12th International Congress on the Deterioration and Conservation of Stone
Columbia University, New York, 2012

MARBLE STATUES AND PANELS OF SAN PETRONIO FAÇADE IN BOLOGNA – STATE OF CONSERVATION AFTER 40 YEARS SINCE RESTORATION

Susanna Bracci,[1] Monica Galeotti and Daniela Pinna[2*]

[1]Istituto per la Conservazione e la Valorizzazione dei Beni Culturali – CNR, Via Madonna del Piano, 10, 50019 Sesto Fiorentino (FI), Italy
[2]Opificio delle Pietre Dure, Ministero per i Beni e le Attività Culturali, viale Filippo Strozzi 1, 50129, Firenze, Italy
[*]Contact author's e-mail address: daniela.pinna@beniculturali.it

Abstract

In the 1970s the marble statues and panels on the façade of San Petronio Church in Bologna were restored by Ottorino Nonfarmale. The cleaning and treatment operations were chosen after an accurate scientific examination performed by Raffaella Rossi Manaresi and other conservation scientists. The façade of San Petronio Church will again undergo restoration and this event has been the occasion for studying the conservation state of statues and panels after about 40 years since the past restoration. Some samples taken in the 1970s, before Nonfarmale's intervention, from panels and sculptures of the facade have been examined focusing on the existing patinas and deposits. The results have been compared with those obtained from samples taken in 2010.

The final step of the restoration carried out in the 1970s consisted of the treatment of marble surfaces with a mixture of an acrylic resin copolymer (Paraloid B72) and a partially pre-polymerized dimethylpolysiloxane (Dri Film104) in solvent, which gave both water-repellency and consolidation to the stones. Thus a further aim of this study has been the evaluation of the treatment after about 40 years of natural ageing.

Both past and recent samples have been analyzed with various techniques: stereoscopic observations, microscopic examination of both thin- and cross-sections under visible light and UV radiation, FTIR spectrometry on KBr micro pellets, micro FTIR on cross-sections, ESEM connected to an EDS probe. Moreover, petrographic analyses were performed on thin-sections.

The results allowed to assess the present state of conservation of marbles and to compare it with the one before the past intervention. Moreover the penetration depth and distribution of the treatment as well as its long-term water-repellency has been evaluated.

DRAFT

1. Introduction

The Gothic Church of San Petronio is dedicated to Petronio, the 5th century bishop and patron of Bologna. Dominating the south side of the city's main square Piazza Maggiore, San Petronio Church was begun in 1390 as a civic project and was completed in 1663 (M. Fanti, 1983). The façade - 51 metres in height and 60 metres in width - is only less than half covered in polychrome stones and decorations. The rest, made of bare bricks that should have been covered with marble, remained unfinished. Nevertheless, the finished half is of exquisite beauty with sculptures by Jacopo della Quercia decorating the Porta Magna, the main doorway, between 1425 and 1438. They depict the Madonna and Child, San Petronio, St. Ambrose and biblical scenes (R. Grandi, 1983). The side portals were erected between 1518 and 1530. The lunette of the left portal is decorated with the Resurrection carved by Alfonso Lombardi, while the right one shows the Deposition of Christ by Amico Aspertini, the Virgin by Tribolo and St. John by Ercole Seccadenari (M. V. Brugnoli, 1984).

The church underwent over time several restructuring and restoration interventions. The first documented restoration on the stone façade was conducted by the restorer Ottorino Nonfarmale from 1972 to 1979. At that time the facade was covered with a dark, compact, homogeneous crust detached only in some jutting out and exposed areas. In some sculpted parts of side portals, pieces of carved stone had fallen off (Fig. 1) (C. Gnudi, R. Rossi Manaresi, O. Nonfarmale, 1979).

Fig. 1. Panel depicting "The Expulsion from the Garden of Eden" before the 1970s restoration (R. Rossi Manaresi, 1981). The dark crust homogeneously covering the stone had fallen off in some of the most exposed areas.

In view of the 350th anniversary of San Petronio's completion in 2013, the "Fabbriceria" (council of maintenance) worked out a special intervention for completing the restoration work that was already carried out in many other parts of the church. The intervention consists in an extraordinary restoration plan of pieces of art and architecture, to be carried out between 2010 and 2013. The project has been named "Felsinae Thesaurus" (the treasure of Bologna), as this is how San Petronio is defined in an inscription engraved on a memorial tablet present on the exterior wall of the chapel consecrated to him in Archiginnasio street in Bologna: "Pone lapidem Felsinae Thesaurus". After about forty years since the last restoration, the façade of San Petronio Church is to be restored again. The conservation project started in September 2010 and included preliminary scientific investigations, run by the "Opificio delle Pietre Dure" in collaboration with the Institute for the Conservation and Valorization of Cultural Heritage - CNR. The scientific study focuses on the three portals, but the conservation state of the whole façade was evaluated, including the upper part made of bricks. OPD is nowadays in charge of the restoration of the façade.

