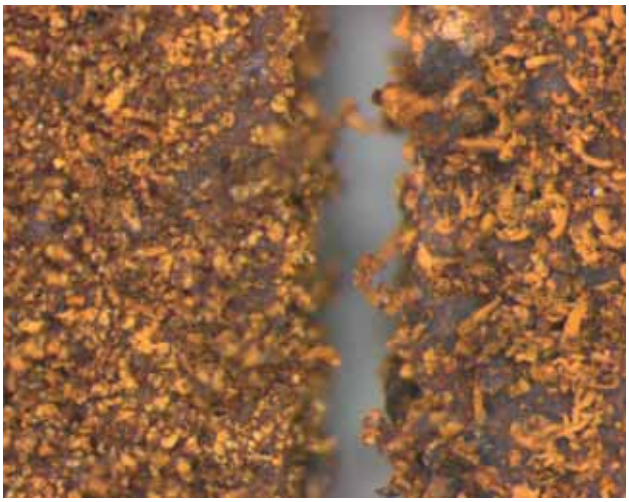

FIGURE 8. Stereo microphotograph of control foils exposed at 54% RH for six months, showing akaganéite formed on the industrial iron (left) was less developed than that formed on wrought iron (right). Image width: 3.5 mm

Rates of corrosion

The corrosion rate can be evaluated by the mass gain of the iron foils covered with iron(II) chloride, or the mass loss of the foils alone after they were cleaned. The mass gain at different RH levels is shown in Figure 9 and the mass loss of the foils alone shown in Figure 10. The mass gain and the mass loss show a similar trend, although there are small differences in the figures at each RH level. The mass gain is very useful in evaluating the deterioration rate of archaeological iron objects because mass loss cannot be measured for archaeological objects without causing damage.

The mass loss of the foils versus time is shown in Figures 11 and 12. At 75% RH, the industrial iron foils were more corroded than the wrought iron for each exposure period, except after one week, Figure 11. At 54% RH, the wrought iron was more corroded than the industrial iron, a pattern repeated at lower RH levels, Figure 12. The rough surface of the wrought iron (compared to the smooth industrial foil) is probably the major factor contributing to a greater degree of corrosion. However, at 75% RH, the rapid corrosion that caused pitting of the industrial iron foil could have accelerated its deterioration. The mass loss of the foils was nearly

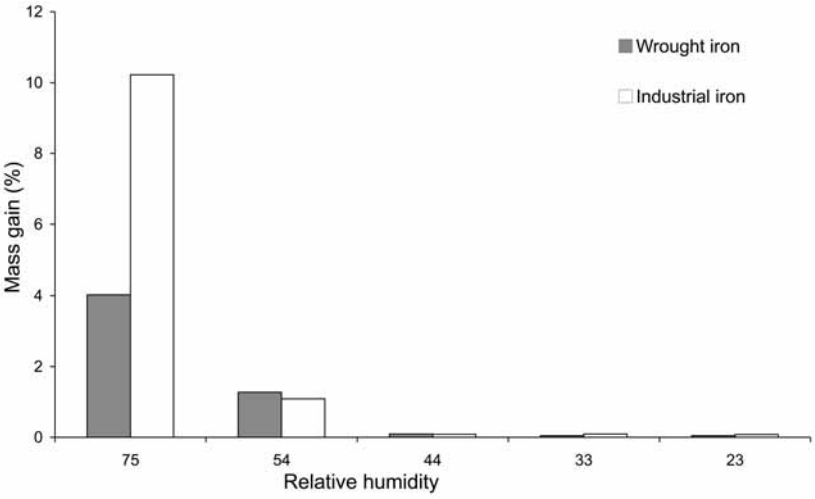

FIGURE 9. Mass gain of the two types of iron foil covered with $FeCl_2 \cdot 4H_2O$ exposed to different RH for six months

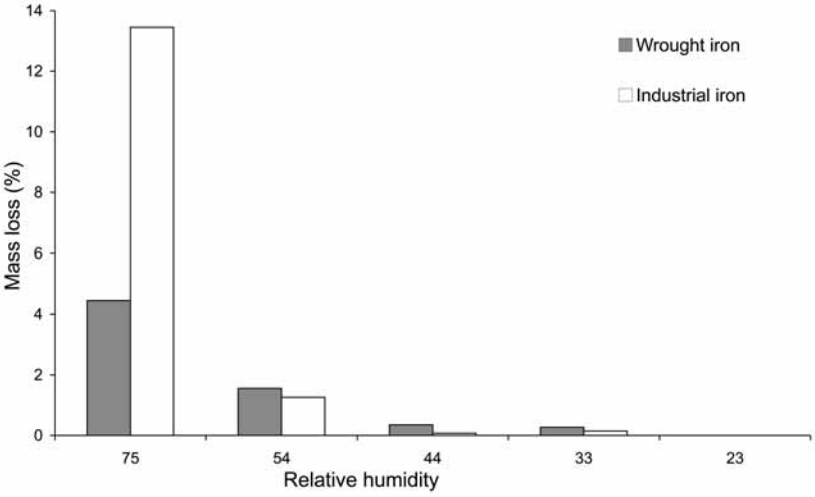

FIGURE 10. Mass loss of the two types of foils exposed at different RH for six months

