A multi-analytical diagnostic approach to study patinas, trace of colours and degradation process on the stone surface of a Renaissance Piety from the Museum of Ancient Art (Castello Sforzesco, Milan)

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Abstract

Alteration dark patinas and traces of colours present on the surface of a marble Piety dating to the Renaissance period and stored at the Castello Sforzesco-Museum of Ancient Art (Milan, Italy) were studied and chemically characterized. For 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. The statue has been recently submitted to a restoration before an exhibition at the Louvre Museum and the original appearance of the marble surface recovered thanks to the patina removal. Through the analytical characterization carried out before and after the marble cleaning, the presence of a degradation layer composed by gypsum was evidenced on the stone surface. The origin of this layer is probably ascribable to the exposure of the statue to outdoor environment and interaction with atmospheric pollution. The chemical nature of the coating applied at the end of 19th century and responsible for the patina formation was hypothesized. Finally, the use of pigments originally applied by means of an organic binder was also highlighted.

Introduction

The issue of conservation and restoration of work of arts in stored in museum collections is of great concern for several decades (Brimblecombe 1992). The present research focuses on the investigation of the alteration patinas and the colour residues present on the surface of a marble Piety dated to the Renaissance period and stored in the Museum of Ancient Art at the Castello Sforzesco in Milan (Italy) (Fiorio 2014). The monolithic sculptural group, carved in a single block of rock, represents five figures forming a Piety or a Lamentation over the Dead Christ. It is traditionally attributed to Gasparo da Cairano (Zani 2010), a Renaissance sculptor from the Lombardy or Veneto area (Northern Italy) even if the origin is still uncertain. According to other critics, the statue could be attributed to a sculptor influenced both by the sculpture of the Duchy of Milan and the artistic workshops of the Republic of Venice (Sgarbi 2006).

Marble sculptures are often characterised by the presence of surface layers applied in the past as protective coating also with the aim to provide an aesthetic finishing or applied as restoration treatment (Lanteri et al. 2021).

The marble group object of this study shows traces of, at least, one maintenance intervention due to the application of a protective paint. At the turn of the 19th and 20th centuries, in fact, it was common to apply an organic protective coat on the statues, bringing during time to the formation of a dark patina. As a consequence, the entire surface of the monolithic group appeared coated with a non-original altered restoration layer which after a century had to be removed. This coat, also known among the experts as “*colletta*” (a kind of glue most likely made of rabbit glue) was often applied by museum conservators at the end of the 19th century to protect and enhance the brightness of the marble artworks.

Regardless of where the work was stored in the past (not documented and probably exposed outdoor for long periods), it is useful for diagnostic purposes to point out that, according to the traditional bibliography, it became part of the museum's collection of Milan in 1883, by purchase. During 2020 a restoration was carried out by *Centro studio e conservazione opere d’arte Piccolo chiostro*, having a wide experience in the restoration of marble and other works of art (Colella 2005; Colella 2008), since the sculptural group had to be moved at the Louvre Museum (Paris, France) for an exhibition entitled "The Body and the Soul", from Donatello to Michelangelo, with

140 Italian Renaissance sculptures exposed, organised in collaboration with the Castello Sforzesco Museum in Milan and having as main focus the masterpieces from the second half of the 15th century. During this period the shapes and movements of the body became of great interest for some of the main artists of this period, starting from Michelangelo. In the exhibition at the Louvre Museum, we discover less famous but no less important artists, such as Gasparo da Cairano, and we find all together works of art that are not always accessible because of their usual location in churches, small towns or museum reserves. The exhibition was scheduled to be visible from March to June 2021 at the Castello Sforzesco Museum in Milan but unfortunately due to the situation caused by the Covid 19 pandemic this was not possible at the moment. Some preliminary investigations (Comite et al. 2020a) have been recently carried out on the Piety in some selected points and carrying out just some preliminary measurements allowing to formulate some hypotheses on the chemical natures of the patinas which needed further investigation. The research was therefore continued with the aim to reconstruct the history of the statue also from the point of view of its conservation. So, from one hand the aim was disclosing the patinas' nature and from the other hand assess the possible presence of traces of colour on the marble surfaces. To disclose the chemical nature and the origin of the residues present on the marble surfaces, a diagnostic investigation has been expanded taking into consideration not only the patinas but also the areas where traces of colours could be present. For this purpose, different techniques, both non-invasive, such as portable X-Ray Fluorescence (XRF) and portable colorimetric analysis, and micro-invasive such as FTIR-ATR (Attenuated Total Reflection - Fourier Infrared Spectroscopy) and SEM-EDS (Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy) were employed.

Materials And Methods

The work of art object of the present research is a sculptural group representing a Piety attributed to Gasparo Cairano (1489?-1517), or to his workshop, dated to the Renaissance period. The dimensions of the statue are: height 40 cm, width 83.5 cm and depth 25.5 cm.

Gasparo Cairano (Zani 2010) was an outstanding artist of the Milanese cultural world at the end of the XV century. He pursued a successful career that soon turned him into the leading exponent of the Renaissance sculpture in Brescia.

The use, for the realization of the statue, of one of the calcium-silicate dolomitic marbles that became very popular in the Po Valley from the Renaissance onwards, is due to the difficulties of importing the traditional Apuan limestones. These pre-Alpine marbles are less translucent than Apuan marbles. The Piety marble has a fine grain and a fairly heterogeneous appearance. The marble employed was probably white marble of Crevola or Crevaldossola (Moro 2017), from the name of the place of the quarries (this marble was also known as Palissandro marble). These marbles were very popular in Lombard sculpture, especially in the years when the Duchy of Milan was established.

The statue, belonging to the *Raccolte Artistiche del Castello Sforzesco di Milano*, appeared strongly dark and yellowed (Fig. 1) and was submitted to restoration in view of an exhibition at the Louvre Museum, Paris. The restoration coat applied probably at the end of the 19th century has made the surface so yellow and dark due to the progressive absorption of atmospheric dirt. In Fig. 1a it is shown how the sculptural group appeared before the cleaning (on the left side) and in an intermediate phase after a first removal of the patina (on the right side).