This paper deals with the study of some samples taken in the 1970s, before Nonfarmale's intervention, from panels and sculptures of the facade focusing on the existing patinas and deposits. The results were compared with those obtained from samples taken in 2010.

2. Materials and methods

A large number of samples - 6 collected in the 1970s and 39 in 2010 - were examined, but only the results referring to the most significant ones are discussed in this contribution, i.e. three samples of the portals collected in the 1970s before the intervention, and three samples taken in 2010.

The following analyses were carried out on the samples:

- observation under stereo- and optical (visible and ultraviolet radiation) of thin (30–40 µm) and cross-sections; the sections were obtained after including the samples in polyester resin;
- Fourier Transform Infra-red Spectrophotometry on KBr micropellets using an IR CONTINUUM™ microscope; micro FTIR in reflection mode was performed on the surfaces of some samples. Micro ATR was carried out on some thin-sections to detect and better localize organic compounds on selected layers;
- examination of thin and cross sections with an energy dispersive X-ray spectrometer (EDS) connected to the scanning electron microscope (ESEM Quanta200 - Environmental Scanning Electron Microscopy) to study the interactions between patinas and stones, as well as the conservation state of the latter. The instrument allows non-conducting specimens to be imaged and analysed without coating them since it is possible to acquire either SEM images or EDS analyses in low vacuum (0.1 torr).

Moreover, thin sections were petrographically studied with a polarizing light microscope (Zeiss Axioscope A1).

DRAFT

3. Results

3.1 Diagnostic investigation preliminary to the restoration of the 1970s

At the time of San Petronio façade restoration, the studies on alteration and conservation of stone were very rare in Italy and abroad. Cesare Gnudi took the opportunity of San Petronio restoration to promote the research in this field founding in Bologna the *Centro per la Conservazione delle Sculture all'aperto*. Thus, in that occasion, historical researches and scientific investigations were carried out before the intervention in order to identify the materials of the façade, to define their state of conservation and the causes of alteration, and to elaborate a correct method of restoration. Dr. Raffaella Rossi Manaresi supervised and coordinated the work with the collaboration of several research institutes. Hereinafter the main results, obtained with the techniques available at that time, are summed up.

The analyses carried out on samples from panels and sculptures of the central portal showed that the marble was generally well preserved and still compact, and a dark superficial crust was distinctly overlying on it (Fig. 2) (C. Gnudi, R. Rossi

Manaresi, O. Nonfarmale, 1979). The marble was of good quality, compact, with low porosity. However, the state of preservation could hardly be explained only with the stone's good quality. According to the researchers a hydrophobic material was probably applied preventing the penetration of water and thus avoiding alteration processes took place. Actually they detected a brown film on the stone, which penetrated micro-fissures at a depth of few microns, suggesting the hypothesis of an ancient, perhaps original treatment (R. Pellizzer, R. Rossi Manaresi, 1970). The brown film was covered by a dark crust, made of two layers in some samples. The crust contained black particles, traces of ferric oxides, a little amount of calcite and quartz and a great amount of gypsum (in some cases 43 % of gypsum, 2.5 % of calcite and traces of magnesium, sodium and potassium salts) (M. Tabasso Laurenzi, 1971). On the other hand only calcite (and no gypsum) was detected under the crust. Such observations led the researchers to hypothesize that the crust couldn't have caused by the deterioration of the stone, and to suggest that it should have been linked to treatments (R. Pellizzer, R. Rossi Manaresi, 1970).

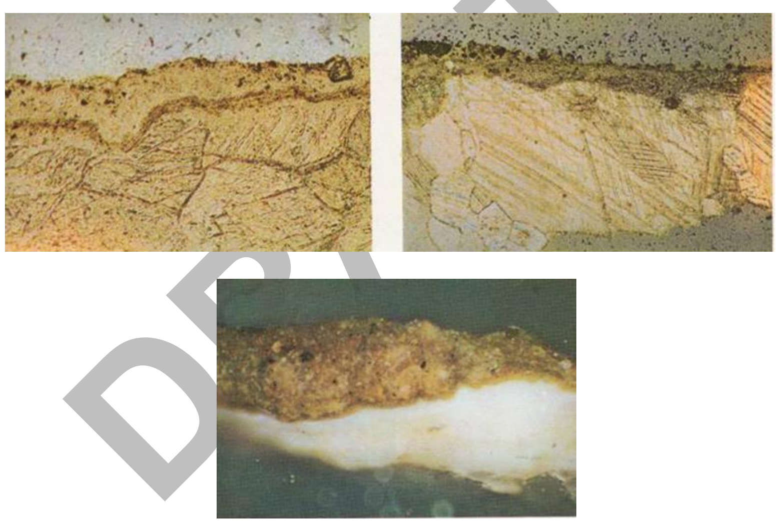


Fig. 2. Cross-sections of samples from central portal. The division between the dark crust and the underlying stone is clearly distinct (R. Rossi Manaresi, 1981).

