

The New York Public Library: Protective Treatment for Sugaring Marble

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Abstract

The marble of the New York Public Library was found to be in a fairly good state of conservation except for the more exposed elements, such as quoins and the many delicately carved elements that decorate the building. This paper focuses on the treatment developed for areas that showed significant sugaring. For this purpose, laboratory examinations and analyses were carried out and preliminary tests were made with silicate ester-based consolidants. These, however, did not perform well in test studies and therefore an approach using inorganic materials was developed. The treatment consisted of spray application of an ammonium oxalate solution that reduced the intensive sugaring of the marble. To further protect these eroded surfaces, a shelter coat based on Type S hydrated dolomitic lime was also applied. This method is fully compatible with the marble substrate and follows the overriding principle of minimum intervention, as stated by the Venice Charter.

Introduction to marble and its deterioration

Marble has always been one of the most prized stones used for carving and in the construction of important buildings. The term marble usually refers to any stone that acquires a polish, although more accurately it refers to those rocks resulting from the metamorphism of limestones, including dolomitic limestones. Therefore, it is mainly constituted of calcite crystals sometimes mixed with dolomite.

As a carbonate material, marble is susceptible to weathering even by pure rain, since the presence of carbon dioxide in the air and its solubility

in water can reduce rainwater to an acid pH level of 5.6. Consequently, marble used in outdoor buildings and sculptures in pre-industrial times is already being slowly eroded by precipitation. Except for very pure marbles in which erosion is uniform, marbles that are not highly metamorphosed present uneven erosion. This reflects their heterogeneous structure, in which some areas have larger crystals and others smaller crystals. The rate of dissolution will be proportional to the exposed surface so the erosion occurs faster in the smaller crystal areas because of their higher specific surface; this leaves behind the larger crystals in relief (Figure 1).¹

The presence of air pollutants, such as sulphur and nitrogen oxides, increases the aggressiveness of the attack by rainwater and results in the formation of a relatively soluble salt, calcium sulfate dihydrate. It crystallizes as gypsum on the marble and within subsurface pores, causing deterioration of the marble by sugaring, and in some cases by flaking, depending on its structure and texture (Figure 2). Since gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is a hundredfold more soluble than calcite, CaCO_3 , it is removed from the areas that are regularly washed by rainwater and therefore these areas show disaggregation but not flaking.

Sugaring of marble is also induced by thermal cycling, a result of the anisotropy of the calcite crystal, which has significantly different expansion coefficients along the *c* axis and the *a* and *b* crystal axis. Upon heating, the crystal elongates along the *c* axis while contracting across the other axes (Figure 3). Repeated thermal cycling loosens the texture of the marble, increasing its porosity and in turn accelerating its solubilization in rainwater.

Consequently, a weathered marble will present a weakened, eroded outer surface with a higher porosity subsurface as compared to the sound interior. When dealing with conservation interventions, it is desirable to preserve this weakened skin and find the means to protect it and to reduce its deterioration rate. The surface treatments of the marble carried out on the most eroded marble areas of the New York Public Library had the key objective of slowing down the erosion and sugaring process of the marble that primarily affects highly exposed areas of the building.

Marbles at the New York Public Library

Historical background

The original marble stone used to build the New York Public Library, henceforth NYPL, was a commercial white marble originally quarried by the Norcross-West Marble Company, from a quarry near the foot of Mount Aeolus and Dorset Mountain in Dorset, Bennington County, Vermont.² Of the four varieties that were quarried, 500,000 cubic feet of 'White



Figure 1 Marble erosion and disaggregation at sculpture relief.



Figure 2 Marble erosion, sugaring and flaking at scroll brackets supporting the cornice.

