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Towards the study of alteration patinas on the marble surface of a Renaissance sculptural group from the Museum of Ancient Art (Castello Sforzesco, Milan)

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***Abstract* – Aim of the present research is the characterization of the alteration patinas present on the surface of a marble Piety dating to Renaissance period and stored at the Castello Sforzesco of Milan. During the last century, a treatment was applied on the statue bringing to the formation of a dark patina which had to be removed. At this purpose a multi-analytical approach, based on both portable non-invasive (XRF and colorimetric measurements) and micro-invasive techniques (FTIR/ATR and SEM-EDS), has been applied in order to make available to restorers useful information that allow them to adopt a suitable procedure for the removal of the patina and to recover the statue original appearance.**

I. INTRODUCTION

This research focuses on the investigation of surface alteration patinas and colour residues present on the surface of a marble Piety (or Lamentation on the dead Christ) dated to the Renaissance period and stored in the Museum of Ancient Art at the Castello Sforzesco in Milan.

The marble group shows traces of at least one maintenance intervention attributable to the application of protective paints common to all the conservative tradition at the turn of the nineteenth and twentieth centuries. In fact, the entire surface of the monolithic group appears painted with an old but not ancient restoration paint.

In the present study, a multi-analytical approach through portable X-ray fluorescence analysis (XRF), FTIR/ATR (Attenuated Total Reflection - Fourier Infrared Spectroscopy), colorimetric analysis by a portable instrument and SEM-EDS analysis (Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy) was performed. The application of these techniques allowed us to disclose the chemical nature of the residues present on the marble surface providing restorers with very precious information which served as a guide in the intervention.

II. MATERIALS AND METHODS

The investigated statue is a marble group representing a Piety or Lamentation of the dead Christ, attributed to Gaspare Cairano (or to his workshop) and dated to the Renaissance period. The statue, belonging to the *Raccolte Artistiche del Castello Sforzesco di Milano,* appeared strongly dark and yellowed (Fig. 1) and needed restoration also in view of an exhibition at the Louvre

Museum, Paris.

Non-invasive colorimetric and XRF investigations were performed with portable instruments on different areas of the statue. Furthermore, some micro-fragments were taken from the surface by means of a scalpel in order to obtain information through FTIR/ATR and SEM-EDS analyses.

Fig. 1. The sculptural group: the three left figures as they appeared before the conservative intervention while the right one (Nicodemus?) and the third female figure already appear in the cleaning phase.

Four micro-samples were taken from different areas before the restoration procedure. Furthermore, in three out of four points, further withdrawals were performed after the cleaning intervention (the samples taken after the cleaning operations are indicated with the same name followed by "a" in Fig. 2). Sample P1 was taken on the back of the statue near an area where some stucco was applied; sample P2 on the back of the Madonna's head; P3 on Maddalena's shoulder and sample P4 on the thong of Christ.

Fig. 2. Image of the statue as it appears after the restoration; the sampling points (P) are displayed in red.

Colorimetric analyses were carried out, directly on the different areas of the marble surface, before and after the restoration, by means of a Konica Minolta CM 2300d portable spectrophotometer, referring to the CIE L*a*b* chromaticity diagram and to the Normal recommendation 43/93, (1933) [1]. L* is luminosity or lightness, which varies from black (value = 0) to white (value = 100); a* ranges from +a* (red) to –a* (green) and b* varies from +b* (yellow) to –b* (blue). The instrument was calibrated with its white reference (100% reflective) and zero calibration box (0% reference) in the 400–700 nm range. Three measurements were performed on each area and the mean values of colorimetric parameters were calculated as representative for that area.

The micro samples taken from the statue surface were analysed by SEM-EDS to obtain qualitative/semiquantitative information on the chemical composition. The instrument employed was a Hitachi TM1000 equipped with an energy dispersive X-ray spectrometer (Oxford Instruments SwiftED). Measurements were directly performed on samples since no metal coating was required.

