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Surface Stratigraphy on Limestone of Venetian Palaces

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Abstract

The surfaces of Venetian palaces are a testimony to a long history of maintenance. Documents from nineteenth-century restoration projects assign dates and reveal some reasons for treatments explaining, for example, the use of aggressive cleaning and then the addition of pigments so that the newly restored façade did not appear 'too white'. Restoration during the twenty-first century has presented the opportunity to study the stone surface of three palaces and their stratigraphy. Three types of layers were identified (pollution deposit, silica/wax treatment and corrosion) which overlay the original stone and show distinct elemental signatures. The texture of the outermost deposit showed that the particle size was greatest when it was derived from areas of greatest exposure to the wind compared with calmer sheltered parts. Waxy treatment layers contained strata that probably derived from the brush used to apply the treatment. These treatment layers were warmer in tone than the superficial deposit or underlying stone. Improved understanding of the stratigraphy can inform decisions as to what layers should be protected during restoration.

Introduction

The façade of a palace, especially a historical one, resembles a palimpsest,[1] codifying the environment experienced by the architecture. A key to this code is the chemical transformation, deposition and treatment revealed in layers on the stone surface. The surface may be seen as offensive black crusts, which disfigure the building, or in some cases as a sympathetic patina. Both are evidence of the building's history. Here we examine the stratigraphy of stone surfaces at some Venetian palaces to assess the mode of formation and explore how this might offer guidance to the sensitive restoration of building façades.

Weathering and treatment of stone

History

As soon as stone is cut from a quarry, the fresh surface begins to change. Classical writers such as Vitruvius and Pliny the Elder were well aware of this and the need to protect the stone from weathering. They suggested that stone could be preserved through the use of waxes or resins. While Pliny the Elder was an encyclopaedist, Vitruvius was an architect, so it is likely that the techniques suggested in his work are probably closer to real practice.

Roman traditions for stone protection were also apparent in the Middle Ages, when the writings of Cennino Cennini gave advice on the protection of stone.[2] Few great buildings were built in the Italy of this period as people preferred to adapt earlier buildings to new functions. They felt no sense of history and thus buildings were spaces to be used, without any intention to preserve them as if they were from the past. The products used to preserve stone were always natural materials (waxes, resins, oils, etc.). When these layers decayed, they could be removed and replaced.

It was only by the nineteenth century that architects (and artists) had become conscious of the gap between the present and the past, and no longer treated buildings as simply useful spaces but saw them as physical reminders of the past which should be preserved. But even in this period, superficial layers on the external surface were considered sacrificial and not important to the history of buildings. Many monuments received extensive cleaning during the nineteenth century, resulting in the complete loss of the surface treatments applied during construction. Hence the earliest traces we find today are the remnants of the nineteenth century.

Nineteenth-century architects, aware of their duty, confronted the problem of stone conservation with great energy, aiming to preserve cultural heritage. Their restoration work often focused on the cultural worth of the architecture rather than restoring functionality, which had been a key concern of restorers of the medieval period or the Renaissance.[3] This has developed into the more recent focus on detail and artistic value, such that restorers have become preoccupied with architectural surfaces and their cleaning and treatment.

By the nineteenth century a wide range of stone preservatives were available.[4,5] In the United Kingdom, the construction of the Houses of Parliament from soft stone that weathered badly in the polluted atmosphere created considerable interest in preservation and cleaning techniques.[6] The treatments were typically based on natural organic materials that repelled water such as waxes or oils, or inorganic artificial products such as silicates and fluorosilicates.

The use of such materials continued in Venice to the early twentieth century, with the city of this period becoming a centre for testing ideas. The aim was to preserve the ancient buildings and reinforce a pride in the architectural achievements linked to the Republic of Venice (Serenissima Republica di Venezia, late seventh century to 1797). Many of the treatment methods proposed sought to cover the surface with thin layers to limit direct contact between the stone and the atmosphere. In Venice, the concept of maintenance was more widespread than the concept of restoration: the Venetian palaces were subjected to continuous maintenance to avoid rapid deterioration. Details of maintenance work are recorded in the documents preserved in archives such as Archivio di Palazzo Reale, Archivio di Stato di Venezia and Archivio Storico del comune di Venezia.

Today deteriorated stone is often preserved and consolidated. Two centuries ago such stones were often replaced with new stone of the same kind and the surface was treated to resemble the original (e.g. at Procuratie Nuove).[7,8,9] Thus nineteenth-century treatment aimed to imitate the older surfaces (usually blackened), thus preserving the contemporary appearance. In this period, there was a lengthy discussion about the way in which restoration should proceed:

- Whether to completely clean the surface or to preserve ‘the patina of time’?
- Should damaged stone be substituted?
- What kind of treatment should be used after surface cleaning?

The façades of the palaces in Venice suggest a variety of nineteenth-century answers to these questions. For example, there are palaces with many indents of substitute stone and others where they are absent. The accounts in *Giornali di Cantiere* of routine work on the palaces do not report the exact formulations of treatments and materials applied. The treatments adopted depended on ownership of the building (i.e. public: Procuratie Nuove and Libreria Marciana, or private: Ca´ Rezzonico) and the availability of materials.