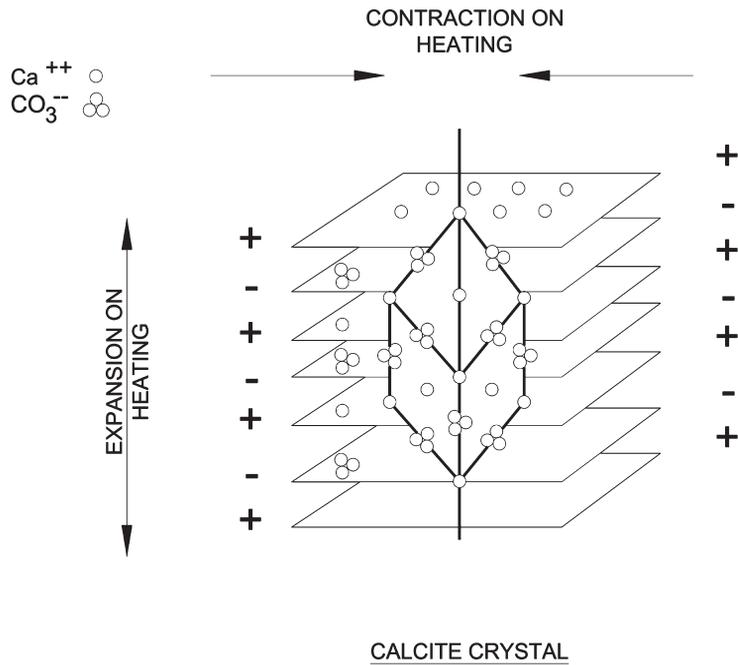


Figure 3 The expansion of a calcite crystal along the c axis and the contraction along the a and b axes with temperature increase (redrawn from Torraca, G., *Porous Building Materials*, ICCROM, Rome, 1981).

Mountain' marble were used in the exterior and interior construction of the NYPL³ in the period until the completion of the building in 1911.

The marble is Ordovician in age (430–500 million years old) and is part of the Bascom Formation, which includes interbedded dolomite and calcite marble, calcareous sandstone, quartzite and limestone breccias.

Analysis and characterization

Prior to the commencement of the restoration of the NYPL in 2008, marble core samples were removed from 28 representative locations on the main building façades. The samples were taken from various exposures of the building, and from locations with different conditions. The cores were found to all be composed of Danby marble. Visual examination as well as stereobinocular microscopy and polarized light microscopy showed some inter- and intra-core variation in the size of the calcite grains. It was also observed that the individual calcite grains in the body of the cores were typically well interlocked. Very minor amounts of accessory minerals were detected such as pyrite, quartz, actinolite (a ferri-ferrous amphibole), muscovite (a mica) and a trace of feldspar (probably microcline). In some of the marble cores, the foliation detected indicated that in all likelihood

individual stones were dressed and installed without particular regard for orientation. A stone unit installed with foliation oriented parallel to the exposed surface may contain planes of weakness that can contribute to an increased rate of weathering during normal exposure.

Some cracks were observed beneath the surface, with localized weathering adjacent to them. This suggests that they had been present for a prolonged period of time. These microfractures could be visually observed as planes of incipient delamination (Figure 4).

Scanning electron microscopy (SEM) examination confirmed that the surface relief had been affected by differential dissolution of the exposed calcite grains, as mentioned previously, and that this variation in relief has greatly increased the exposed surface area.

Possible treatments considered

The rationale used in the selection of the treatment had to address the key problems, which were the sugaring and flaking of the surface marble. Although the surface was much eroded, especially at corners and on decorative elements with fine carving, this deteriorated layer was less than a centimetre (about 0.25 to 0.75 cm) in thickness and the remaining large portion of the marble was in good condition. The marble in its sound condition



Figure 4 View of surface loss resulting from delamination.

showed a very low porosity of 0.14% on average. It was felt that the application of a consolidation treatment such as a silicate ester would tend to form a surface layer with different mechanical properties from those of the underlying marble. In fact, the laboratory tests carried out to evaluate this approach showed that none of the silicate ester-based consolidants tested were able to penetrate far enough to achieve the required bonding to the sound stone nor were they capable of filling the microfissures that cause the surface sugaring.

Silicate esters were specially developed for the more porous sandstones and have been used effectively on porous limestones.^{4, 5} However, consolidating a loose, thin surface layer and ensuring that it behaves in a similar way to the sound stone is difficult; the chances of failure, with the consequent loss of the consolidated surface, are relatively high given the aggressive environmental conditions, with frequent freeze–thaw cycles and intense traffic pollution.

It could be argued that the application of a siloxane water repellent would in part mitigate the effects of the air pollution and water infiltration. However, it is also known that water repellents, especially on sculpted objects, tend to form preferential water paths that result in concentrated soiling, or even biocolonization, along them.^{6, 7} The unaesthetic effect of the striped patterns that may result was considered a risk that could not be taken for a building with the aesthetic value of the NYPL. A further consideration against the use of water repellents on the vertical walls is the uneven aging of these products leading to a blotchy and possibly darkened appearance.⁸ However, a water repellent treatment was applied on horizontal surfaces along the building parapets and exposed horizontal ledges at the cornice level.