DRAFT

The examination of the brown film overlying the carved stone resulted in a complex issue. Beeswax, a natural resin such as sandarac or colophony, substances identified as belonging to rue leaves and, only in one sample, calcium oxalates were detected. There was also a high amount of triglycerides, higher than that of standard beeswax. Since triglycerides are the fundamental constituents of fats and oils, they might be linked to those substances. Moreover proteins in samples from two panels of the main portal were detected (S. Barcellona, M. Tabasso Laurenzi, 1971).

The use of both sandarac and rue oil was reported in documents attesting a payment to Jacopo della Quercia on July 15th 1428 *per vernixe e per ollio de ruda da unzere le colonne rosse (for varnish and rue oil to spread on the red columns)*. An analogous document for the sculptures was unfortunately not found. Moreover it is worth mentioning that wax-based treatments applied to protect the outdoor sculptures are documented since ancient times. Vitruvius for example suggested a mix wax and oil, and also wax and resin (R. Pellizzer, R. Rossi Manaresi, 1970).

Samples from the side portals were also examined (R. Rossi Manaresi, 1973). They were covered with a homogeneous very compact dark crust. Some details of the sculptures were detached or damaged. The crust had a composition very similar to the one of the central portal, but it contained also casein. As it hadn't the characteristics of an alteration crust, it was probably caused by a treatment of the sculpted surfaces. The presence of iron-based pigments and of casein, which could acts as binding medium, confirmed this latter hypothesis. The brown organic film in contact with the stone and the beeswax, found on the central portal, were not detected.

All the three portals had surely undergone many treatments over the centuries (C. Gnudi, O. Nonfarmale, R. Rossi Manaresi, 1981). The analyses showed at least two coatings. One is the brown film containing beeswax and detected on the main portal only. The general treatment (over the brown film) was hypothesized to be coloured (red-orange) and made of a mixture containing gypsum, or calcium hydroxide transformed into carbonate and then into gypsum by atmospheric action; casein was used as binding medium (C. Gnudi, R. Rossi Manaresi, O. Nonfarmale, 1979). Ceresin (a synthetic wax, which came into use in the nineteenth century), found on samples from the statue of Madonna (main portal), could explain the presence of hydrocarbons detected on all the portals. It could have been applied perhaps when the last retouching had been done, even just to obtain an aesthetic effect (C. Gnudi, R. Rossi Manaresi, O. Nonfarmale, 1979).

Oil, rarely identified in samples, could have been the binding medium of a coloured mixture used to "retouch" the previous "painting". This hypothesis was based on the microscopic observations, which showed two distinct layers corresponding to two successive treatments.

Thanks to historical studies and investigations, and to a comparison between some photographs of the same panels taken on different dates, it was supposed that the first casein-based treatment was applied in the period between the two World Wars while the retouching was done between 1950 and 1974 (C. Gnudi, R. Rossi Manaresi, O. Nonfarmale, 1979).

The aforementioned conclusions made it possible to elaborate the appropriate restoration methods. The main goals were: the removal of the black crust, the consolidation of the materials in the most degraded areas, the protection of the entire surface with a water-repellent product.

Cleaning operations were then performed using poultices of attapulgite with water, and poultices of carboxymethylcellulose containing basic salts, EDTA, a surfactant (Desogen), and triethanolamine. The consolidating and water-repellent treatment was obtained by mixing Paraloid B72 (copolymer methyl acrylate-ethyl methacrylate, 30% w/w in nitre diluent), a silicon-based compound (Dri Film 104, 70% w/w in white spirit), 1,1,1-trichloroethane and acetone in ratio 15/5/40/40 v/v, respectively (C. Gnudi, O. Nonfarmale, R. Rossi Manaresi, 1981).

3.2 Diagnostic investigations carried out in 2010-2011

DRAFT

As mentioned, the restoration project “Faelsinae Thesaurus” included also preliminary scientific investigations which started in September 2010. The statues of the main portal are made of Candoglia marble, the ones of the side portals and the panels of Carrara marble, the lintels are composed by Oolitic Limestone from San Vigilio (G. C. Grillini, 2011).

A number of samples, both collected in the 1970s and in 2010, has been examined for this study, but only the most significant ones are mentioned in this article. The re-examination of the 1970 samples and their comparison with the ones taken in 2010 were aimed at checking the past results and deepening their study with the aid of other techniques in particular ESM/EDS and microFTIR, able to provide further information on the composition of the single layers. Moreover the samples’ comparison revealed either the effect of the restoration on stone surfaces or the past and present state of conservation.