Some guidance on the range of treatments can be found in articles, letters and patents.[10] The Venetian architect Giacomo Boni (1859–1925) and his friend Ruskin were against the extreme cleaning (*scorticamento*) of façades and substitution of damaged stone. Boni preferred to use consolidants for damaged stone and protective treatments for cleaned surfaces. He advocated silicates as a consolidant (Ransome’s patent formulation)[11] along with waxes. Where substitution was absolutely necessary (as with the capitals at Palazzo Ducale), he suggested colouring the stone with carbon black[12] to imitate the appearance that had been erased by decay and cleaning.

Boni was the last of a series of men who influenced the debate on conservation in Venice during the nineteenth century. Federico Berchet, Pompeo Molmenti and Giovanbattista Meduna were also key figures in early conservation.

Berchet worked to recover the Fondaco dei Turchi, but was strongly criticized (especially by Boni and Ruskin) because he rebuilt part of the building, on the basis of ancient drawings, instead of preserving what had remained. He was also criticized for the use of nut oil on the column surfaces, which was judged as unsuitable and bad for marble. Pompeo Molmenti wrote *Delendae Venetiae*, a pamphlet where he denounced the destruction of the city under restoration. For him, buildings were to be conserved and not rebuilt, a belief shared by both Boni and Ruskin. Giovanbattista Meduna was the architect who restored Ca' d'Oro and the San Marco basilica. Ruskin and the Society for the Protection of Ancient Buildings (founded in 1877 by William Morris in Britain) fought against this latter work because Meduna proposed rebuilding the edifice. To his opponents, this building was unique and could not be restored.

Such debate animated architects and created a strong interest in the principles of conservation and restoration just before the end of the nineteenth century. Boni was probably unique in his strong stance against the creation of historic fakes (i.e. recreated buildings). At the same time, he wished to stop the decay, yet remained convinced of the need to preserve the past; he wanted even patina to be conserved to give a sense of history.

Surface crusts

Surface crusts are typical of nineteenth- and early twentieth-century cities. Their morphology and characteristics vary depending on the underlying material and exposure.[13] Typically there are white crusts in areas exposed to the direct action of precipitation (i.e. washed areas) and black crusts, which form in partially sheltered areas. The latter show wide variation in terms of morphology, thickness and texture depending on the deposition of particles such as soot, dust, salts, etc. Although these crusts are typically black, other forms are found such as thin grey crusts or thick black crusts with a yellow layer of variable thickness.[14] The surface deposits on the façades are for the most part made up of unburnt carbon particles, silicates (sand), iron particles and calcium sulfate (gypsum). Other compounds are specific to different parts of the building. The surface crust is not necessarily a sign of the stone's decay because, in some cases, it represents accreted material.

There are many examples of buildings with surface crusts which represent part of the building's history such as the Church of St Trophime in Arles,[15] Palazzo d'Accursio in Bologna[16] and the Tower of London.[17] On the stone surface of the Venetian monuments, a range of different types of layers were found including black crusts, diverse deposits and treatments. Black crusts (i.e. gypsum-rich corrosion layers or superficial deposits) were usually found overlaying the treatment layers.

Treatment layers

Two different types of treatments were used on the three palaces studied:

- wax-based treatments between 1860 and 1874 on Palazzo Rezzonico and Procuratie Nuove;[18,19]
- a silica-based treatment on Libreria Marciana around 1883–84.[20]

To avoid any confusion this paper uses the term 'treatment' instead of 'patina'. A patina is the result of the natural aging of a surface whereas a treatment is something intentional added to a surface.[21]

The use of silica became common during the last two decades of the nineteenth-century and is confirmed in letters from Giacomo Boni to John Ruskin. In samples from Libreria Marciana, silica was found lying directly on stone surfaces suggesting that the earlier treatment of Jacopo Sansovino (sixteenth century) described as nut oil, sandarac, incense and alum was no longer evident. Any of this earlier treatment remaining was no doubt removed during the nineteenth century restoration, which began by cleaning with strong acid or alum. Alum seems to have a variety of meanings in addition to the potassium/aluminium double salt; it is sometimes referred to as 'allume di feccia', which seems to have been anything from salts from calcinations, grapes[22] or just potassium carbonate.

Methodology

Sites

The outer layers of stone were sampled from three Venetian palaces: Libreria Marciana, Procuratie Nuove and Palazzo Rezzonico (Figure 1). These three buildings can be considered representative of the city notably as public buildings (Marciana Library), a chamber of government of the Venetian Republic (Procuratie Nuove) and a private house (Palazzo Rezzonico or Ca' Rezzonico). The palaces are all built in Istrian stone, a limestone originating from quarries belonging to the Venetian government in the Istria region of the Balkans. The stone was used because of its well-known resistance to the severe climate of the lagoon.

Libreria Marciana

The Libreria Marciana (Figure 2) was built between 1537 and 1588. It was started by Jacopo Sansovino and completed by Vincenzo Scamozzi along

Figure 1 The city of Venice seen from satellite showing the location of (a) San Marco Square and (b) Palazzo Rezzonico.

Figure 2 Libreria Marciana, San Marco Square, Venice.

the lines proposed by Sansovino. To protect the stone surface, especially the sculpture, Sansovino used a special mixture reported in 'Secreti Diversi' (a manuscript conserved in the Libreria Marciana and known as the 'Marciana' manuscript).[23] The mixture was composed of sandarac, nut oil, incense resin and alum. The library was restored during the following centuries using a different treatment from that adopted by Sansovino. The Bell Tower collapsed in 1902, destroying the corner of the library. This was repaired and treated, but our samples are from an undestroyed part of the building.