Another consolidation system that was considered was the treatment developed in Bologna, Italy, three decades ago, which is generally referred to as the ‘Bologna cocktail’. This system is based on an acrylic resin (Acryloid B72) mixed with a silicone resin (Dry Film 104) in a mixture of various solvents.^{9, 10} The acrylic resin provides superior adhesion for loose particles but experience gained over the years showed that areas treated with this system tend to soil more rapidly than untreated surfaces.^{11, 12, 13} This can be attributed to the relative low glass transition temperature of this acrylic resin (T_g 40°C). Around this temperature, which can definitely be attained by white marble surfaces when the sun shines on them on hot summer days, the resin tends to become sticky and therefore soiling will be enhanced. This negative feature would be enhanced by the exposure of the NYPL to traffic pollution.

In view of these considerations it was decided to evaluate an inorganic treatment based on the application of ammonium oxalate to consolidate and protect the surface.

Protective treatments

Historical background

Since antiquity, marble has received protective finishes and treatments, wax being preferred to enhance the brilliance of marble. Some ancient marble monuments such as the Parthenon were even painted, based on the presence of colour traces and historic records.

The presence of oxalates in many of the colour traces ranging from pale yellow to orange has prompted many studies and resulted in two international conferences devoted to the presence of calcium oxalate in patinas.^{14, 15} There are various mechanisms that lead to the formation of oxalate patinas, depending on the substrate, treatments applied to it, and environmental conditions, as summarized elsewhere.¹⁶

In the specific case of the NYPL, pale yellowish patinas were found in areas protected from direct rain and water run-off. However, the two samples, taken from the pediment at the south-west corner of the building, analysed by Raman spectroscopy did not show the presence of oxalates.

Complementary analyses by X-ray fluorescence spectroscopy¹⁷ showed the presence of silicon, aluminium and potassium, consistent with the trace minerals in the marble, as well as that of sulfur and phosphorus, to be expected from the deposition of air pollutants, in addition to titanium, iron and calcium, the latter mostly due to the substrate. The presence of iron and titanium, with that of other metals, has previously been identified by this same technique in atmospheric particulate matter as well as in black crusts or coloured surface deposits.^{18, 19}

Development of oxalate-based protective coatings

The persistence of the calcium oxalate compounds found on so many ancient and historic monuments prompted the idea of using them as a protective coating. By the mid-1980s this approach was being used successfully on mural paintings.^{20, 21} The good performance of this method suggested the logical extension of applying it to deteriorating limestones.^{22, 23, 24}

The treatment consists of applying a poultice containing a saturated solution of ammonium oxalate in its monohydrate form, approx. 5–7% w/v, for several hours. At this concentration, longer application times have shown no significant improvement in the resulting calcium oxalate formation (mostly the monohydrate whewellite, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$).²⁵

Other studies evaluated the treatment as a protective coating for dense limestone and marbles.²⁶ Those authors applied it by poulticing with a 5% w/v concentration solution for different time lengths of up to 36 hours. It was found that only after fifteen hours does a layer of calcium oxalate (mostly the monohydrate whewellite) become visible in

a cross-section. This layer presents good adhesion to the marble substrate and is variable in thickness, between 0.5 and 2.1 μm , regardless of the poultice application time (between fifteen and 36 hours). Although the authors considered that by ten hours a sufficient coating of the more stable calcium oxalate, whewellite, is achieved, the fact that the layer only becomes visible in cross-section after fifteen hours suggests that a longer application time is required to form a thicker layer and therefore they recommended a 24-hour poultice application. Their study also included an evaluation of the resistance to acid attack where they were able to confirm that even a treatment with a 0.4% w/v concentration, applied for 24 hours, reduces the initial attack significantly. This was the lowest ammonium oxalate concentration at the 24-hour application time that provided a protective action to the marble.

Following the laboratory studies carried out in Florence, Italy, the treatment was applied to various works of art. For example, the marble statues of Farinata degli Uberti, Pier Capponi and Andrea Ocagna in the Loggia of the Uffizi were treated in 1989–99.²⁷ At about this time, the conservation intervention of the cloister of the Jeronimos Monastery in Lisbon, Portugal, was being undertaken. A saturated solution of ammonium oxalate was sprayed onto the exterior surfaces until saturation. The treated surface was in turn coated with a pigmented translucent lime-wash and, finally, with an oligomeric siloxane water repellent.^{28, 29} The former served to homogenize the surface colouration and the latter as a protective treatment.