Fig. 3 shows the cross section of a fragment taken in the1970s from the back of the basement of St. Ambrogio statue (main portal). In the visible light image a patina, composed by two layers, covers the marble. The layer in contact with marble is 30-60 μm thick and brownish coloured, while the other one overlying it, is discontinuous, 40-50 μm thick, light-grey coloured, and externally darker with black airborne particles. Both layers contain red-orange particles (Fe silicates and Fe oxides). UV light images (not shown) reveal a whitish fluorescence in some areas of the patina and inside the grains of marble. Examinations of the thin section show that the stone is affected by inter and intra-crystalline micro-fractures and that the layer in contact with the stone penetrates marble’s micro-fractures. FTIR and EDS analyses enabled to differentiate materials of the external layer of the patina from the ones of the inner layer. Amide I and amide II bands, featuring protein substances, and phosphorus were detected on a brown material, perhaps belonging to the layer in contact with the stone. Moreover, oxalates were specifically identified in the external layer of the patina. Phosphorous and proteins may be associated to the treatment with casein used as binding medium, as reported in the literature (C. Gnudi, R. Rossi Manaresi, O. Nonfarmale, 1979) (R. Rossi Manaresi, 1973).

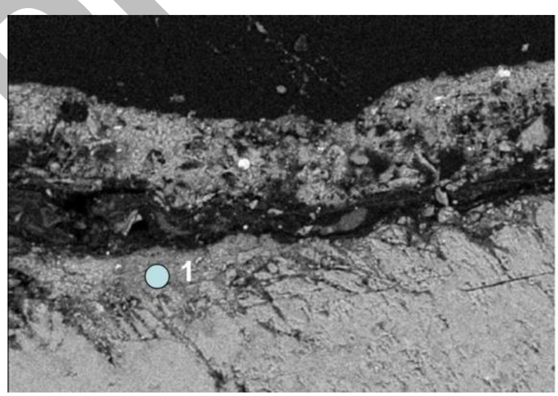
DRAFT

Fig. 3. Cross-section of a sample taken in the 1970s from the statue of St. Ambrogio (main portal).

The cross-section of a fragment collected from the same statue in 2010 is shown in Fig. 4. Despite this sample comes from a different area, a comparison between the two samples can still provide insights into the changes occurred since the previous investigation. The marble, again micro-fractured, is covered by a compact, light brown patina 30 µm thick (labelled 1 in Fig. 4).

Fig. 4. Cross-section of a sample taken in 2010 from the statue of St. Ambrogio: 1- light brown patina (30 µm), 2- non-colored layer with gypsum, siloxane and acrylic resin (some glass spheres are visible on the right), 3- top black layer.

It is not continuous even though, when present, it looks adhering very well to the stone and partly penetrating the inter grain fissures (Fig. 5).



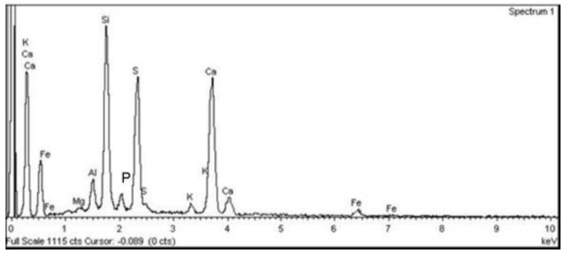


Fig. 5. Back- scattered electron micrograph of a detail of the cross-section of in Fig. 4. The compact, well adhering patina is visible. The EDS spectrum shows Ca, Si, S, Fe, Al, Mg, K and P.

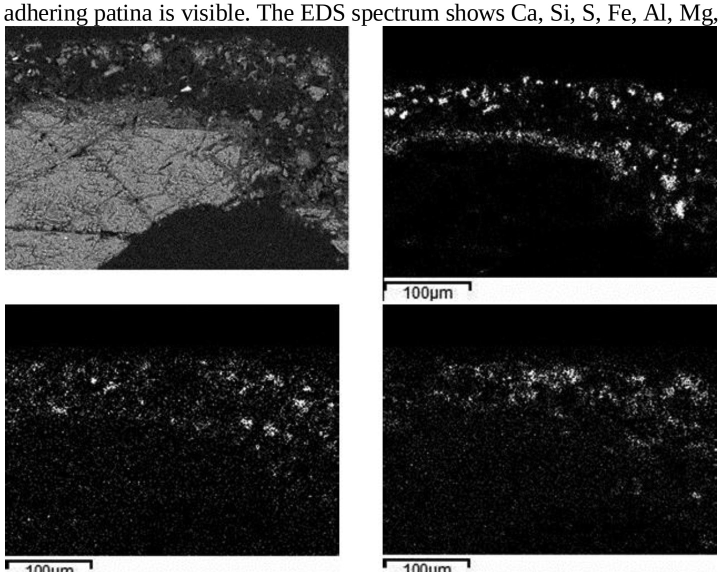


Fig. 6. Back- scattered electron micrograph of the cross-section of a sample from the Madonna statue (main portal). EDS maps of Si (top right), Al and S (bottom left and right).