Procuratie Nuove (also known as Procuratorie Nuove)

The construction of houses for the Procuratori di San Marco (magistracy of the Republic of Venice) began in 1586 with Vincenzo Scamozzi and was finished in 1640 by Baldassarre Longhena. The building (Figure 3) underwent continual maintenance and restorations during the nineteenth century, so the appearance of the façade (recorded in archive pictures) remained unchanged for at least two centuries. When these continuous works were halted between the First and Second World Wars, the front of the palace showed immediate signs of decay.

Figure 3 Procuratie Nuove, San Marco Square, Venice.

Palazzo Rezzonico

Palazzo Rezzonico or Ca' Rezzonico (Figure 4) was started in 1649 by Baldassarre Longhena and completed in 1756. The palace was restored several times, particularly during the twentieth century. The latest restoration (1986) involved the removal of most of the nineteenth-century wax-based treatments.

Methods

The samples taken from the three palaces (Libreria Marciana, 111 samples; Procuratie Nuove, 83 samples; and Ca' Rezzonico, 57 samples) originate from areas in which treatments were evident. Surfaces showing extensive deterioration were avoided and samples were chosen to represent different surface textures, exposures and architectural elements (sculptures, columns, etc.). The samples were detached from the surface mechanically and cut

Figure 4 Ca' Rezzonico, Canal Grande, Venice.

as cross-sections supported in an epoxy bi-component resin (CONCHEM CA 400/L-pm <700) and subsequently polished.

A range of techniques was used to study the apparent stratigraphy and composition of the samples:

- optical microscopy (Leica MZ75, Leica DM2500P);
- Nexus Nicolet infrared analysis via Fourier transform spectroscopy (FT-IR) using tablets of KBr for both powdered samples and acetone extracts;
- scanning electron microscopy (Jeol JMS 5600 LV) and electron microprobe analysis (SEM-EDX);
- Raman analysis using a Labram instrument by Jobin Yvon-Horiba with red laser (632.8 nm) and Edge filters for cross-sections.

Texture was explored by counting and sizing particles in images obtained by optical microscopy. This allowed particles present in the superficial deposits or crusts to be compared using statistical methods in an attempt to establish a relationship between exposure and the size of particles. The relationship eventually found between exposure and the size of particles is useful in order to understand how much direct exposure to the atmosphere influences the deposit.

Optical microscopy also offered the potential to undertake a colorimetric analysis using RGB values inherent in digital photomicrographs. These data, crudely calibrated, were expressed as percentages of lightness, the red–green and yellow–blue components. In the end we tended to use the yellowness of samples as defined by the formula $100 \times (G/255 - B/255)$ where G and B represented the green and blue intensities on the RGB scale.

Results

Composition

Optical microscopy showed the stratigraphy of the cross-sections. In general the samples showed several layers, characterized by different thicknesses, morphology and colour. This is illustrated in Figure 5, which shows a typical layering. The different layers observed with optical microscopy have a different chemical composition.

The outer layer is principally a deposit of gypsum, which includes particles of silica and traces of iron (as revealed by SEM-EDX analysis and FT-IR). The next layer derives from the treatment. This may be silicaceous in some cases (Figure 6) or organic (Figure 7). Table 1 lists the total number of samples analysed, and the treatments and deposits found.

Using acetone extracts analysed by FT-IR, the organic layers were identified as beeswax. Raman analysis also revealed small particles sometimes identified as hematite within the silicaceous layers or carbon particles in the waxes. The beeswax treatment may have been rather effective in

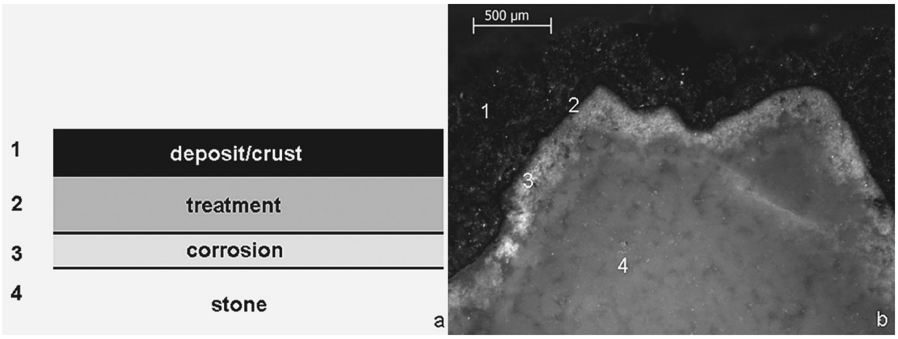

Figure 5 (a) A general scheme for layers found on the building stone. (1) Layer in contact with the atmosphere, sometimes not present. It is characterized by coarse red and black particles, or by black crystal-like material. It is not homogeneous. Its thickness varies between 2–3 μm and 250 μm. (2) Treatment layer (thickness 2–3 μm up to 100 μm) yellow or grey–black in colour, sometimes containing small pigment particles. (3) Corrosion layer (thickness between 2–3 μm and 10 μm), sometimes discontinuous or separated from the underlying stone, characterized by whitish particles and thickness not regular. (4) Istrian stone. (b) The micrograph of a sample from a sheltered area of Procuratie Nuove illustrates the visual appearance of these layers. The image of sample pp66 was obtained by optical microscopy equipped with a digital camera at 50× magnification; white numbers on the micrograph identify the layers described in scheme (a).