Although the characteristics of the stone used in the cloister (dense Lioz limestone) are different from those of the NYPL, their chemical nature is similar. Both are mainly composed from calcite crystals with low porosity (<1%), very small and compact in the case of the Lioz limestone and large and medium crystals for the Danby marble.

Shelter coats

Shelter coats have been used traditionally as a means of preserving weaker materials that may be more susceptible to deterioration. Particularly in the UK, where the ‘lime method’ for conservation of limestone was developed,³⁰ and in Austria, for outdoor sculptures in limestone,³¹ this approach has been, and still is, implemented.

The purpose of a shelter coat is to protect the substrate by providing a sacrificial layer that will undergo the effects of erosion and weathering, thus reducing the loss of original material. Furthermore, by filling surface pores and fissures of the stone, shelter coats provide a smoother surface improving water run-off while reducing the accumulation of pollutants.

Laboratory and field tests

Oxalate test treatments

Sample preparation for laboratory evaluation

For testing purposes, fragments from marble blocks that needed to be replaced at the NYPL were used. These were mostly taken from the west elevation and from the south-west corner of the building, near the parapet. The samples were weathered, showing a rough surface and sugaring when rubbed. Two sets of experiments were carried out on these weathered samples. All solutions used in the testing were prepared from the ammonium oxalate monohydrate at a 5% w/v concentration. In practice, due to the extent of the surfaces to be treated, the solution was applied by brushing or spraying, so only these methods were evaluated in the laboratory.

In the first test, the surfaces of two weathered samples were brushed with a 5% w/v ammonium oxalate solution. The first sample was brushed only once, while the second one was brushed three times, with 30-minute intervals between the brushings.

For the second test, five weathered marble samples were treated, respectively, with one, two, three, four and five applications of a 5% w/v ammonium oxalate solution. This solution was sprayed on, with a two-hour waiting time between successive applications.

Finally, a third unweathered quarry sample received a single brushing of the 5% w/v ammonium oxalate solution.

Analytical procedures

Raman spectroscopy analyses were carried out in situ on the surfaces of the different samples. After the in situ analyses, the samples were mounted as cross sections in a synthetic resin, polished and examined using both polarized light microscopy and scanning electron microscopy (SEM).

Results

Both hydrated calcium oxalates, the mono- and the dihydrate, whewellite and weddelite, respectively, were detected on the surfaces of all the treated samples by Raman spectroscopy.³² The amount of calcium oxalate crystals was found to increase with the number of applications. Similar results were obtained for both the sprayed and brushed samples.

When the samples were examined in cross-section, it was found that the calcium oxalate deposit had not formed a uniform layer on the surface. Some ammonium oxalate crystals were observed on the surfaces of the treated samples, both brushed and sprayed. Comparatively fewer

ammonium oxalate crystals were found on the surfaces of the sprayed samples, as this compound decomposes into volatile materials, i.e. CO₂ and NH₃, especially when exposed outdoors.

The presence of the calcium oxalate confirms that the application method is sufficient to produce a reaction of the oxalate solution with the marble, very likely in the fissures and cracks given the preferential absorption of the solution by capillaries, but it is not sufficient to produce a uniform coating on the surface. Nonetheless, the reaction results in the consolidation of the 'sugared' marble, as visually observed as a uniform cohesion of calcite crystals that previously lay apparently loose over the marble surface. Neither spraying nor brushing, as applied on these samples, resulted in any loss of surface grains. Tangible sugaring was produced only with a higher pressure, such as rubbing.

Field tests

Field tests were also carried out on actual marble blocks at the NYPL. For this purpose, the areas where the ammonium oxalate was to be applied were previously cleaned by using very low pressure dry steam, i.e. only the vapour reached the surface. Tests were carried out on quoin blocks that presented a very weathered quoin surface on one side, where the marble surface had sugared intensely, and a smoother marble surface on the other side. The sugaring was made evident when the surface was rubbed by hand, but neither the soft-cleaning method used nor the ammonium oxalate solution spraying induced any significant loss of surface grains.