Infrared spectra were collected on the micro samples by a Nicolet 380 spectrophotometer coupled with ATR accessory Smart Orbit equipped with a diamond crystal. Spectra have been acquired in the range 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

Non-invasive and in-situ EDXRF analysis were carried out on the areas of interest showed in Fig.3, partially selected in correspondence of the sampling regions. The measurements were performed with the portable EDXRF spectrometer ELIO (XGLab srl, Milan, Italy) equipped with a low-power X-ray tube with Rh anode. The sensitivity range of the spectrometer is 1–40 keV, and it is therefore able to detect elements heavier than Na. The measurements parameters were set at time 120 s, tube voltage 40 kV, tube current 40 μA, and acquisition channel 2048. Data were processed using the ELIO 1.6.0.29 software.

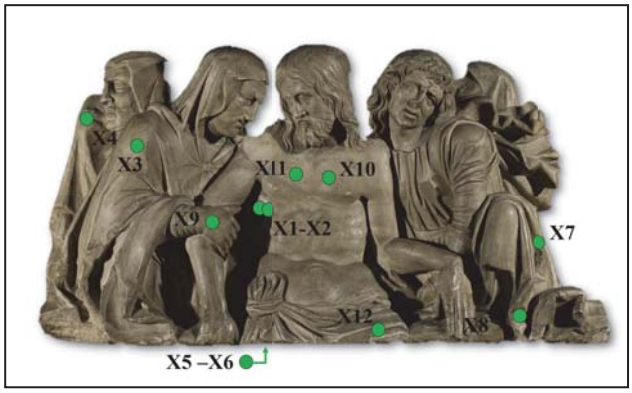

Fig. 3. Image of the statue as it appears after the restoration; the XRF measuring points (X) are displayed in green.

III. RESULTS AND DISCUSSION

Micro-morphological and chemical characterizations were performed by means of SEM-EDS on the samples taken from the different areas before and after restoration (Fig. 2).

Sample P1 showed the presence of S and Ca and minor amount of Fe which has been attributed to the presence of a red pigment. P2, P3 and P4 samples showed even higher concentrations of S and Ca (variable values in the different samples in the ranges 35-45 wt% for Ca and 20-25 wt% for S); lower values were obtained for Si, Fe, K and P.

As for the widespread presence of Ca and S on the marble surface, two different hypotheses could be formulated: 1) the application of a thin preparatory layer of gypsum on which an iron base pigment was subsequently applied; 2) the formation of a sulphation layer because of interaction between the marble and the atmospheric pollution (in particular SO_2 and aerosol carbonaceous particles) to which the monumental group has been exposed during the centuries (the sculptural group has most likely been exposed externally for some time). In fact, it is well known that large quantity of SO_2 together with soot particles were emitted in the past mainly from coal combustion and these pollutants are the responsible for carbonatic stone sulphation, i.e. a process leading to the chemical transformation of the substrate into gypsum [2]. This process that commonly takes place in outdoor environments, can also bring to black crusts formation [3-14].

The presence of other elements on the marble surface, such as P, could be due to the application of restoration products [15].

It is worth to notice that the analyses performed on samples P2a, P3a and P4a, i.e. the same samples taken after the restoration on the same areas previously analysed, showed an increase in the concentrations of Ca and S (variable values in the different samples in the range 55-60 wt% for Ca and 25-35 wt% for S). Furthermore, lower concentrations of Si, Al and Fe were found while P disappeared (see for example sample P3 before and after restoration, as reported in Fig. 4). These differences in the chemical composition of the outermost layer of the statue before and after restoration, indicate that the cleaning procedure carried out has eliminated the deterioration patina or the restoration product previously applied. On the contrary, the cleaning procedure has highlighted the presence of gypsum.

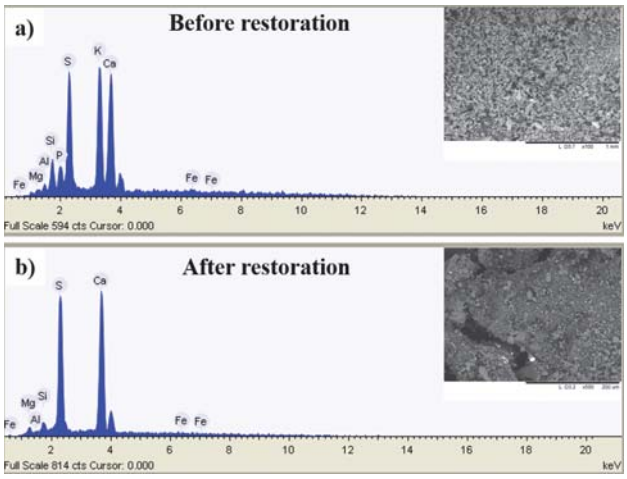

Fig. 4. Representative SEM-EDS analysis performed on sample; a) P3 (before restoration); b) P3a (after restoration)