A more in-depth removal was then performed on the whole surface to bring the statue as it appears in Fig. 1b, c, d.

Some micro shards were taken from the marble surface (see Table 1) from different areas both before and after the restoration. In particular in three points out of four, the sampling was performed also after the cleaning intervention (the samples taken after the restoration are indicated with the same name followed by “a” in Fig. 1b). It is important to point out that the samples were taken in the form of powders which were not suitable for preparing cross-sections.

Table 1
Samples collected from the statue surface before and after the restoration

	Sampling location on the statue
Sample P1	Sampling performed of the statue basement
Sample P2 - P2a	Sampling performed on the back of the Madonna's head
Sample P3 - P3a	Sampling performed on Maddalena's shoulder
Sample P4 - P4a	Sampling performed on the thong of Christ
a = after restauration	

Colorimetric analyses were carried out, directly on the different areas of the marble surface before and after the restoration on the points indicated in Fig. 1c where C1-C5 refer to the measurements before the restoration while C1a-C5a refer to the measurements on the same points after the cleaning. A Konica Minolta CM 2300d portable spectrophotometer was employed. The measurements refer to the CIE L*a*b* chromaticity diagram and to the Normal recommendation 43/93 (Normal 1993) where 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). Further information on the experimental details are reported elsewhere (Comite et al. 2020a; Guglielmi et al. 2020).

By SEM-EDS semiquantitative analyses were performed on the micro shards (Table 1) by means of a Hitachi TM1000 instrument equipped with an energy dispersive X-ray spectrometer (Oxford Instruments SwiftED).

Infrared spectra were also collected on the micro shards (Table 1) in ATR mode by a Nicolet 380 spectrophotometer in the range 4000 – 500 cm^{-1} at a resolution of 4 cm^{-1}.

Non-invasive and in-situ EDXRF analysis were performed, on the points indicated in Fig. 1d, with the portable EDXRF spectrometer ELIO (XGLab srl, Milan, Italy) equipped with a low-power X-Ray tube with a Rh anode. The sensitivity range of the spectrometer is 1–40 keV, and it is therefore able to detect elements heavier than Na (Albano et al. 2017; Albano et al. 2020). 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. In Fig. 1d, the measurement points are shown and highlighted in green.

Results And Discussion

The paint making dark the statue surface (Fig. 1a) was applied probably at the end of 19th century with the intention of giving the surface a "wet" effect, to close the porosity of the material and finally also to create a sufficient barrier to protect the work during moulding operations.

Different methodologies are available for restoration interventions (Matteini et al. 1999; Cremonesi 2002). In the present case in order to remove the dark layer, a treatment based on the use of the commercial product Phytagel (by Bresciani srl, http://www.brescianisrl.it/newsite/ita/home.php) was used. This system allows the cleaning of the surface thanks to its adhesion and the subsequent tearing, removing in this way the dirt layer. Phytagel is a gelling agent, substitute for the well-known agar-agar, used in paper restoration for gentle wet cleaning. It is important pointing out that Agar-agar turns yellow whereas Phytagel produces a totally transparent gel. In this way the result shown in Fig. 1b-c was obtained.

After the removal of the dark layer some very fain traces of colour appeared, and the hypothesis of the possible and intentional presence of colour on the marble surfaces was considered. At this purpose we decided to start with non-invasive analyses such as colorimetric and XRF investigation. Subsequently we went further on with the analysis of the micro shards.

The colorimetric measurements were performed on the Madonna’s mantle (C1 and C1a before and after restoration respectively), the hand of Christ (C2 and C2a before and after restoration respectively), the Madonna's dress (C3 and C3a before and after restoration respectively), the angel’s hair (C4 and C4a before and after restoration respectively) and the angel’s dress (in this case 3 measurements were taken: C5 before restoration, C5i during an intermediate stage of the restoration - as represented in Fig. 1a - and C5a after restoration). Additional areas of the monument were not analysed due to the impossibility of performing accurate measurements because of the non-regular surface.

The values of the colorimetric coordinates are reported in Table 2. An increase in the L* coordinate (luminosity) occurred after the restoration, pointing out a change of the surface shade from dark to a lighter tone. Moreover, L* values after cleaning are very homogeneous indicating that the restoration was successful.

Table 2
Colorimetric coordinates (L*, a*, b*) calculated for the analysed areas before and after restoration.

		L*	a*	b*
C1	before restauration	43,06	4,62	11,83
C1a	after restauration	74,62	1,02	5,52
C2	before restauration	51,43	4,24	15,29
C2a	after restauration	74,56	2,83	16,93
C3	before restauration	55,72	2,25	16,23
C3a	after restauration	76,67	4,15	16,98
C4	before restauration	47,17	4,73	13.47
C4a	after restauration	75,97	3,76	17,34
C5	before restauration	57,03	2,63	12,69
C5i	intermediate restauration	73,44	3,96	17,91
C5a	after restauration	75,33	4,15	17,94

The colorimetric coordinate a* increased for areas C3 and C5 while for C1, C2 and C4 a decrease was observed. Since higher values of a* means that the colour is moving towards red, it could be hypothesized that traces of red pigments were present in C3 and C5. As far as colorimetric parameter b*, it slightly increased for all the analysed areas except for C1 (the mantle of the Madonna) where b* clearly decreases. Taking into account that negative values of b* are associated with blue colour, the decrease of this coordinate could indicate the presence of traces of a blue colour on the mantle. This is confirmed by the reflectance spectra reported in Fig. 2 where for C1 an increase of the reflectance in the blue region of the spectrum after cleaning (C1a) is clearly observable. Furthermore, for sample C5 a clear increase of b* was also detected corresponding to a yellower colour, i.e. the use of a yellow pigment.