Consequently, the effectiveness of oxalate formation on two types of surfaces could be assessed. The saturated ammonium oxalate solution (approximately 5% w/v) was applied by spraying until saturation. After a period of twelve hours, it was found that when rubbed by hand the treated surfaces on the smoother marble surface were much less friable. This was also the case for very weathered surfaces, indicating that the amount of calcium oxalate formed was sufficient to bond the loose grains of the marble surface. Tactile evaluation has been shown to be a reliable method for comparison of stone surface roughness.³³

Shelter coats testing

The laboratory and field tests suggested that the ammonium oxalate treatment applied by spraying, while increasing the cohesiveness of the outer, weathered layer of the marble, would not provide sufficiently long-term protection, as a uniform coating of calcium oxalate was not developed. Therefore, to further protect and smooth out much-eroded surfaces, a shelter coat was applied over the marble surface once it had been treated using the ammonium oxalate solution. Several types of shelter coats were tested based on formulations of either

lime putty, dispersed hydrated lime or hydrated hydraulic lime. These were tested and evaluated in the laboratory to select the optimal system for site testing at the NYPL. The shelter coat is an effective and low-cost traditional treatment that generally improves weathering performance over time.

Laboratory evaluation

The lime putty shelter coat formed a white layer over the marble surface. While the coating was observed to be quite thick over the low spots of the marble surface, the highest points of the surface were observed to protrude from the baseline of the coating. After curing, the lime putty coating in areas covering the low spots of the marble showed significant cracking. However, these did not extend to the high spots because the coating was thin. The dispersed hydrated lime also formed a white layer over the marble surface coating; however, it had a somewhat blotchy appearance. In comparison to the lime putty coating, it was not as thick, did not develop cracks, and conformed better to the surface of the marble. The observed difference is most likely due to the specific characteristics of the material itself, including its deposition process. The marble surface appeared to be well coated and filled in by the shelter coat. The hydrated hydraulic lime (Natural Hydraulic Lime NHL 2.0) coating was deposited as a thin, white coating with a slightly more uniform appearance. No cracks were apparent on the surface. While the coating appears thicker than the dispersed hydraulic lime and thinner than the lime putty coating, the low spots of the marble were well covered and smoothed out and the high spots appeared to extend through the coating. The appearance of the shelter coat in these samples more closely matched the appearance of the marble than that provided by the lime putty or the dispersed hydrated lime coated samples.

During laboratory trials, all shelter coats were observed to add significantly more material and assisted in conserving the marble by filling the surface pores, thus improving water shedding abilities of the marble while reducing the exposed surface area. From an aesthetic point of view, the hydrated hydraulic lime shelter coats provided the best match to the marble. The limited number of test samples evaluated in the laboratory suggested that while this shelter coat was visually distinguishable from the adjacent uncoated marble, its aesthetic appearance could be improved during application in field trials by varying the water-binder ratio used and the addition of pigments.

Field testing

During the field trial applications, the chosen hydrated hydraulic lime shelter coat did not perform as well as in previous laboratory testing. Variations on the above formulations were tested in the field and, based on field

evaluation, a shelter coat formulation based on a Type S dolomitic hydrated lime including casein was selected.³⁴ As the early formulations tended to produce a yellowish appearance in the shelter coat, a titanium dioxide (rutile) pigment was added for colour matching. Each subsequent shelter coat was prepared suspending the binder in various aqueous dispersions and using 1 part of the hydrated lime powder mix with from 3 to 6 parts water. It was noted that the resulting shelter coat was quite milky in appearance.

Six formulations of the above shelter coat were applied in situ along the lower courses of marble masonry that showed signs of sugaring and that had been thoroughly steam-cleaned of dirt and grease, with no ammonium oxalate treatment applied. Each coating was applied and evaluated for ease of application, appearance and possible colour variation. After a short drying period of 24 hours, uniform results could already be observed. The shelter coat that best matched the white marble in appearance was the 1:4 formulation, consisting of 1 part hydrated dolomitic lime to 4 parts water, with an addition of titanium dioxide pigment.

It was noted that the shelter coats were best applied by brushing over the clean surface to saturation, with perimeter boundaries feathered to blend in with surrounding stone. This was the procedure used for the selected formulation on all the areas that required this protection.