As concerns the analyses performed after the restoration action, a non-invasive campaign was accomplished by portable XRF. The measurements areas, reported in Fig. 2, were selected in correspondence of the sampling regions and in the areas of interest showing the presence of a pigmented patina. In particular: X4 and X12 were collected respectively in the same region of the P3 and P4 sampling; X5 and X6 could be considered as a reference since were acquired in an area at the bottom of the sculpture thus protected by the atmospheric interaction and in which no treatments or coatings should be present; X1 and X2 correspond to the most reddish area identified with the cut in the Christ's ribs. The normalized values of the net are counts related to the characteristic elements are reported in Tab. 1: high values of Ca were mainly detected together with significative counts of S and Fe. In addition, the signals of Ti, Mn, Zn and Sr were highlighted in few cases.

Ca, Mn, Sr, and Fe are expected due to the non-treated original stone, whereas the uniform distribution of S and the variability of the Fe detected by each acquisition, could be informative about the presence of a surface treatment or patina. As for the presence of Fe, the increase in correspondence of the pigmented areas (X1, X2, X4, X8, X9, X11 in Fig. 3), could be related to the presence of red earth pigments, as highlighted by SEM-EDS analysis. In addition, the slight correlation between S and Ca allowed us to hypothesize the presence of spread gypsum. The scatter plot in Fig. 5 shows the position of X1, X2 and X11, far from the others which are, instead, scattered in a narrow region. For those areas is possible to suppose the presence of a red Fe-based pigment, probably combined with a preparation layer of a different composition and Ca/S ratio.

Table 1. Net area count estimation of the peak Kα of the elements detected by XRF on the different areas. Each value was normalized to the mean value - calculated on the whole XRF data set - of the net area counts of the Rh peak (Kα). Areas marked with an asterisk (*) were selected as non-treated areas and can be considered as spectral background.

Area	*S*	*Ca*	*Ti*	*Fe*	*Sr*
X1	5,63	63,92	1,60	1,00	3,50
X2	6,10	58,14	1,05	1,05	3,77
X3	14,44	50,86	0,12	0,36	4,17
X4	15,37	63,08	0,17	0,67	4,13
*X5**	13,13	43,29	-	0,17	3,45
*X6**	12,50	42,60	-	0,18	2,76
X7	9,11	34,89	-	0,19	2,98
X8	9,17	40,26	0,16	0,83	2,88
X9	10,59	44,35	0,19	1,60	5,81
X10	12,60	46,33	0,12	0,16	4,69
X11	7,51	58,91	0,74	0,73	3,78
X12	9,32	46,00	0,13	0,24	3,47

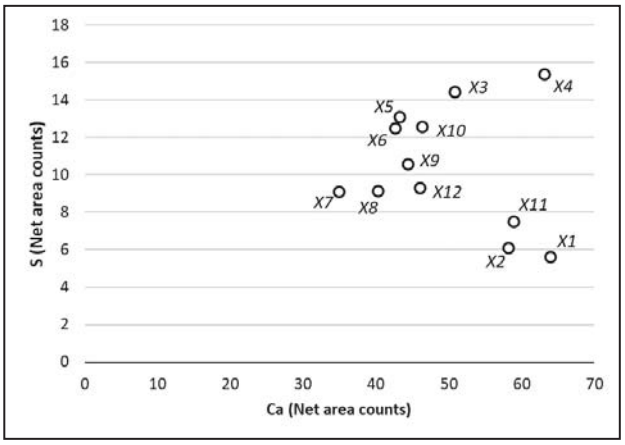

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Fig. 5. Scatter plot of Ca and S.