Combining ESEM-EDS and FTIR results, gypsum, alumino-silicates, a small amount of phosphorus and oxalates were detected in the patina. The non-colored layer over the patina (labelled 2 in Fig. 4) contains instead gypsum, siloxane and acrylic resin. Acrylic resin was identified by IR bands at 1730, 1480 and 1380 cm^{-1}, and siloxane by IR bands at 1274, 850 and 780 cm^{-1}. Other bands, which according to Favaro et al., (A.E. Charola, A. Tucci, and R.J. Koestler, 1986) are useful to evaluate the degree of degradation of the polymer mixture, are hidden by gypsum and silicates vibrations, and analyses of the extracts are still in progress. Nevertheless, the well detectable 1274 cm^{-1} band, assigned to the Si-C stretching of the group $Si\text{-}CH_3$, indicates that un-reacted alkoxy groups are still present in the polymeric mixture.

The top black layer contains mainly round-shaped carbon particles, gypsum and silicate, likely a deposit of airborne material. Furthermore glass spheres, 50 µm in diameter, are present under the black external layer (Fig. 4). They are an evidence of the mechanical cleaning carried out with air-abrasive during the 1970s restoration.

Thus the re-examination of the 1970s sample and its comparison with the one taken in 2010 show the two-layered patina occurring on stone before the restoration (confirming the 1970s investigations). The new examination brought to a more precise definition of its origin and composition. It was indeed the result of two intentionally applied treatments based on organic substances: a protein-based treatment for the first layer and an oil-based one for the second layer (as it can be inferred by the oxalates). Since the first layer penetrates the marble micro-fractures, it is unlikely that it was originally applied on the sound marble. Moreover the analyses show that it was partially preserved during the cleaning carried out in the 1970s, probably because it had proven to be effective against the marble’s decay. The glass spheres and the mixture siloxane-acrylic resin are mostly embedded in it or laid on its top, confirming that the removal of the superficial material was limited to the dark external layer. The current outer black layer was therefore formed over the last decades as a result of dry deposition while the marble underneath was not affected by a further weathering.

On the statue of the Madonna on the main portal, the marble is covered by a mono-layered grey-brownish coloured patina (40-50 μm), containing orange and black particles, visible both in the 1970s sample and in the one of the 2010. Combining ESEM-EDS and FTIR results, gypsum, alumino-silicates, Fe oxides, phosphorus and oxalates were detected in the patina. The composition is similar to that of the previously discussed samples. The 2010 sample contained also siloxane and acrylic resin. A dark powdered atmospheric deposit with inhomogeneous thickness is visible on the patina. In both samples the marble is highly weathered but not affected by gypsum formation in between the grains. While gypsum occurs mainly inside the black deposit, silicon is instead layered into the patina as siloxane (see EDS maps of Si, Al and S in Fig. 6) and also dispersed in the deposit as silicate particles. Fig. 7 shows an ESEM picture of the patina’s surface, where some flat areas composed of acrylic resin and siloxane are visible. They are covered by acicular and tabular (to a less extent) gypsum crystals and alumino-silicates aggregates. The coating covering the marble is still quite uniform and its appearance is similar to a newly treated surface (A.E. Charola, A. Tucci, and R.J. Koestler, 1986). It is worth mentioning that the whole depth of the superficial layer (patina + deposit) in both samples, is less than 150 μm and that the morphology of the cross-section is quite the same even after many years and an extensive conservation work. It seems that the marble has not undergone a further decay since the 1970s.

DRAFT

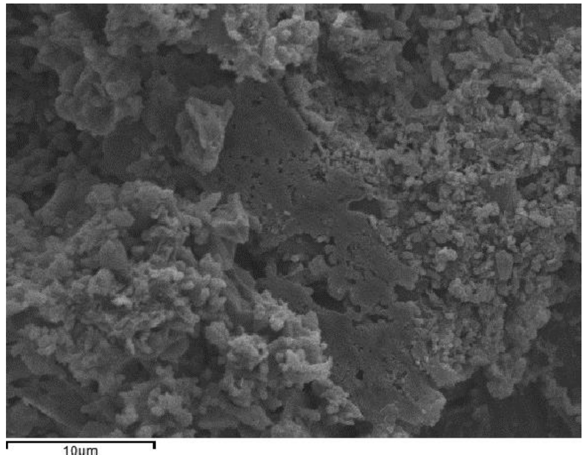


Fig. 7. ESEM micrograph of the surface of a sample from the Madonna statue. The polymer coating and acicular and tabular gypsum crystals are shown.

DRAFT

Carrara marble panels of the side portals are much more jutting out than the statues which are protected by the lunettes. Two samples from the panels of the right portal have been compared. The investigations carried out in the 1970s on samples' cross-sections showed two layers (more rarely three) over the stone. This result is observable in the cross-sections of a sample taken in the 1970s from the panel depicting "the Coronation of the Virgin" (Fig. 8) and of a sample taken in 2010 from the panel depicting "The Flagellation of Christ" (Fig. 9). In both of them, over the micro-fractured stone, a two-layered patina is visible, where the layer in contact with marble is thin (10-20 μm), compact, brown coloured and partially penetrating the marble micro-fractures.