Discussion and conclusions

The practical solution implemented on the NYPL was the application of the developed protective surface treatment to highly exposed areas such as corners, quoins and some decorative architectural features throughout each building façade. Prior to application of the surface treatment these areas were cleaned to remove all dust, soiling and surface deposits, as tested during the field trials, and care was taken to minimize loss of material from the more friable surfaces. The purpose of this process was to leave the marble surface clean to receive the treatment.

The surface treatment was based on a two-step approach: first, the application of the ammonium oxalate solution to consolidate the sugaring surface, followed by the application of a lime shelter coat to protect the exposed surface.

In practice, the ammonium oxalate treatment was applied by spraying to saturation, i.e. until the surface would no longer take up solution. In the field, spraying to saturation implies several spray applications over a given area, with overlaps. Based on the effectiveness of consolidation that was achieved, this was equivalent to an oxalate surface formation that was obtained in the laboratory with two to four sprayings. After twelve to 24 hours, it was followed by a careful application of the shelter coat by brushing, taking care to colour match the shelter coat to adjacent areas of the marble.

The surface treatment carried out on the most eroded marble areas of the New York Public Library had the key objective of slowing down the erosion and sugaring process that primarily affected highly exposed areas of the building. The use of the ammonium oxalate treatment served to increase the surface cohesion of the marble, thus significantly reducing the surface sugaring. To further protect the surface, the traditional shelter coat method was used. The inclusion of the titanium dioxide pigment in the shelter coat may have the additional advantage of contributing self-cleaning properties and air-purifying properties,³⁵ although rutile is not as efficient for this purpose as anatase.³⁶ By reducing the exposed surface area and providing a sacrificial surface layer that may reduce the soiling rate, the long-term effectiveness of the intervention was potentially increased.

The conservation intervention implemented to consolidate and protect the sugaring marble at the NYPL can be considered an 'extraordinary maintenance' intervention, as defined by the Italian NORMAL Commission (Normal 20/85).³⁷ This designation reminds those responsible for the building that it will still require future maintenance, even after a conservation intervention. Ideally, the time required between interventions will remain constant; however, in some cases it can decrease because the 'conserved' building material is more complex than the original material. One of the advantages of the oxalate treatment is that it is closely related to the inorganic nature of the stone substrate, in comparison to silicate ester treatments. For the present case, considering that over a century went by without a major intervention, aside from a comprehensive cleaning of the façade in 1989, it is likely that under present conditions and assuming that air pollution will continue to decrease in the future, 25 to 50 years may go by before another 'extraordinary maintenance' intervention, such as this one, will be needed.

The selected approach is considered an optimum solution for treating the deteriorated marble surfaces since it respects the three primary ethical criteria of conservation. It complies with the minimum intervention principle. Furthermore, it utilizes materials that are totally compatible with the marble substrate. Finally, the mineral nature of the oxalate reaction products will not interfere with the application of any conservation product that may be developed in the future; therefore the third ethical criterion, re-treatability, is also respected.

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Notes

- 1 Charola, A. E. and Koestler, R. J., 'SEM study of the deterioration of monumental stones in Vienna', *Wiener Berichte über Naturwissenschaft in der Kunst*, Vol. 2/3, eds. Vendl, A., Pichler, B. and Weber, J., Hochschule für Angewandte Kunst, Vienna, (1985–86), pp. 176–85.
- 2 West, E. H., 'Vermont marble, Part I, quarries of the Norcross-West Marble Co., Dorset, Vermont', *Mine and Quarry*, Sullivan Machinery Co., Chicago, Illinois, March, 1909, pp. 271–75.
- 3 Bender, B. J., Norcross & West Marble Co., South Dorset. Postcard dated 23 February 1907, University of Vermont, Special Collections, Bailey Howe Library, Wilbur Collection.
- 4 De Witte, E., Charola, A. E., and Sheryll, R. P., 'Preliminary tests on commercial stone consolidants', *Proceedings, 5th International Congress on Deterioration and Conservation of Stone*, ed. Felix, G., Presses Polytechnique Romandes, Lausanne, 1985, pp. 709–18.
- 5 Oliver, A. B., 'The variable performance of Ethyl Silicate: Consolidated stone at three National Parks', *APT Bulletin*, 33, no. 2/3, 2002, pp. 39–44.
- 6 Roby, T., 'In situ assessment of surface consolidation and protection treatments of marble monuments in Rome of the 1980s, with particular reference to two treatments with Paraloid B72', *Proceedings, 8th International Congress on Deterioration and Conservation of Stone*, ed. Riederer, J., Möller Druck und Verlag, Berlin, 1996, pp. 1015–28.
- 7 Charola, A. E., Delgado Rodrigues, J. and Vale Anjos, M., 'Disfiguring biocolonization patterns after the application of water repellents', *Restoration of Buildings and Monuments*, Vol. 14, No. 5, 2008, pp. 365–72.
- 8 Roby, *op.cit.*
- 9 Nonfarmale, O., 'A method of consolidation and restoration for decayed sandstones', *The Conservation of Stone I*, Centro per la Conservazione delle Sculture all'Aperto, Bologna, 1975, pp. 402–10.
- 10 Rossi Manaresi, R., 'Effectiveness of conservation treatments for the sandstone monuments in Bologna', *The Conservation of Stone II*, Centro per la Conservazione delle Sculture all'Aperto, Bologna, 1981, pp. 665–88.