Therefore, on the base of this first overview carried out by colorimetric investigation, that demands further confirmation by the other techniques, the use of pigments on the surface can be assumed.

in Fig. 2 for all the investigated areas the reflectance spectra before and after cleaning are shown together with the colour appearance (in the box inside each figure). All samples show an increase in reflectance in the yellow and red areas of the spectrum with a shift of the colour towards warmer tones after restoration.

To verify the presence of inorganic colorants or pigments and to assess whether the variation of the chromatic properties of the surface could be attributable to an intention of the artist nor an alteration, a non-invasive campaign was accomplished by portable XRF. Data are shown in Table 3. The measurements areas X4 and X12, as reported in Fig. 1d, were collected respectively in the same region of the P3 and P4 sampling (Fig. 1b); X5 and X6 could be considered as a reference, acquired at the bottom of the sculpture protected by the atmospheric interaction and where no treatments or coatings were expected; X1 and X2 correspond to the cut in Christ's ribs. The normalized values of the net area counts related to the characteristic elements (Table 3) featured high

values of Ca 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.

Table 3
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) (Invernizzi et al., 2020) Areas marked with an asterisk (*) were selected as non-treated areas and can be considered as spectral background. Non-detected elements are marked with n.d.

Area	S	Ca	Ti	Mn	Fe	Zn	Sr
X1	5.63	63.92	1.60	n.d.	1.00	1.52	3.50
X2	6.10	58.14	1.05	n.d.	1.05	0.83	3.77
X3	14.44	50.86	0.12	0.25	0.36	0.04	4.17
X4	15.37	63.08	0.17	0.18	0.67	n.d.	4.13
X5*	13.13	43.29	n.d.	n.d.	0.17	n.d.	3.45
X6*	12.50	42.60	n.d.	n.d.	0.18	n.d.	2.76
X7	9.11	34.89	n.d.	n.d.	0.19	n.d.	2.98
X8	9.17	40.26	0.16	n.d.	0.83	n.d.	2.88
X9	10.59	44.35	0.19	n.d.	1.60	0.15	5.81
X10	12.60	46.33	0.12	n.d.	0.16	n.d.	4.69
X11	7.51	58.91	0.74	n.d.	0.73	0.44	3.78
X12	9.32	46.00	0.13	n.d.	0.24	n.d.	3.47

If Ca, Mn, Sr, and Fe are expected for the original limestone, the even S distribution and the variability of Fe detected by each acquisition are highly informative about the presence of a surface treatment or patina (Invernizzi et al. 2021). The scatter plot of the normalized net area counts Ca/Fe displayed in Fig. 3a, allow us to infer the presence of yellow or red earth pigments. An increase of the Fe counts is recognizable in correspondence to the presumed pigmented areas where reddish or yellowish hue was observed. Those areas, namely X1, X2, X4, X8, X9, X11, are scattered in a narrow region far from the other group of measurements that are arranged closer to the reference points X5 and X6. In particular, area X8 is quite near to area C5 where, by colorimetric analysis, an increase of the yellow component, associated to the use of a yellow pigment, was observed. Besides, the slight correlation between S and Ca showed in Fig. 3b allowed us to hypothesize the presence of gypsum probably employed in a preparation layer or, more likely, due to an alteration patina formed by the weathering, as discussed below.

In order to assess the chemical composition of the micro-shards taken from the surface (Table 1), a characterization was performed by SEM-EDS both before and after the cleaning procedure. In Table 4 the semi-quantitative data acquired on all the samples are reported. From EDS results it can be observed that in all the

analysed points an increase of both Ca and S concentration is evident after the cleaning procedure. Some representative EDS spectra taken before and after restoration are shown in Fig. 4.

Table 4
chemical composition detected by SEM-EDS on some selected areas (and reported as average values) on the fragments taken from the statue surface before and after the restoration (relative standard deviations were in all cases lower then 10%)

Sample		**Mg (w%)**	**Al (w%)**	**Si (w%)**	**P (w%)**	**S (w%)**	**Cl (w%)**	**K (w%)**	**Ca (w%)**	**Fe (w%)**	**Pb (w%)**
P1	before restauration	0.23	1.30	3.60		36.15			57.28	1.45	
P2	before restauration	0.33	0.40	3.20	0.40	28.07	0.53	2.07	61.83	3.20	-
P2a	after restauration	0.30	0.30	2.30	-	30.13	-	-	62.20	4.77	-
P3	before restauration	1.10	0.97	3.87	1.40	25.07	-	30.35	35.65	1.60	-
P3a	after restauration	0.90	0.13	2.63	-	29.04	-	-	66.80	0.53	-
P4	before restauration	1.57	1.0	4.70	-	29.77	-	-	62.97	-	-
P4a	after restauration	0.27	-	1.47	-	30.73	-	-	63.57	-	3.97

Analysis performed on sample P1 confirms that gypsum had been applied to the sampled area to fill a fracture-lacuna. The sample shows high values of sulphur (36.15%) and calcium (54.4%). Moreover, the punctual analysis performed on some white particles (Fig. 5) has shown the presence of strontium which is correlated to natural gypsum composition (so not gypsum of neo-formation) indicating a restoration intervention (Barbieri et al. 1976).

Together with analyses carried out on selected areas, some punctual analyses were also performed on single particles (Fig. 6). Pb was found in sample P3a and Pb and Fe in sample P4a. The not negligible concentration of lead in P4a on selected areas (Table 4) allowed to hypothesize the use of lead pigments even if further investigation is recommended for the identification of the specific pigment (for instance lead white). It is worth noting that P3a and P4a correspond to the areas X4 and X12 characterized, on the base of Fe/Ca, by a more red or yellow hue for X4 and a white hue that could match with the use of a white lead for X12.

In the case of sample P3, a high quantity of K together with a lower signal of P is observed. The presence of phosphorus can be attributed to the composition of the *"colletta"* applied to the surface, as described in the introduction. In fact, this glue was prepared using animal glues produced from rabbit bones.