Fig. 8 (left) Cross-section of a sample taken in the 1970s from the panel depicting "the Coronation of the Virgin" (right portal).
Fig. 9. (right) Cross-section of a sample taken in 2010 from the panel depicting "The Flagellation of Christ" (right portal).

Combining ESEM-EDS and FTIR results, gypsum, alumino-silicates, Fe oxides, traces of oxalates and a natural wax (identified by the bands at 1730 cm^{-1}, ~1465 cm^{-1} and ~1053 cm^{-1}) were detected in the layer in contact with marble. The 2010 sample contained also siloxane and acrylic resin. Micro-FTIR with ATR on thin-section of the older sample reveals, along with silicates signals, bands at ~1540 and 1504 cm^{-1} assigned to carboxylates. These last results are likely an evidence of altered oil or wax. The 2010 sample also contained lead and phosphorous, both detected by EDS (Fig. 10).

Over the layer in contact with stone, a thicker (from 70 to 100 µm in both samples) grey coloured one is visible. Despite the fact the elemental composition (Ca, S, Si, Al, Fe) of both layers is the same, the external one contains a larger number of orange, white and black particles.

The grey layer of the 1970s sample goes under the stone fragment just like if it had entered fractures of the stone, favouring the detachment of little scales. It is covered by a black deposit.

The EDS map of the 2010 sample shows that gypsum is mainly located on the outmost surface. It is probably connected to dry deposition along with black particles also observed. The results obtained on samples from the side portals do not fully match those of the1970s research reporting a mono-layered patina and in particular the lack of the beeswax protective coating detected instead on the main portal. On the contrary our examinations of old and recent samples from the side portals clearly show a thin, organic-based treatment, which preserved the underlying marble over time. Lead detected in the sample from “The Flagellation of Christ” could be related to a remnant of a “scialbatura” layer.

DRAFT

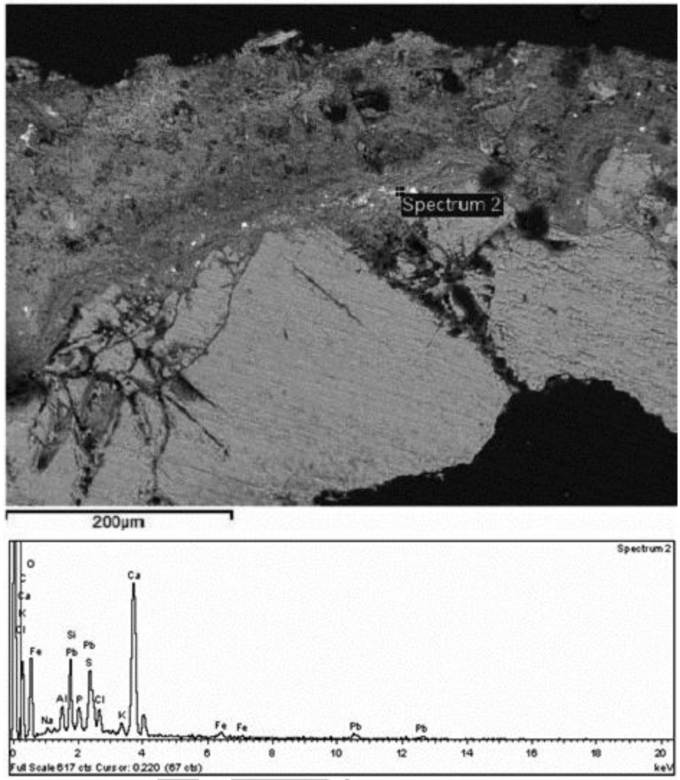


Fig.10. Back- scattered electron micrograph of a detail of the cross-section in fig.9. EDS spectrum of a spot where Pb was detected.

Over the layer in contact with stone, a thicker (from 70 to 100 µm in both samples) grey coloured one is visible. Despite the fact the elemental composition (Ca, S, Si, Al, Fe) of both layers is the same, the external one contains a larger number of orange, white and black particles.

The grey layer of the 1970s sample goes under the stone fragment just like if it had entered fractures of the stone, favouring the detachment of little scales. It is covered by a black deposit.

The EDS map of the 2010 sample shows that gypsum is mainly located on the outmost surface. It is probably connected to dry deposition along with black particles also observed. The results obtained on samples from the side portals do not fully match those of the1970s research reporting a mono-layered patina and in particular the lack of the beeswax protective coating detected instead on the main portal. On the contrary our examinations of old and recent samples from the side portals clearly show a thin, organic-based treatment, which preserved the underlying marble over time. Lead detected in the sample from “The Flagellation of Christ” could be related to a remnant of a “scialbatura” layer.