	Number of samples with sandy crust (deposit)	**Number of samples with black crystals* in crusts**	**Number of samples where crusts or deposits were virtually absent**
Inorganic treatment	Libreria Marciana (10) Procuratie Nuove (3)		
Organic treatment (or mixture of organic and inorganic)	Libreria Marciana (1) Procuratie Nuove (5) Ca' Rezzonico (8)	Procuratie Nuove (2)	Procuratie Nuove (10)
Absence of treatment	Libreria Marciana (4) Procuratie Nuove (4) Ca' Rezzonico (3)	Procuratie Nuove (1)	

* Crystals refers to particles of gypsum in the crusts as seen by optical microscope.

Table 1 Samples from the palaces classified on the basis of the type of treatment and crust.

protecting the stone, as its semi-fluid nature means it would have adapted to the complex profile of the surface whereas the inorganic silica would have been more rigid.

The presence of a treatment on the stone enables the growth of surface deposits which are completely detached from the stone. It also means that

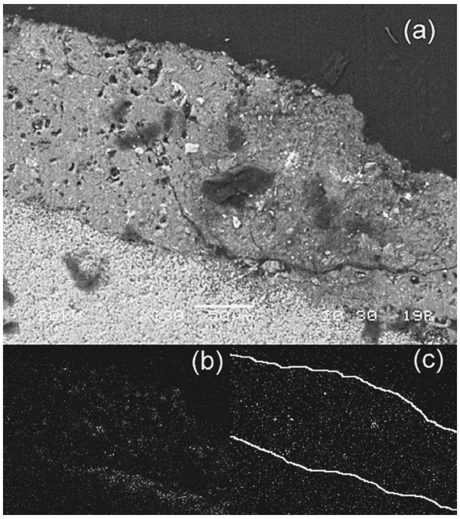

Figure 6 Cross-section from Procuratie Nuove sample pp53 with a diagonal orientation with the outside of the stone in the upper right. (a) Scanning electron micrograph showing the presence of a large compact layer on the top of the stone. (b) Mapping of sulfur X-ray intensity from pp53 showing the presence of a thin sulfur-rich corrosion layer beneath the treatment. (c) Mapping of iron X-ray intensity from pp53 showing the borders to the presence of silicon (from the silica treatment). The iron shows the distribution of iron pigment (in this case hematite) in the treatment layer, while the silica borderlines mark the layer of treatment.

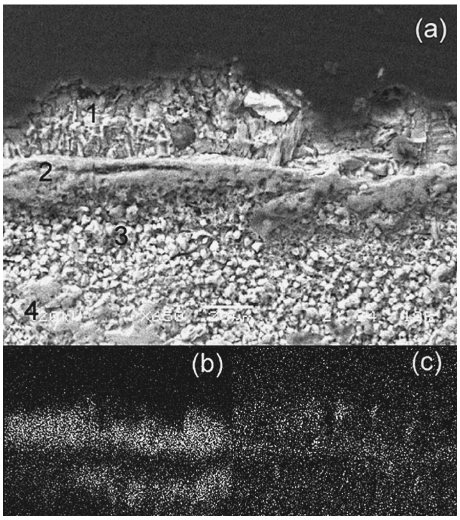

Figure 7 Cross-section from Ca' Rezzonico sample cr33. (a) Scanning electron micrograph showing the typical layering suggested in the scheme presented in Figure 1(a). The numbers mark the layers described in Figure 5. (b) Mapping of sulfur X-ray intensity from sample cr33. (c) Mapping of silica X-ray intensity from sample cr33. The maps are only semi-quantitative but show the presence of an upper deposit consisting of silica cemented in a gypsum matrix. A thin gypsum corrosion layer, low in sulfur, is found below the wax treatment layer.

products of decay do not form on the underlying stone unless the treatment layer is damaged or absent. In these situations, often found where the stone is badly damaged, the formation of corrosion products from the stone is generally mixed with particles deposited on the surface.

Underneath the treatment layers, a gypsum layer is often found which sometimes becomes detached from the underlying stone by a few microns (Figure 8). The gypsum under the treatment layer usually reveals no siliceous or carbon particles. This means that this thin layer is unlikely to be a remnant of earlier decay from deposited sulfur dioxide, or the product of sulfur dioxide deposition after the surface was cleaned. It might be possible for sulfur dioxide to diffuse through the waxy treatment layers, although this would be quite slow. Moreover, the gypsum crystals in this layer have a different morphology and are smaller than those found in the thick deposits. It seems the thin layer may be a short-term product of cleaning with sulfuric acid or alum. Thus this gypsum layer may be a frozen relic of the aggressive pretreatment adopted during the late nineteenth century.

In general, the outermost layers are more porous. Thus in summary we found:

- a dark gypsum and silica outer deposit, which is the most porous and friable;
- a beeswax or silicaceous treatment layer;
- a more compact thin gypsum layer;
- the underlying original stone.