Furthermore, on the samples, after the restoration, lower concentrations of Si, Al were detected (Table 4) probably because of the removal of some dust embedded in the patina. The presence of higher concentrations of Ca and S after the restoration, in accordance with what highlighted by XRF analysis, could suggest, the presence of a

preparation layer or of some degradation products, like gypsum of neo formation due to the reaction between the marble and atmospheric pollution (Belfiore et al. 2013; Barca et al. 2014; Vidorni et al. 2019).

The widespread presence of Ca and S on the statue surface is also attested by the fact that for all the three examined shards, comparing the FT-IR spectrum acquired before and after the restoration (Fig. 7), gypsum appears more evident after the cleaning as attested by the signals at 3525, 3400, 1627, 1109, 667 and 590 cm^{-1} (signals labelled in Fig. 7a). Together with gypsum also oxalate signals at 1630, 1450, 1380, 1320 and 780 cm^{-1} are evident for samples P2 and sample P4 but not for sample P4. Accordingly, to the literature oxalate (signals labelled in Fig. 7a) is attributed to the previous restoration interventions or to some biological degradation (metabolism of microorganisms) (Sabbioni et al. 1991; Rampazzi et al. 2004). Thanks to the comparison with a spectra data base (https://spectrabase.com/spectrum/4gc0KO4vgqP) it was also verified that no traces of the cleaning product applied on the surface, i.e. Phytagel, remained after its removal.

Another common feature of the three samples is that after cleaning the signal due to calcite (at about 1420 and 871 cm^{-1}) and due to the original limestone are more evident. In the case of sample P4 (Fig. 7c) the signals due to calcite appear only after cleaning (P4a) indicating a greater thickness of the overlying "*colletta*" forming the patina which was not completely homogenously on the marble surface (on the contrary, as previously evidenced by colorimetric analysis, the cleaning operation made the surface very homogeneous). In sample P4 the signals at about 2900 cm^{-1} (due to C-H stretching) and at about 1730 cm^{-1} (carbonyl group stretching) together with some quite weak signals at 1530 and 1440 cm^{-1} are indicative of the presence of organic substances due to the proteinaceous binder of the "*colletta*". In fact, the signals at about 1730, 1530 and 1440 cm^{-1} are characteristic of amide I, II and II (Fermo et al. 2020a) present in the amino acid groups of proteins. In fact, this kind of "*colletta*" was prepared, as mentioned in the introduction, starting from some animal glue which is a proteinaceous binder. An evident decrease of this signals is observable in sample P4a confirming that, with cleaning, the organic coating was removed.

However, in samples P3a and P4a stain peaks due to organic substances (at about 1730 cm^{-1} as well as at about 2900 cm^{-1}) are still present probably indicating the use of a compound that was applied to the surface and was not completely removed after cleaning. A possible hypothesis is that this substance was an oil used as a binder and mixed with pigments in order to apply some colour to the stone surfaces. It is known that FT-IR spectroscopy is only indicative of the kind of binder. Nevertheless, the highlighted signals are consistent with the use of an oil, as confirmed by the comparison with some references (https://spectra.chem.ut.ee/paint/binders/).

Sample P3 shows two signals at 749 and 650 cm^{-1} which are no longer present after cleaning. They could be assigned to a compound containing phosphorus and potassium that was found on this area before cleaning but after no longer appeared (Table 4). These signals could correspond to some hydrated potassium phosphate, but the degree of hydration is not known and therefore it is difficult to determine the precise position of the bands, which are, however, compatible with the presence of a phosphate.

As far as the diffused presence of gypsum on the statue surface, on the base of the preliminary results reported in Comite et al. 2020a, as before mentioned, we made two different hypotheses. The first one was that a thin preparatory layer of gypsum was applied on the surface before the colour application. However, this hypothesis would seem to be discarded because there is no clear evidence in the literature of this kind of procedure applied to decorate marble surfaces. Furthermore, as previously discussed, traces of an oily binder probably used in

combination with pigments and that allowed the colour to adhere to the surface, were evidenced; conversely gypsum was not able to do so.

A second hypothesis seems to be much more likely: a sulphation layer has formed during the century on the limestone because of interaction between the surface and atmospheric pollution (the Piety has most likely been placed outdoor for centuries although its history is not well documented).

In fact, it is known that cultural heritage is submitted to a high corrosion risk (De Marco et al. 2017). SO_2 was responsible, together with other pollutants, of the deterioration of marble statues stored in archaeological museums (Agelakopoulou et. al 2009). It is also well known that in presence of SO_2, humidity and aerosol carbonaceous particles, a sulphatation process can occurs on carbonatic stones. This process corresponds to the chemical transformation of the substrate into gypsum, as well documented in the literature (La Russa et al. 2017; Comite et al. 2017).

Nowadays SO_2 air concentration significantly decreased but in the past large quantity of this pollutant were emitted mainly from coal combustion used as an energy and heating source (Ielpo et al. 2019). The sulphatation process that commonly takes place in outdoor environments, can also bring to different forms of deterioration including black crusts formation (Gulotta et al. 2013; Antonelli et al. 2016; La Russa et al. 2017; Comite et al. 2017; Comite et al. 2020b). However SO_2 is not the only component responsible for this degradation and other atmospheric pollutants such as black carbon and heavy metals are also involved (Fermo et al. 2015; Fermo et al. 2020b).

The "*colletta*" applied to the surface of the statue during 19th century, when it became part of the Castello Sforzesco museum collections, may also have favoured the growth of this layer of gypsum, since this coating certainly did not make the surface of the statue completely impermeable to the permeation of gaseous pollutants and humidity. It is worth noting that, in order to protect stone surfaces from such deterioration phenomenon, nowadays a wide variety of protective coatings are available (Fermo et al. 2014; Germinaro 2019; Pargoletti et al. 2019). It is also worth to note that, in order to better investigate the origin of the sulphation layer, the possibility to have a cross-section available would have allowed to better understand the interaction between the gypsum and the underlying stone surface but sampling of a shard of adequate size suitable for this purpose was not permitted in this case. Nevertheless the hypothesis advanced as for as gypsum presence seems quite reliable and is also in accordance with the opinion of the conservators involved into the project.