The cleaning carried out in the 1970s did not intentionally affect the layer in close contact with marble, whose preservative efficiency seems to be indeed strengthened by the resin mixture used by Nonfarmale. As a matter of fact, siloxane and acrylic resin were extensively detected by FTIR on almost all the 2010 samples, not only on marble but also on Verona stone slabs, which are not sheltered. The EDS distribution maps of silicon in cross-sections show that it is located in the first layer on the stone where, not being associated with aluminium and other elements of silicate compounds, it is therefore related to siloxane. In some cases, depending on the preservation state of the underneath stone, silicon penetration in the marble is around 0.8 mm. On the other hand, sulphur inside the marble and at the interface with patina is rarely detected, showing that sulphation occurred only at a minor extent. *In situ* reflectance FTIR spectroscopy (data not shown) allowed to much enlarge the number of investigated areas in a non-invasive way and to confirm the widespread distribution of Dri Film 104 and Paraloid B72. Tests with the sponge contact method were performed (data not shown) to evaluate the long-term performance of siloxane (D. Vandevoorde, M. Pamplona, O. Schalm, Y. Vanhellemont, V. Cnudde, E. Verhaeven. 2009). The results showed that the values of treated surfaces are close to the ones of sound marble, demonstrating the treatment is still performing in terms of water-repellency.

DRAFT

4. Conclusions

The stone surfaces of San Petronio façade, treated about 40 years ago with a mixture of an acrylic polymer and siloxane, were investigated and the results were compared with those ones related to the examination carried out before the 1970s restoration. Moreover, samples taken at that time were re-examined, and stone's changes as well as treatment performance over time were assessed. A thin, organic-based layer in close contact with marble was detected on samples before and after the 1970s intervention, both from the central and the side portals. A second thicker layer was placed over it. The layers contained, among other compounds, oxalates, i.e. the end-products of chemical transformation over time of more complex organic substances applied to protect the stone (G. Alessandrini, 2005). Thus they were related to an intentional treatment with organic substances mixed with red-orange particles (Fe silicates and Fe oxides). The thin organic-based layer in close contact with marble, detected before Nonfarmale restoration, resulted to be partially left after that. Dark airborne deposits affected the outmost surfaces while sulphation phenomena seemed to be very limited.

Siloxane and acrylic resin impregnated the pre-existing treatments and penetrated the micro-fractures of marble, thus performing a further protective and consolidating action, avoiding in this way more massive alteration of the stone. The components of the mixture applied in the 1970s are indeed still present in a fairly high content and, as far as the analytical results achieved so far allow to infer, are not affected by deterioration or strong molecular changes. Studies on monuments treated in the 1980s with Paraloid B72-Dri Film 104 mixture (M. Favaro, R. Mendichi, F. Ossola, S. Simon, P.A. Vigato, 2007; S. Haake, M. Favaro, S. Simon. 2004, M. Favaro, S. Simon, C. Menichelli, V. Fassina, P. A. Vigato. 2005, L. Appolonia, F. Bevilacqua, C. Di Francesco, D. Pinna. 2000) provided evidences of loss of water-repellency of treated stone, strong reduction of the content of siloxane, formation of low molecular weight compounds originating from alteration of the acrylic component (cross-linking and chain scission). These results were confirmed by the examination of marble specimens treated with Paraloid B72-Dri Film 104 mixture and artificially aged through photo-oxidation (M. Favaro, R. Mendichi, F. Ossola, S. Simon, P.A. Vigato, 2007). On the other hand R. Rossi Manaresi herself studied the effect of acid fog (using 0.02 M H_2SO_4) and UV radiation on limestone samples treated with Paraloid B72-Dri Film 104 mixture and then artificially aged (A. Tucci, R.J. Koestler, A. Charola, R. Rossi Manaresi, 1985). While UV radiation did not alter the morphology of the treated surfaces, significant changes appeared instead after acid fog exposure resulting in a three-dimensional network of the treatment, thicker than non-aged one, with small cells. This change was observed though only on surfaces directly exposed to acid fog and the authors ascribed the result to the fact that *in situ* polymerization of the silicone is triggered by the weathering itself.

Actually the results obtained examining San Petronio façade are partially in contrast with the mentioned literature. This can be tentatively explained by noticing that the photo-oxidative deterioration of the mixture is strongly affected by the application method. Tests reported by Favaro et al. (M. Favaro, R. Mendichi, F. Ossola, S. Simon, P.A. Vigato, 2007) showed that the mixture's degradation is enhanced whenever it is applied as thin film on marble. On the contrary, polymer modifications resulted limited when the mixture is applied as thick coating, as it is likely the case of San Petronio where the bulk of the thick polymer layer is probably not affected by oxygen penetration. Moreover, most sculpted surfaces are nowadays uniformly covered by atmospheric deposits which could have provided a protection from the direct exposure of acid fog. Finally, a synergic action of both the polymer mixture and the old organic treatment could also be invoked to explain the long lasting water-repellency of the surfaces.

DRAFT

Acknowledgements

The authors wish to thank Monsignor Oreste Leonardi, Primicerius of San Petronio Church, for permission to collect samples. The authors acknowledge the support of this work by Maria Cristina Improta Director of the Stone Restoration Department at Opificio delle Pietre Dure, by Roberto Terra and Guido Cavina Directors of the restoration of San Petronio Church, and by Gian Carlo Grillini who carried out the petrographic examinations of stones.