- 11 Roby, *op. cit.*
- 12 Fassina, V., Lazzarini, L., Laurenzi Tabasso, M. and Mecchi, A. M., 'Protective treatments for the reliefs of the Arconi di S. Marco in Venice: Laboratory evaluation', *Durability of Building Materials*, 5, 1987, pp. 167–81.
- 13 Laurenzi Tabasso, M. and Mecchi, A. M., 'Natural and artificial ageing for evaluating waterproofing treatments for marbles', *Materiale de Costruccion*, Vol. 42, 226, 1992, pp. 5–25.
- 14 *The Oxalate Films: Origin and Significance in the Conservation of Works of Art*, Proceedings of the Conference, Centro C.N.R., Gino Bozza, Politecnico di Milano, Milan, 1989.
- 15 Realini, M. and Toniolo, L., eds, *The Oxalate Films in the Conservation of Works of Art*, Proceedings of the 2nd International Symposium, Editeam, Castello d'Argine, 1996.
- 16 Charola, A. E., Aires Barros, L., Centeno, S. A., Basto, M. J. and Koestler, R. J., 'Analysis of the colour traces found on the cloister of the Jeronimos Monastery in Lisbon', *Restoration of Buildings and Monuments*, Vol. 8, No. 5, 2002, pp. 447–74.
- 17 X-ray fluorescence elemental analyses were conducted with a Jordan Valley ExWIN Series energy dispersive Ex3600 X-ray fluorescence unit. Each sample area, approximately 1 cm in diameter, was analysed for 200 live time seconds with direct rhodium radiation with medium throughput (40 μ A, 10 kV).
- 18 Aires Barros, L. and Basto, M. J., 'As particulas sólidas da atmosfera envolvente dos Jerónimos e a mínero-química da suas costras de alteração', *Memórias* No. 3, eds. Noronha, F., Marques, M. M., and Nogueira, P., Universidade do Porto, Porto 1993, pp. 515–18.
- 19 Aires Barros, L., Basto, M. J. and Charola, A. E., 'The stones of the cloister: Nature, deterioration and studies of historic treatments', *Jeronimos Monastery: The Conservation Intervention of the Cloister*, ed. Charola, A. E., IPPAR, Lisbon, 2006, pp. 190–98.
- 20 Matteini, M., Moles, A., and Giovannoni, S., 'Un sistema protettivo minerale per le pitture murali a base di calcio ossalato: Proposta di un metodo e verifiche analitiche', *OPD Restauro*, Vol. 6, 1994, pp. 7–15.
- 21 Matteini, M., Moles, A. and Giovannoni, S., 'Calcium Oxalate as a protective mineral system for wall paintings: Methodology and analysis', *3rd Int. Symposium on the Conservation of Monuments in the Mediterranean Basin*, eds. Fassina, V., Ott, H. and Zezze, F., Soprintendenza ai Beni Artistici e Storici di Venezia, Venice, 1994, pp. 155–62.
- 22 Matteini, M., 'Artificial oxalate in conservation of mural paintings and limestone artifacts', *OPD Restauro*, Vol. 11, 1999, pp. 30–38.
- 23 Matteini, M., 'Durabilità e compatibilità in alternativa a reversibilità nei trattamenti protettivi dei manufatti calcarei all'esterno', *Reversibilitâ? Concezione e interpretazioni nel restauro*, Arkos-UteT, Torino, 2002, pp. 87–94.
- 24 Lanterna, G., Mairani, A., Matteini, M., Rizzi, M. and Scuto, S., 'Mineral inorganic treatments for the conservation of calcareous artefacts', *Proceedings 9th International Congress on Deterioration and Conservation of Stone*, ed. Fassina, V., Vol. 2, Elsevier, Amsterdam, 2000, pp. 387–94.
- 25 Matteini, M., 'Consolidanti e protettivi di natura minerale in uso sui manufatti di interesse artistico ed archeologico costituite da materiali porosi', *Konservierung von Wandmalerei*, ed. Pürsche, J., Vol. 104, Arbeitshefte des Bayerischen Landesamt für Denkmalpflege, Lipp Verlag, Munich, 2001, pp. 240–49.