Conclusions

The application of both non-invasive in-situ analyses and micro-destructive investigation allowed us to collect information on the chemical composition of the alteration patinas present on the Renaissance marble sculptural group by Gasparo Cairano.

A winning strategy was the comparison of analyses conducted before and after cleaning operations. The application of a proteinaceous-based treatment named *"colletta"*, often employed for conservative purpose at the end of the 19th century, has been confirmed in particular thanks to the FT-IR analyses. After the removal of this ancient treatment and thanks to the comparison between XFR and colorimetric analyses, some colour traces have been highlighted in some areas of the statue and, in particular, on the Madonna's mantle and on the thong

of Christ where the presence of lead could be associated to lead white (even if a molecular identification was not performed). It is very likely that these colours could have been applied using an oil as a binder, the presence of which becomes more evident after the removal of the "*colletta"*.

Another important outcome of this study is that the colorimetric analysis carried out by a portable instrument turned out to be a powerful system not only to disclose traces of colour but also to verify the homogeneity of the cleaning procedure. This could be advantageous in marble cleaning operations because it can suggest to the restorer how far to proceed.

Finally, the removal of the *"colletta"* made it possible, above all, to highlight the presence of an extensive layer of sulphation (gypsum) that may have formed over the centuries because of the interaction between the stone surface and atmospheric pollutants, especially during the period when the statue was exposed outdoors.

In conclusion the multi-analytical approach applied has allowed to reconstruct the "conservation story" of this less well known but no less important work of art of the Renaissance period, contributing also to formulate some hypothesis on its original appearance.

Declarations

Ethics approval and consent to participate: Not applicable.

Consent for publication: Not applicable.

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Figures

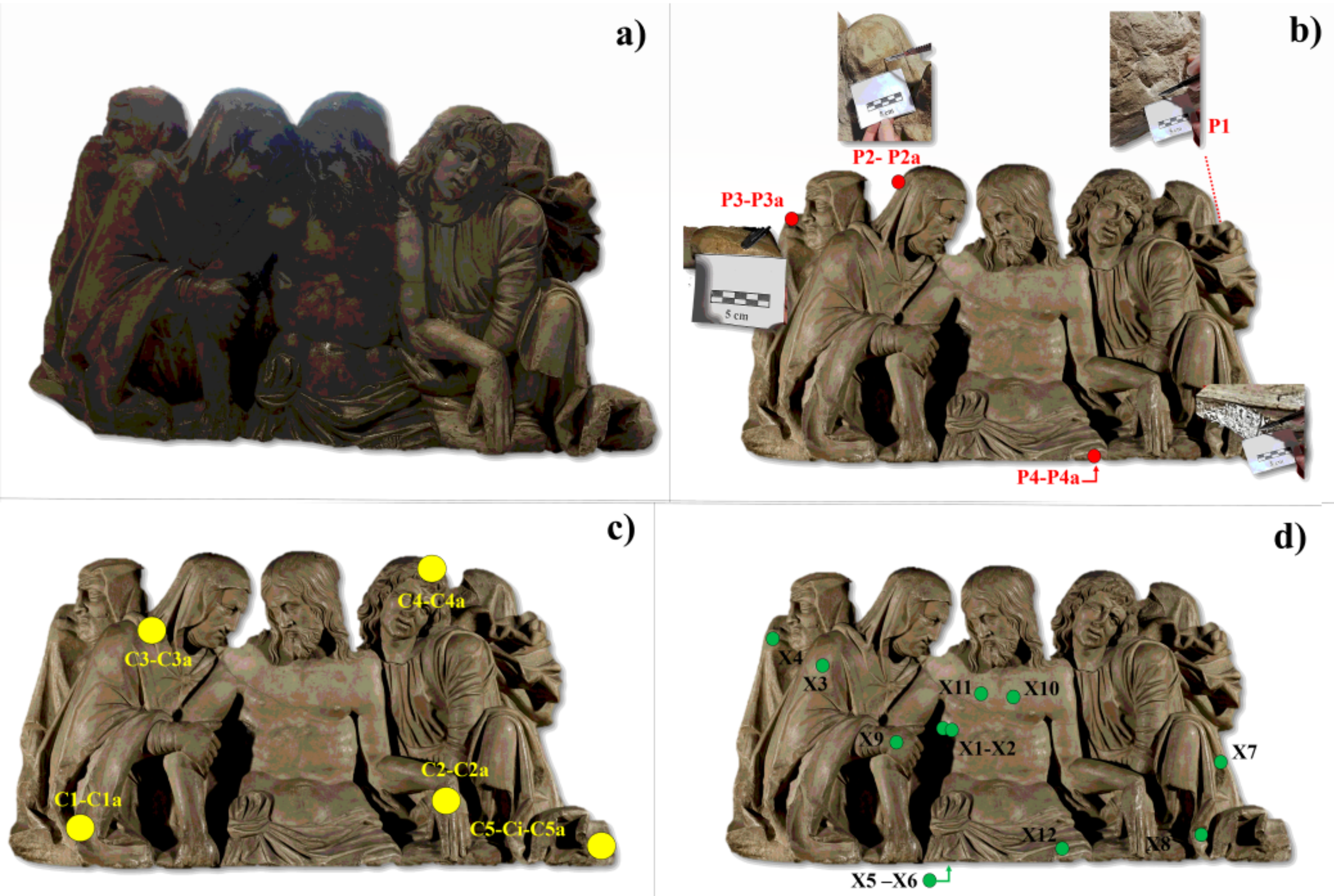


Figure 1

The sculptural group: a) the three left figures as they appeared before the conservative intervention while the right part already appears in the cleaning phase after a first removal of the patina; b) the sampling points (P) from where the micro shards before and after the restoration (indicated with a) were withdrawn are displayed in red; c) the points (C) where colorimetric analysis were carried out before and after the restoration (indicated with a) are displayed in yellow; d) the XRF measuring points (X) are displayed in green