References

G. Alessandrini, 2005. *Patine sui materiali lapidei*, In: P. Tiano, C. Pardini (Eds.), *Le patine – Genesi, significato, conservazione,* Nardini Editore, Kermes quaderni, Firenze, 15-28.

L. Appolonia, F. Bevilacqua, C. Di Francesco, D. Pinna. 2000. *Verifica dello stato di conservazione di monumenti ferraresi dopo alcuni decenni dagli interventi di restauro*. In: Proceedings of the Congress "La prova del tempo", Bressanone, 163-171.

S. Barcellona, M. Tabasso Laurenzi, 1971. *Studio del materiale organico presente sulla superficie del portale centrale di S. Petronio a Bologna*, Internal report, June 1971, ICR, Roma.

M. V. Brugnoli, 1984. *Le porte minori*, In: *La Basilica di San Petronio in Bologna*, Silvana Editoriale, Bologna, v. II: 61-82.

A.E. Charola, A. Tucci, and R.J. Koestler, 1986. *On the reversibility of treatments with acrylic/silicone resin mixtures*, JAIC, Volume 25, Number 2, Article 3, 83-92.

M. Fanti, 1983. *La basilica di San Petronio nella storia religiosa e civile della città – Genesi, vita e significato del monumento*, In: *La Basilica di San Petronio in Bologna*, Cassa di Risparmio di Bologna, Bologna, v. I: 9-27.

M. Favaro, R. Mendichi, F. Ossola, S. Simon, P.A. Vigato, 2007. *Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part II: Photo-oxidative and salt-induced weathering of acrylic-silicone mixture.* Polymer Degradation and Stability, 92: 335-351.

M. Favaro, S. Simon, C. Menichelli, V. Fassina, P. A. Vigato. 2005. *The four virtues of the Porta della Carta, Ducal Palace, Venice. Assessment of the state of preservation and re-evaluation of the 1979 restoration.* Studies in Conservation, 50(2), 109-127.

C. Gnudi, O. Nonfarmale, R. Rossi Manaresi, 1981. *Il restauro della facciata di San Petronio*, In: A. M. Giusti (Ed.), *Atti del convegno sul restauro delle opere d'arte –* Firenze Novembre 2-7, 1976, Edizioni Polistampa, Firenze, 213-220.

C. Gnudi, R. Rossi Manaresi, O. Nonfarmale, 1979. *Report on the conservation of the facade of S. Petronio,* Centro per la conservazione delle sculture all'aperto, Edizioni Alfa, Bologna.

R. Grandi, 1983. *Cantiere e maestranze agli inizi della scultura petroniana*, In: *La Basilica di San Petronio in Bologna*, Cassa di Risparmio di Bologna, Bologna, v. I: 125-131.

G. C. Grillini, 2011. Facciata della Chiesa di San Petronio. Identificazione dei litotipi. Technical report, 2011, (not published).

S. Haake, M. Favaro, S. Simon. 2004. *The Bologna Cocktail and evaluation of past consolidation treatments.* In: Proceedings of the X Int. Congress on Deterioration and Conservation of Stone. Stockholm, Sweden, ICOMOS, 423-430.

R. Pellizzer, R. Rossi Manaresi, 1970. *Sullo stato di conservazione del portale maggiore della chiesa di S. Petronio a Bologna*, Atti Acc. Fisiocritici Siena, Serie XIV, v. II, 269-283.

R. Rossi Manaresi (editor), 1981. *Jacopo della Quercia e la facciata di San Petronio a Bologna. Contributo allo studio della decorazione e notizie sul restauro.* Edizioni Alfa, Bologna.

R. Rossi Manaresi, 1973. *Sullo stato di conservazione dei portali laterali della Chiesa di S. Petronio a Bologna,* In: *Problemi di conservazione*, ICR, Roma, Editrice compositori, Bologna, 395-402.

M. Tabasso Laurenzi, 1971. *Studi e osservazioni sullo stato di conservazione del portale centrale di San Petronio a Bologna,* Proc. of the Int. Congress La conservazione delle sculture all'aperto, Bologna 23-26 ottobre 1969, Ente bolognese manifestazioni artistiche, 117-132.

A. Tucci, R.J. Koestler, A. Charola, R. Rossi Manaresi, 1985. *The influence of acid rain and UV radiation on the ageing of acrylic and silicone resin*. In: Proceedings of the 5th Int. Congress on Deterioration and Conservation of Stone. Lausanne, Switzerland, Press Polytechniques Romandes, 891-898.

D. Vandevoorde, M. Pamplona, O. Schalm, Y. Vanhellemont, V. Cnudde, E. Verhaeven. 2009. *Contact sponge method: performance of a promising tool for measuring the initial water absorption*. Journal of Cultural Heritage, 10(1), 41–7.

DRAFT

DRAFT