Some differences after the cleaning procedure have been evidenced by means of FTIR measurements. In Fig. 6 as an example the results obtained by FTIR/ATR analysis performed on sample P2 is reported

All the samples showed the characteristic absorption peaks due to gypsum, calcite and oxalate. In particular, the presence of gypsum (peaks at 3525, 3400,1627, 1109, 667 and 590 cm^{-1}) has been observed for all the samples, confirming SEM-EDS and XRF results. Furthermore, the signals due to calcium carbonate (at 1409 and 871 cm^{-1}), related to the marble substrate, were present. Oxalate was recognized due to the typical absorption peaks at 1630, 1320 and 780 cm^{-1} which, according to the literature, can be attributed to previous restoration interventions or to a biological degradation (metabolism of microorganisms) [16-18].

Finally, the presence of signals at 1735, 2853 and 2922 cm^{-1}, observed in all the samples, allowed us to hypothesize the presence on the surface of a mixed proteinaceous and oleic binder confirming the application of the so called "*colletta*" during a previous restoration of the statue. This layer has progressively adsorbed the aerosol particulate matter, mainly carbonaceous particles, leading the surface to a dark brown colour.

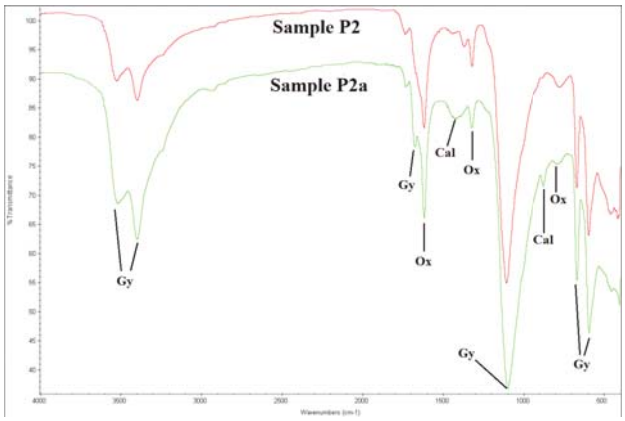

Fig. 6. FTIR spectra of the representative sample P2 (before restauration) and P2a (after restauration).

The colorimetric investigation carried out before and after the surface cleaning, allowed to point out that for all the analysed areas the surface of the statue after cleaning underwent an increase in the L* coordinate (luminosity) with a change of the shade surface from dark to a lighter shade. The values of the colorimetric coordinate a* increased for almost all the analysed areas except for an area (lower part of the mantle of the Madonna), indicating a change in colour towards a more intense red. Finally, the colorimetric parameter b* increased for all the analysed areas, except for the mantle of the Madonna (where b* slightly decreases).

IV. CONCLUSIONS

Thanks to the application of both non-invasive in -situ analyses together with micro-destructive investigation, some preliminary information on the composition of the alteration patinas present on a Renaissance marble sculptural group have been acquired.

The application of a treatment, typical at the turn of the nineteenth and twentieth centuries and based on a mixture of oleic and protein binders, has been confirmed. Colour

traces have been also highlighted.

An in-depth study of the results will allow to better clarify both the nature of the sulphation layer and the use of colour on the sculptural group.

REFERENCES

[1] NORMAL 43/93 Misure colorimetriche di superfici opache. CNR-ICR, Roma (1933).

[2]D.Gulotta, M.Bertoldi, S.Bortolotto, P.Fermo, A.Piazzalunga, L.Toniolo. "The Angera stone: a challenging conservation issue in the polluted environment of Milan (Italy)". Environ. Earth Sci. vol.69, 2013, pp.1085–1094

[3]V.Comite, D.Barca, C.M.Belfiore, A.Bonazza, G.M.Crisci, M.F.La Russa, A.Pezzino, C.Sabbioni "Potentialities of spectrometric analysis for the evaluation of pollution impact in deteriorating stone heritage materials" Rendiconti Online Soc. Geol. Ital. vol 21, Issue part 1, 2012, pp 652-653

[4]C.M.Belfiore, D.Barca, A.Bonazza, V.Comite, M.F. La Russa, A.Pezzino, "Application of spectrometric analysis to the identification of pollution sources causing cultural heritage damage", Environ. Sci. Pollut. Res., vol.20, 2013, pp.8848–59.

[5]M.F.La Russa, C.M.Belfiore, V.Comite, D Barca, A.Bonazza, S.A.Ruffolo, G.M.Crisci, A.Pezzino, "Geochemical study of black crusts as a diagnostic tool in cultural heritage", Appl. Phys. A Mater. Sci. Process., vol.113, 2013, pp.1151–1162.