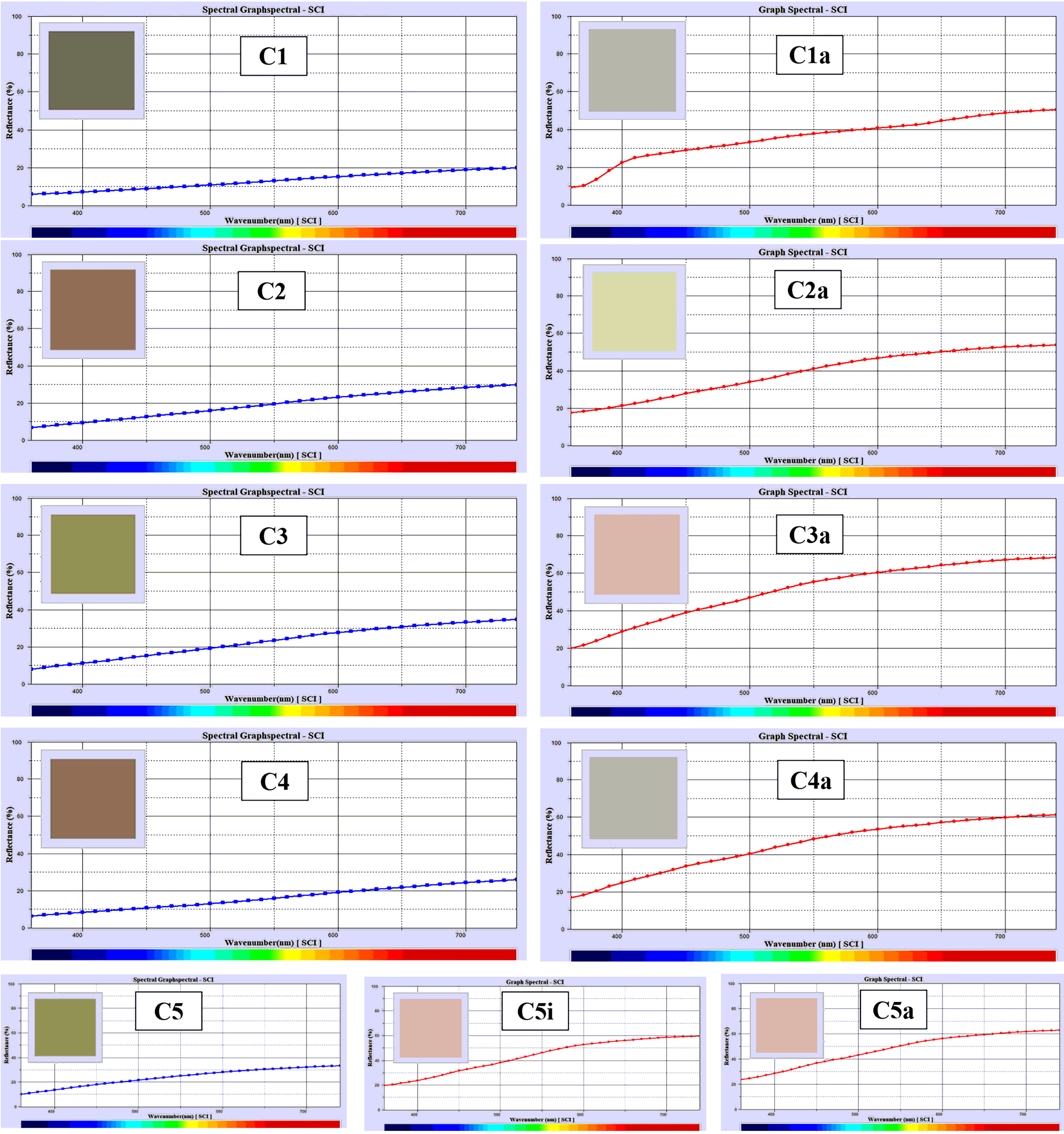


Figure 2

Reflectance spectra of the analysed areas before and after restoration; the squares inside the spectra represent the field of colour

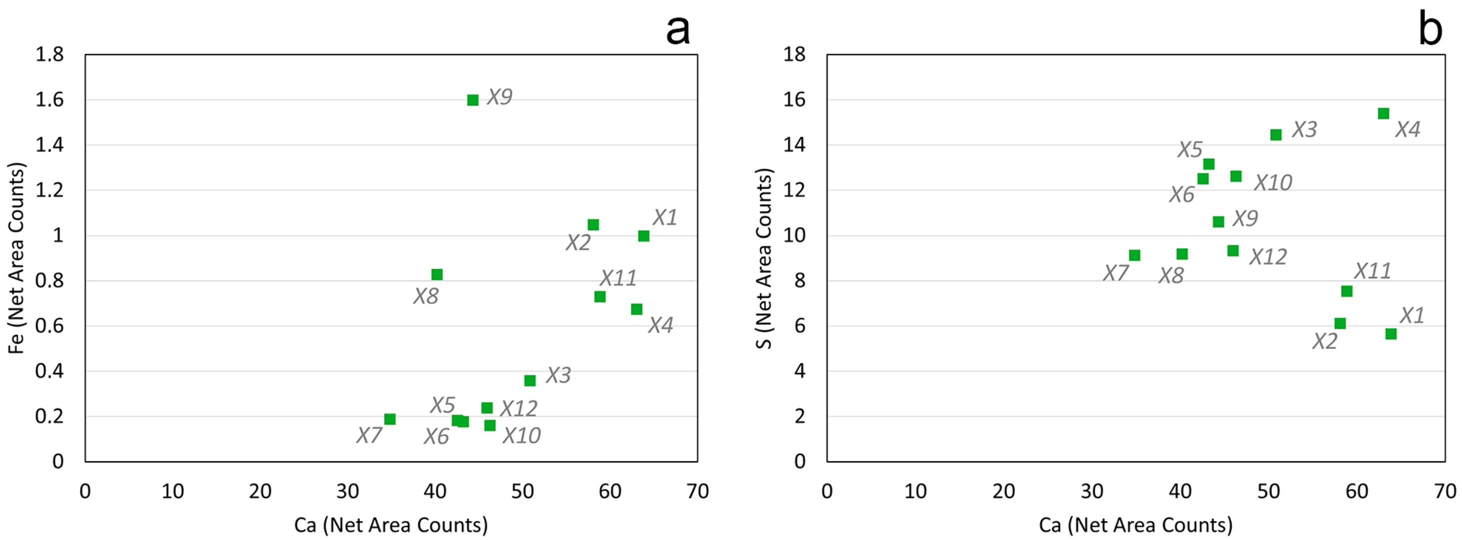


Figure 3

Scatter plot of Ca/Fe (a) and of Ca/S (b)