Chemical characterization has refined our understanding of the nature of the layers. The outermost layer, characterized by gypsum and small lumps of silica in the superficial deposit, is made up of deposited materials and their sulfation products, which may act as a cement (calcareous dust, with silicaceous and iron particles are recognized as deposits at other sites such as Burgos).[24] The underlying treatment layer is beeswax (Ca' Rezzonico and Procuratie Nuove) or inorganic silica (Procuratie Nuove and Libreria Marciana); both are low in sulfur. These materials were typically applied to stone surfaces in the nineteenth century with a brush, so the treatment layer is visible as a detailed stratified structure (Figure 8).

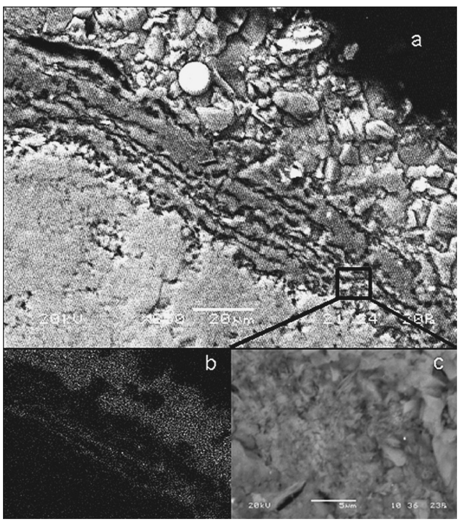

Figure 8 Layers from Ca' Rezzonico sample cr10 with a diagonal orientation with the outside at the upper right. (a) Scanning electron micrograph showing a spherical iron particle (white sphere, upper centre) in the upper coarse deposit layer, a wax layer with linear features lying on top of the corrosion layer, and stone. (b) A map of sulfur (chosen rather than a calcium map for clarity) showing high concentrations in the deposit and low amounts in the wax, except for some linear features and thin corrosion layers with sulfur at the upper edge of the stone. (c) Crystals of gypsum in a layer within the wax that appear to have been detached from the corrosion layer at the stone surface, perhaps during application of the wax.

Texture

The layers present different textures in addition to varying compositions. Microscope images were used to obtain measurements of particle size as a guide to texture. Particles within the upper layer show a wide variation in size. Particle size (see Table 2) is greater in deposits that derive from samples collected from exposed areas than those from sheltered ones. This is shown in Figure 9 as box-whisker plots relating particle size to exposure. The coarse texture probably results from the greater size of wind-driven particles deposited at exposed sites compared to those in the calmer sheltered areas (e.g. under porticoes).

Image analysis based on Fourier transforms can also be used to identify textural differences between the layers; fine-scale structures have a high frequency and coarse features a low frequency.

Sample	Position	Average particle size (μm)	Standard deviation
cr10	not exposed (portico on Canal Grande)	9.71	3.24
cr17	not exposed (portico on Canal Grande)	4.06	2.46
m1	not exposed	9.62	0.88
m110	not exposed	13.79	8.99
cr2	partially exposed	14.49	5.65
cr33	partially exposed (internal court)	10.53	3.60
m4	partially exposed	21.44	11.37
m6	partially exposed	15.42	3.24
m28	partially exposed	6.55	2.02
m87	partially exposed	19.22	4.25
m105	partially exposed	17.57	6.72
pp5	partially exposed	9.61	3.79
pp66	partially exposed	24.28	8.20
pp71	partially exposed	12.98	3.08
pp73	partially exposed	12.06	5.95
pp74	partially exposed	20.98	5.92
pp81	partially exposed	18.25	5.66
pp82	partially exposed	19.59	7.58
cr8	exposed	41.77	16.79
cr20	exposed (internal court)	24.29	8.54

cr = Ca' Rezzonico, pp = Procuratie Nuove, m = Libreria Marciana.

Table 2 Average particle sizes and their standard deviation in superficial deposits on samples.

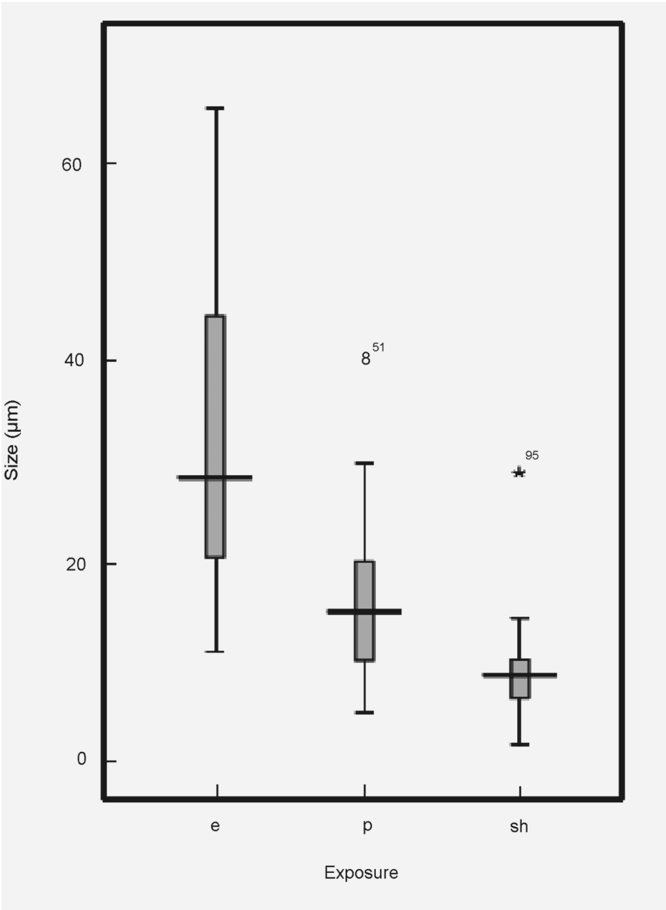

Figure 9 Box whisker plot of particle size in the superficial deposits (e = exposed, p = partially exposed, sh = sheltered). The numbers lying beyond the box and whiskers are the values of the outliers.