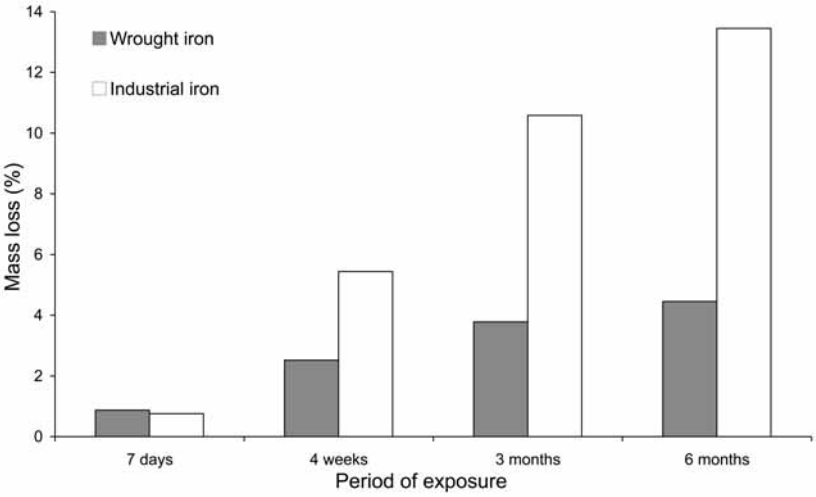

FIGURE 11. Mass loss of the foils exposed at 75% RH versus time

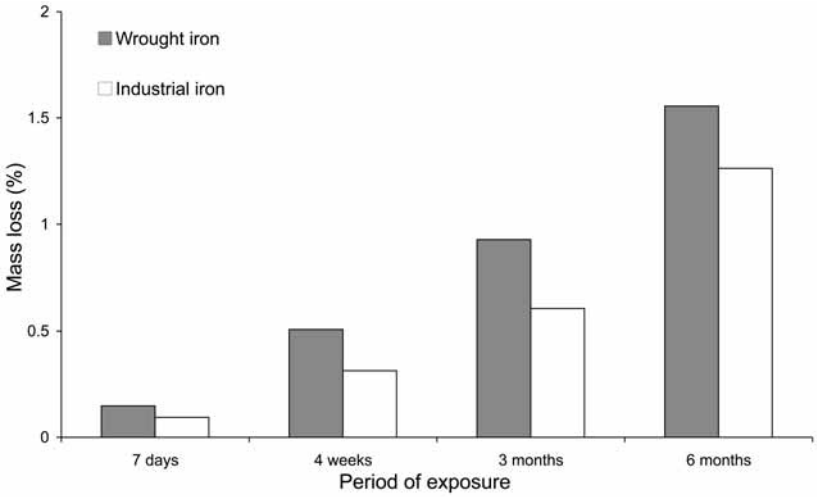

FIGURE 12. Mass loss of the foils exposed at 54% RH versus time

14% at 75% RH and 1.6% at 54% RH after six months of exposure, but even after one year of exposure, was less than 0.4% at RH levels of 44% and below.

CONCLUSIONS

Experiments on iron(II) chloride powder were carried out for a year at 75 and 54% RH and two years at the lower RH levels. It was found that the formation of akaganéite bubbles occurred within hours at 75% RH and within a month at 54% RH. Akaganéite was also detected in the powder after six months at 44% RH and after ten months at 33% RH, although the powder had not liquefied and its mass was still decreasing.

Experiments on iron foils covered with iron(II) chloride were carried out for six months at 75 and 54% RH and one year at lower RH levels. At 75% RH, pitting was visible on the foil after one week and the metal sample, which was 1 mm thick, was corroded throughout its depth after a three-month exposure. Severe pitting was observed on the foils exposed at 54% RH for six months. Corrosion was not obvious on the foils exposed at 44% RH and below, although the $FeCl_2{\cdot}4H_2O$ powder was partially altered to akaganéite.

The wrought iron, with its rough surface, was more corroded than the industrial iron foil with a smooth surface at all RH levels except 75%, which suggests that surface conditions have an impact on the corrosion rates.

The experiments indicated that elongated crystalline akaganéite probably forms at RH levels of 50–60%, and the akaganéite bubbles found on archaeological iron form at higher RH levels. The elongated crystalline akaganéite formed on the control foils exposed at 54% RH indicates that similar crystals formed on archaeological iron could be the result of atmospheric oxidation, even if there is little chloride in the objects. The experimental results suggest that keeping archaeological iron objects in sealed containers with RH levels below 35% can slow down their deterioration significantly.

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MATERIALS AND SUPPLIERS

- Industrial iron foils: Goodfellow Cambridge Limited, Huntingdon PE29 6WR, UK. Email: info@goodfellow.com
- Wrought iron: the wrought iron used in these experiments was provided by Peter Crew of the Snowdonia National Park Study Centre, Maentwrog, Blaenau Ffestiniog, Gwynedd LL41 3YU, UK

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