[6]D.Barca, V.Comite, C. M.Belfiore, A.Bonazza, M.F.La Russa, S.A.Ruffolo, G.M.Crisci, A.Pezzino, C. Sabbioni, "Impact of air pollution in deterioration of carbonate building materials in Italian urban environments", Appl. Geochem., vol.48, 2014, pp.122 131

[7]M.F.La Russa, P.Fermo, V.Comite, C.M.Belfiore, D.Barca, A.Cerioni, M.De Santis, L.F.Barbagallo, M.Ricca, S.A.Ruffolo, "The Oceanus statue of the Fontana di Trevi (Rome): The analysis of black crust as a tool to investigate the urban air pollution and its impact on the stone degradation", Sci. Tot. Environ., vol.593-594, 2017, pp. 297-309

[8]M.F.La Russa, V.Comite, N.Aly, DBarca, P. Fermo, N.Rovella, F.Antonelli, E.Tesser, M. Aquino, S.A. Ruffolo, Black crusts on Venetian built heritage, investigation on the impact of pollution sources on their compos ition", Eur. Phys. J. Plus vol. 133:370, 2018.

[9]V.Comite, M.Álvarez de Buergo, D.Barca, C.M.Belfiore, A.Bonazza, M.F.La Russa, A.Pezzino, L.Randazzo, S.A.Ruffolo "Damage monitoring on carbonate stones: Field exposure tests contributing to pollution impact evaluation in two Italian sites" Constr Build Mater. vol152, 2017, 907–922.

[10]V.Comite, J.S.Pozo-Antonio, C.Cardell, L.Randazzo, M.F.La Russa, P.Fermo. "A multi-analytical approach for the characterization of black crusts on the facade of an historical cathedral" Microchem J, vol.158, 2020, art. no. 105121.

[11]V.Comite, P.Fermo, "The effects of air pollution on cultural heritage: the case study of Santa Maria delle Grazie al Naviglio Grande (Milan)", E.P.J. Plus., vol.133(12), 2018, pp.556.

[12]V.Comite, M.Ricca, S.A.Ruffolo, S.F.Graziano, N.Rovella, C.Rispoli, C.Gallo, L.Randazzo, D.Barca, P.Cappelletti, M.F.La Russa, "Multidisciplinary approach to evaluate the geochemical degradation of building stone related to pollution sources in the Historical Centre of Naples (Italy)". Int. J. Conserv. Sci., vol. 11(1), 2000a, pp. 291-304.

[13]V.Comite, J.S.Pozo-Antonio, C.Cardell, T.Rivas, L.Randazzo, M.F.La Russa, P.Fermo, Environmental impact assessment on the Monza cathedral (Italy): a multi-analytical approach. Int. J. Conserv. Sci. 11(1), 2020b, pp. 291-304.

[14]N.Rovella, N.Aly, V.Comite, S.A.Ruffolo, M.Ricca, P.Fermo, M.Alvarez de Buergo, M.F.La Russa, "A Methodological approach to define the state of conservation of the stone materials used in the Cairo historical heritage (Egypt)", Archaeo l. Anthrop. Sci., 12(8),178, 2020

[15]G.Barone, E.Campani, A.Casoli, M.F.La Russa, Lo A.Giudice, P.Mazzoleni, A.Pezzino. "The Cathedral of St. Giorgio in Ragusa Ibla (Italy): A case study of the use of protective products" Environ. Geol. vol. 54, 7, 2008, pp.1501-1506

[16]M.Del Monte, C.Sabbioni, "Weddellite on limestone in the Venice (Italy) environment" Environ. Sci. Technol., vol.17, 1983, pp. 518–522.

[17]C.Sabbioni, G.Zappia, "Oxalate patinas on ancient monument: the biological hypothesis". Aerobiologia vol.7, 1991, pp. 31–37.

[18]L.Rampazzi, A.Andreotti, I.Bonaduce, M.P.Colombini, C.Colombo, L.Toniolo, "Analytical investigation of calcium oxalate films on marble monuments" Talanta, vol.63, 2005, pp. 966–977.