Figure 10a shows the original SEM image with a grid marking the portions chosen for analysis. The two-dimensional Fourier transform of the deposit layer of the sample is shown in Figure 10b, with the highest of the power (black areas) a rather chaotic signal of between 4 and 16 µm suggesting no preferred dimensions for the coarse particles present in this layer. Note that the length scale is plotted as a reciprocal because the output is scaled in terms of frequency.

The transform of the wax treatment layer (Figure 10c) displays more coherent spatial information, with a stronger periodicity as revealed by the intensity (power) of the Fourier transform at between about 8 and 16 µm. This seems to be associated with the holes in the wax layer.

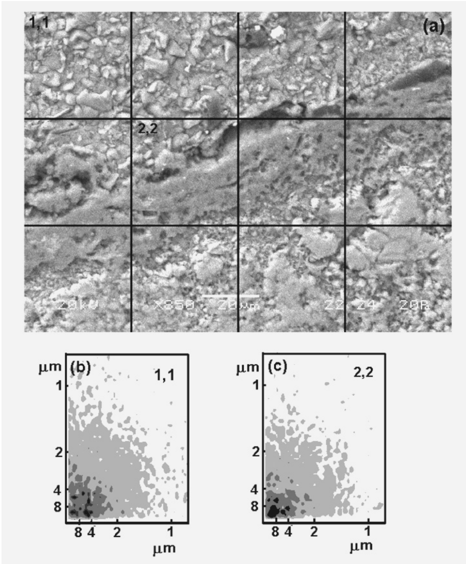

Figure 10 (a) Scanning electron micrograph of sample cr10_6 from Ca' Rezzonico with an added grid. This micrograph shows a coarse layer of deposit at the surface (upper left diagonal) on top of a sloping wax layer, which overlies a layer of decay and the stone. (b) Two-dimensional discrete Fourier transform of the image fragment 1,1 (as labelled on the grid in (a), representing the coarse deposit layer. Here the *x* and *y* axes are in microns (plotted as a reciprocal scale) and the power in the transform is represented in terms of a grey scale, where black signifies the greatest power. There is little evidence of a coherent spatial structure. (c) Two-dimensional discrete Fourier transform of the image fragment 2,2, representing the wax treatment layer. Here there are hints of a stronger periodicity between about 8 and 16 μm, perhaps associated with the holes in the wax.

Colour

Colour was determined by an analysis of the RGB values in digital photomicrographs. The RGB values showed the wax layers to be more yellowish. These layers lie between the two white horizontal lines marked in the inset, which shows a small cross-section of a sample from Ca' Rezzonico. By averaging reduced noise and by using the RGB values of the pixels, it was possible to determine a profile of yellowness as presented in Figure 11. This shows that the wax is more yellow than the black crust or the white limestone. The monochrome inset also shows the stratification that arises from brush strokes during application of the treatment layer.

Discussion

This study points to distinct chemical, textural and colour differences between layers on the surface of stone façades. Particular attention has been paid to differences between surface deposits and crusts, and treatment

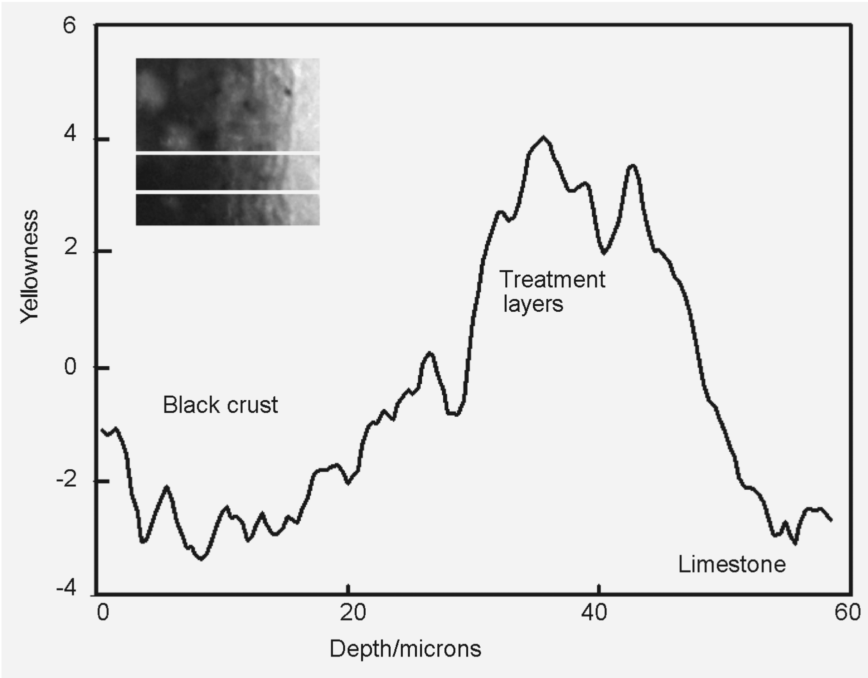

Figure 11 A profile of yellowness through sample cr10_1 from Ca' Rezzonico (each point in the profile represents an average from 30 scans). The inset shows a monochrome micrograph from the cross-section. The area averaged to obtain the profile lies between the two white horizontal lines. The inset also shows fine-scale stratification within the wax layer.

layers. These differences, which are not visible *in situ*, mean that the story recorded on the stone surface is not immediately apparent to conservators working at the building surface.