- 26 Doherty, B., Pamplona, M., Selvaggi, R., Miliani, C., Matteini, M., Sgamellotti, A. and Brunetti, B., 'Efficiency and resistance of the artificial oxalate protective treatment on marble against chemical weathering', *Applied Surface Science*, Vol. 253, 2007, pp. 4477–84.
- 27 Lanterna et al., *op. cit.*
- 28 Henriques, F. M. A. and Charola, A. E., 'The theoretical approach of the conservation intervention at the cloister of the Jeronimos Monastery in Lisbon', *Restoration of Buildings and Monuments*, Vol. 8, No. 5, 2002, pp. 429–45.
- 29 Proença, N., 'Conservação e metodologia na intervenção do claustro do Mosteiro dos Jeronimos', *Jerónimos Monastery: The Conservation Intervention of the Cloister*, ed. Charola, A. E., IPPAR, Lisbon, 2006, pp. 145–75.
- 30 Fidler, J., 'Lime treatments. An overview of lime watering and shelter coating of friable historic limestone masonry', *Stone*, ed. Fidler, J., Vol. 2, English Heritage Research Transactions, James and James, London, 2002, pp.19–28.
- 31 Koller, M., Nimmrichter, J., Paschinger, H. and Richard, H., 'Opferschichten in der Steinkonservierung-Theorie und Praxis', *Restauratorenblätter* 17, Mayer & Comp, Wien, 1996, pp.143–50.
- 32 Calcium oxalate in its different states of hydration can be identified and distinguished from ammonium oxalate by their characteristic Raman bands. The monohydrate whewellite maybe characterized by a doublet at ca. 1461 and 1485 cm^{-1} and the dihydrate weddellite is characterized by a single peak at 1474 cm^{-1} (Doherty, Pamplona et al., 2007). The spectrum of ammonium oxalate monohydrate (Sigma) measured for the present study showed bands at ca. 1474 and 1448 cm^{-1} . The first band of ammonium oxalate overlaps the characteristic peak of weddellite, though no peaks for weddellite or whewellite are observed at 1448 cm^{-1} .
Raman spectra were recorded with a Renishaw System 1000 spectrometer, using a 785 nm laser excitation. The samples were placed in the stage of the Leica microscope attached to the spectrometer and the laser beam was focused on the different areas of the surfaces using a x50 objective lens, allowing spatial resolution in the order of 2 to 3 microns. Powers on the order of 5 mW were used, with accumulation times between 10 to 100 seconds. Identification of the materials was done by comparing the spectra of the unknown material with those published for reference compounds.
- 33 Grissom, C. A., Charola, A. E. and Wachowiak, M. J., 'Measuring surface roughness: Back to basics', *Studies in Conservation*, Vol. 45, 2000, pp. 73–84.
- 34 Type S refers to an autoclaved hydrated lime, Graymont, Richmond, British Columbia. (www.graymont.com/prod_pressure_hydrate_S.shtml)
- 35 Maury Ramirez, A., Demeestere, K., De Belie, N., Mäntylä, T. and Levänen, E., 'Titanium coated cementitious materials for air purifying purposes: Preparation, characterization and Toluene removal properties', *Building and Environment*, Vol. 45, 2010, pp. 832–38.
- 36 Poon, C. S. and Cheung, E., 'No removal efficiency of photocatalytic paving blocks prepared with recycled materials', *Construction and Building Materials*, Vol. 21, 2007, pp. 1746–53.
- 37 NORMAL 20/85 'Interventi conservativi: progettazione, esecuzione e valutazione preventiva', Consiglio Nazionale per la Ricerca and Istituto Centrale per il Restauro, Rome.