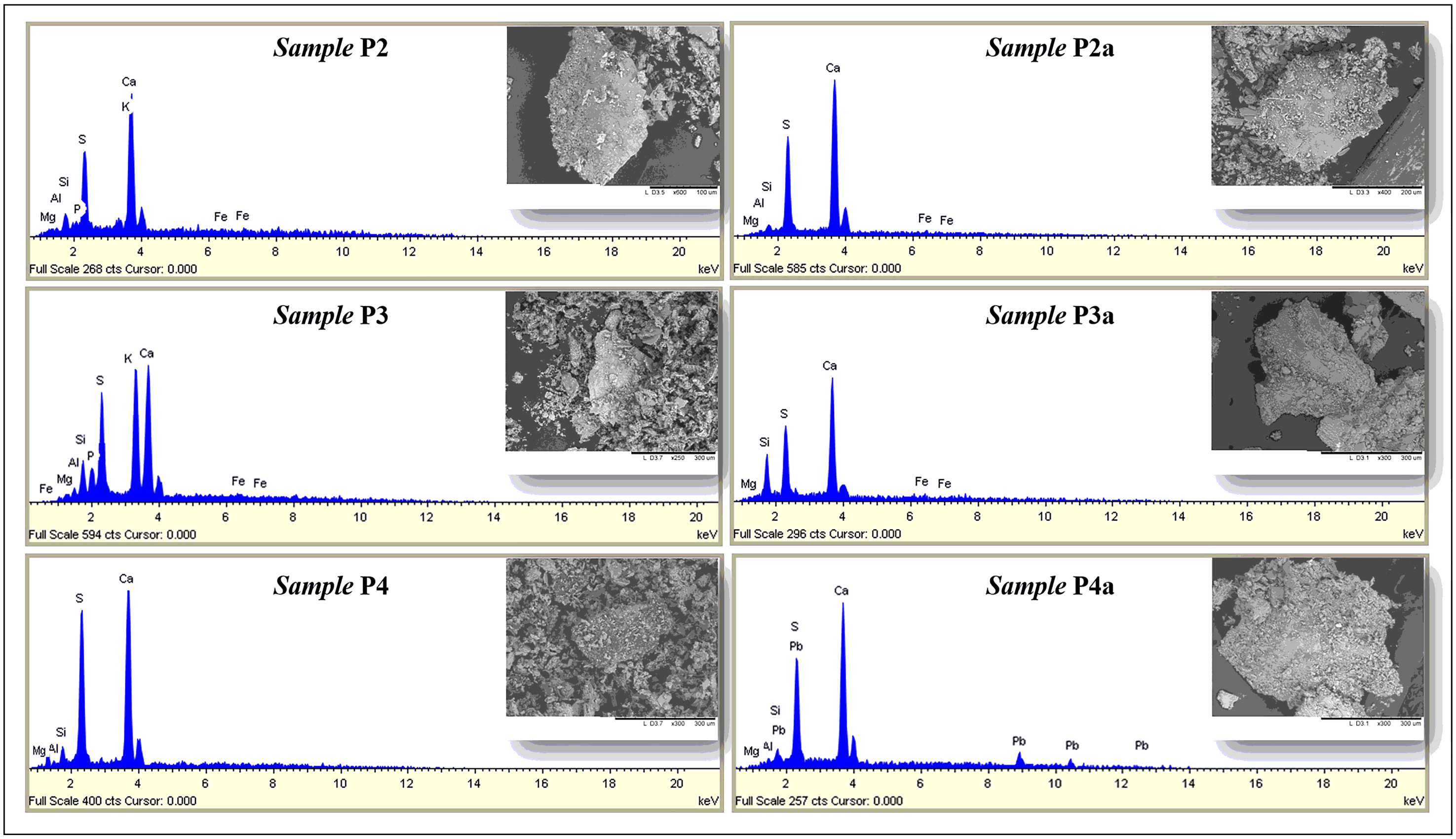
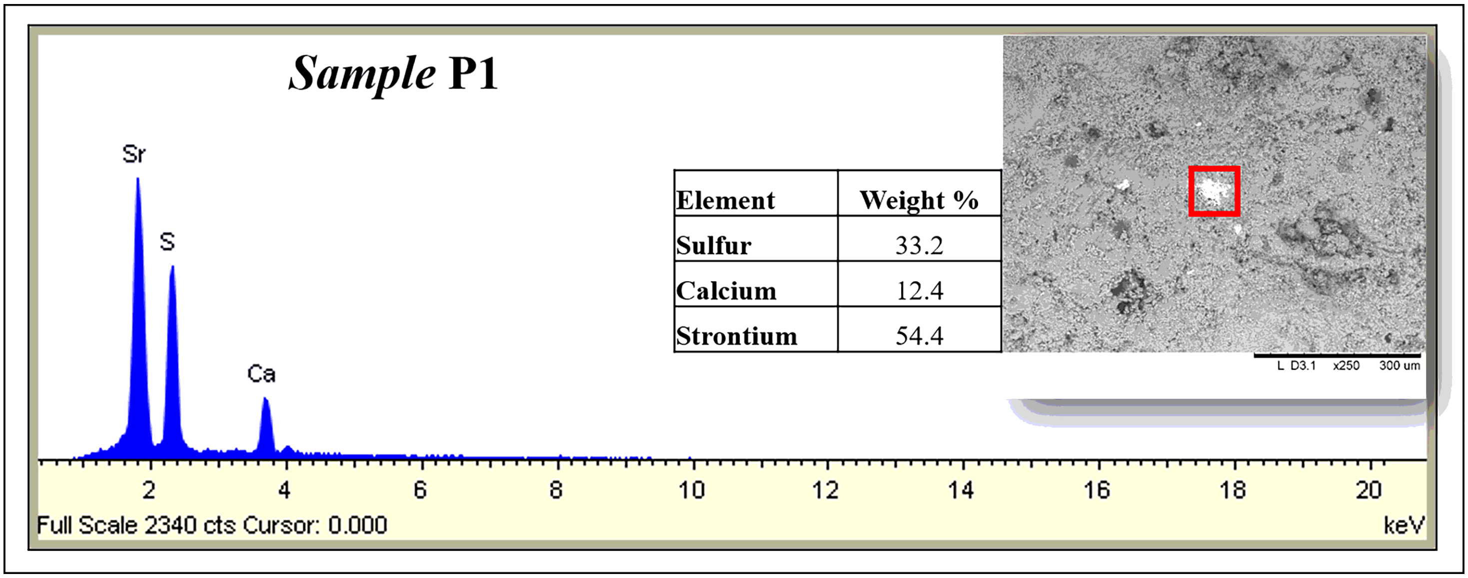