Sometimes, without microscopic examination of cross-sections, it is not even possible to distinguish between treatment and decay because these can appear similar to the naked eye. This creates a difficulty during restoration. While it might be sensible to preserve layers that were evidence of the deliberate actions of nineteenth-century restorers, the case for preservation of layers that developed though accidental corrosion after the cleaning process would seem less worthwhile. It is probably important for conservators working on a building to be clear about what parts of the stratigraphic record they wish to preserve. This established, they could then decide how much effort they would wish to expend in the task of reading the stratigraphy.

An understanding of the surface stratigraphy requires historical knowledge combined with scientific analysis of the layers. Archival documents tell of cleaning methods and materials used, and define a period of time for the various layers. Chemical analysis reaffirms the materials used, while SEM-EDX resolves the fine-scale distribution of elements within the layers. Textural and colour analysis give a sense of the mode of accretion of deposits and how colour changes between the layers. Notably, the analysis of particle size and the coarse nature of some superficial deposits indicate an influence from the exposure of architectural surfaces. Fourier analysis supported this by revealing a chaotic assembly of particles in these coarse outer superficial deposits and a lack of regular spatial features. The colour of the treatment layer depends on its nature (organic or inorganic) (e.g. beeswax is yellow), though oxidation of organic compounds over time can lead to warmer tones.

In the nineteenth century, little attention was paid to pre-existing surface coatings which were considered sacrificial and so aggressive cleaning was employed. The question of whether to preserve the surface never really arose. Thus by the twentieth century, the traces of earlier treatments had usually been erased. If any evidence had survived at the three Venetian palaces studied it could only have come from flexible materials (e.g. wax, tempera or oil) that had become embedded in fissures or cracks. What remains today as a treatment layer can be at the most 150 years' old. So if we preserve these layers, we are preserving not the original appearance but that of an intermediate stage in the history of the building.

The aggressive cleaning (with alum and acids) of the nineteenth century also meant that corrosion products could form on the freshly cleaned stone (as seen in Figure 8). Thus cleaning processes may have produced their own thin layers of gypsum. Although this layer is evidence of an earlier technique, it has no cultural significance as it is simply an accidental product of earlier cleaning. In reality the acids were meant to be washed off before the treatment layer of wax was added.

In spite of continuous maintenance, the palaces were never 'statue di sale' (i.e. made of salt or 'white'). This led Boni[25] to advocate the use of pigments to imitate the previous appearance: 'da poter mettersi cogli anni in armonia di colore colle parti vecchie' [to achieve, with passing of time, harmony in colour with old parts]. Hematite as a pigment is clearly evident in the analyses of the silica treatment (Figure 6) and, although the layers that survive are essentially nineteenth-century ones, they reflect a much earlier practice of colouring surfaces. This was especially true of the statues studied.

Restored façades should not appear too dirty or too clean. Yet, in each case, appearance has a complex interaction with the way architecture is perceived, and so the visitor needs to be informed about the way the building is presented.[26]

Conclusions

Stratigraphy on stone façades is the concealed history of a monument. Debates, mistakes, new products and testing are all encrypted on the surface. When revealed, the stratigraphy tells us not only about past decay but also the whole history of the building and its restoration, both its successes and failings. Furthermore, it offers the potential to see an expression of restoration ethics put into practice.

Reading the story presented on the stone allows us to explore the origin and significance of the layers. However, this requires a range of techniques:

- chemical characterization to understand microscopic cross-sections;
- physical representations of texture and colour.

Combined with historical knowledge, the information obtained from these two types of techniques reveals likely sources of treatments and cleaning residues.

Past restorations (mostly nineteenth century) erased the previous treatments and accidentally added gypsum corrosion layers. Thus contemporary restoration has to consider whether it is appropriate to conserve the traces (deliberate or accidental) left by nineteenth-century restorers. During restoration and preservation of the stone, it is necessary to strike a balance between preserving original intent and the patina accrued by the passage of time. There is also a fundamental question about colour. Black surfaces arose not only from decay, but were also derived from architectural pigments.

Future research should provide a better understanding of the original colour of the façades and might create the need to distinguish traces of carbon pigmentation from combustion particles. Although this paper presents a useful understanding of the stratigraphy, the approach is too time-consuming to be employed directly by those working in situ. Operators need techniques with which to distinguish clearly what is decay and what is treatment as they work. This is an important future direction for research. Attention needs to be given to the development of non-destructive on-site techniques that allow operators to understand the surface of the façade in real time. This research should provide methods to distinguish between treatment and decay, possibly through the use of portable microscopy or Raman spectroscopy. It is also important to be able to provide a statistical understanding that would allow a limited number of observations to be used as a guide to the surface of large parts of a façade. Even once this is established, the choice of what has to be removed and what must remain is an informed heritage management decision which can be justified by our understanding of the stratigraphic layers.

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Notes

1 A palimpsest is a manuscript, often written on parchment, in which later writing has been superimposed on earlier writing that has been incompletely erased.
2 Thompson, D. V., *The Craftsman's Handbook* (translation of *Il Libro dell' Arte* by Cennino d'Andrea Cennini), Yale University Press, New Haven (1933).
3 Rossi Manaresi, R. 'Stone protection from antiquity to the beginning of the industrial revolution', *Science and Technology for Cultural Heritage*, Vol. 2, 1993, pp. 149–59.
4 Brimblecombe, P., 'A brief history of grime: Accumulation and removal of soot deposits on buildings since the 17th century', *Stone Cleaning*, ed. Webster, R. G. M., Donhead Publishing, Shaftesbury, 1992, pp. 53–62.

5 Lewin, S. Z., 'The preservation of natural stone 1839–1965. An annotated bibliography', *Art and Archaeological Technical Abstracts*, Vol. 6, No. 1, 1966, pp. 185–277.
6 Brimblecombe, P., 'Air and architecture: Past, present and future', *Journal of Architectural Conservation*, Vol. 6, No. 2, 2000, pp. 30–46.
7 Archivio di Palazzo Reale, Palazzo Reale, Fabbriche, 1839, 1852, 1856, 1868.
8 Archivio di Palazzo Reale, Busta lavori edili, 1867–1882.
9 Archivio di stato di Venezia, Genio Civile, Busta 781.
10 Guidobaldi, F. and Mecchi, A. M., 'Trattamenti per i materiali lapidei dei monumenti estratti dalla manualistica tecnica del XIX e dell'inizio del XX secolo', *Manutenzione e conservazione del costruito fra tradizione e innovazione*, Bressanone, 1986, pp. 413–21.
11 *Report of the Twenty-Ninth Meeting of the British Association for the Advancement of Science*, John Murray, London (1860), pp. 78–9.
12 Calabretta, M. and Guidobaldi, F., 'Studi e sperimentazioni di Giacomo Boni su prodotti e tecniche per la conservazione dei monumenti', *Proceedings, Manutenzione e conservazione del costruito fra tradizione e innovazione*, Libreria Progetto Editore, Padova, 1986, pp. 81–90.
13 Sabbioni, C., Ghedini, N. and Bonazza, A., 'Organic anions in damage layers on monuments and buildings', *Atmospheric Environment*, Vol. 37, No. 9/10, 2003, pp. 1261–69.
14 Bonazza, A., Sabbioni, C., Ghedini, N., Favoni, O. and Zappia, G., 'Carbon data in black crusts on European monuments', *Proceedings, Air Pollution and Cultural Heritage,* ed. Saiz-Jimenez, C., Routledge, New York, 2004, pp. 39–46.
15 Ausset, P., Bannery, F., Monte, M. D. and Lefevre, R.A., 'Recording of pre-industrial atmospheric environment by ancient crusts on stone monuments', *Atmospheric Environment*, Vol. 32, No. 16, 1998, pp. 2859–63.
16 Ausset *et al*., ibid.
17 Bonazza, A., Brimblecombe, P., Grossi, C. M. and Sabbioni, C., 'Carbon in black layers at the Tower of London', *Environmental Science and Technology*, Vol. 41, 2007, pp. 4199–204.
18 Bretz, S., Baumer, U., Stege, H., Von Miller, J. and Von Kerssenbrock-Krosigk, D., 'A German house altar from the sixteenth century: Conservation and research of reverse paintings on glass', *Studies in Conservation*, Vol. 53, 2008, pp. 209–24.
19 Bensi, M. R. M. and Bensi, P., 'La cera e la paraffina nella pratica della conservazione dei dipinti murali nel XIX e XX secolo', *Manutenzione e Conservazione del Costruito fra Tradizione e Innovazione*, Proceedings of the congress held in Bressanone (24–27 June 1986), Libreria Progetto Editore, Padova, 1986, pp. 53–67.
20 Calabretta and Guidobaldi, *op. cit.*
21 Matteini, M. (ed.), *Le patine. Genesi, significato, conservazione* (series Kermes quaderni), Nardini Editore, Florence (2005).
22 Griselini, F., *Dizionario delle arti e dei mestieri*, Venice, 1768, pp. 99–100.
23 Merrifield, M., *Original treatises dating from XIIth to XVIIIth century on the art of paintings*, Vol. 2, John Murray, London, 1849, p. 630.
24 Esbert, R. M., Diaz-Pache, F., Grossi, C. M., Alonso F. J. and Ordaz J., 'Airborne particulate matter around the Cathedral of Burgos (Castilla y Leon, Spain)', *Atmospheric Environment*, Vol. 35, No. 2, 2001, pp. 441–52.
25 Boni, G., 'Il colore sui monumenti', *Archivio Veneto*, Vol. 25, 1883, pp. 344–60.
26 Brimblecombe, P. and Grossi, C., 'Aesthetic thresholds and blackening of stone buildings', *Science of the Total Environment,* Vol. 349, 2005, pp. 175–89.