Figure 4

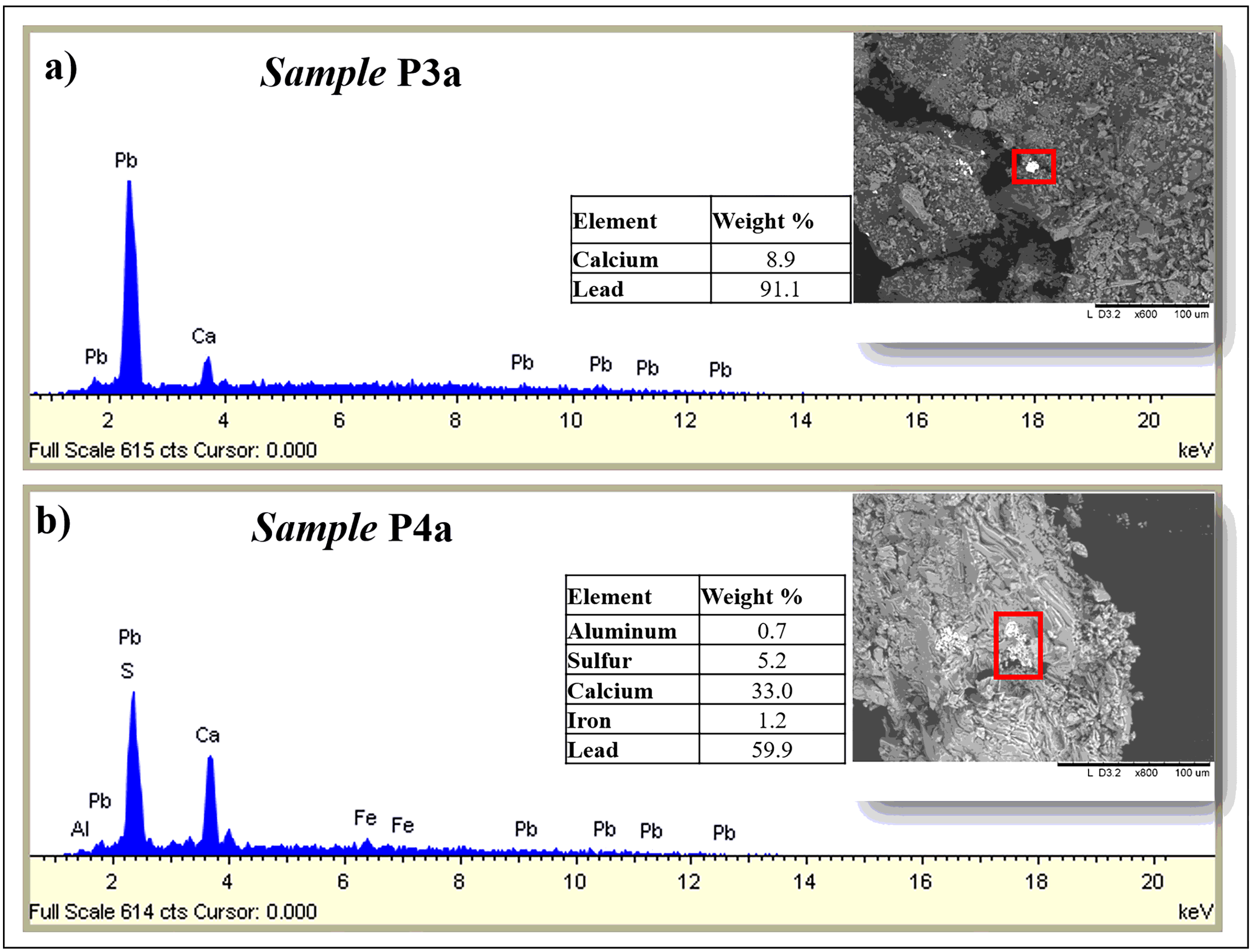
Representative EDS spectra taken before and after restoration on the micro-shards



Element	Weight %
Sulfur	33.2
Calcium	12.4
Strontium	54.4

Figure 5

SEM-EDS analysis performed on a clear particle present on sample P1



Element	Weight %
Calcium	8.9
Lead	91.1

Element	Weight %
Aluminum	0.7
Sulfur	5.2
Calcium	33.0
Iron	1.2
Lead	59.9

Figure 6

SEM-EDS analysis performed on particles present on the shards taken after restoration: a) sample P3a; b) sample P4a.

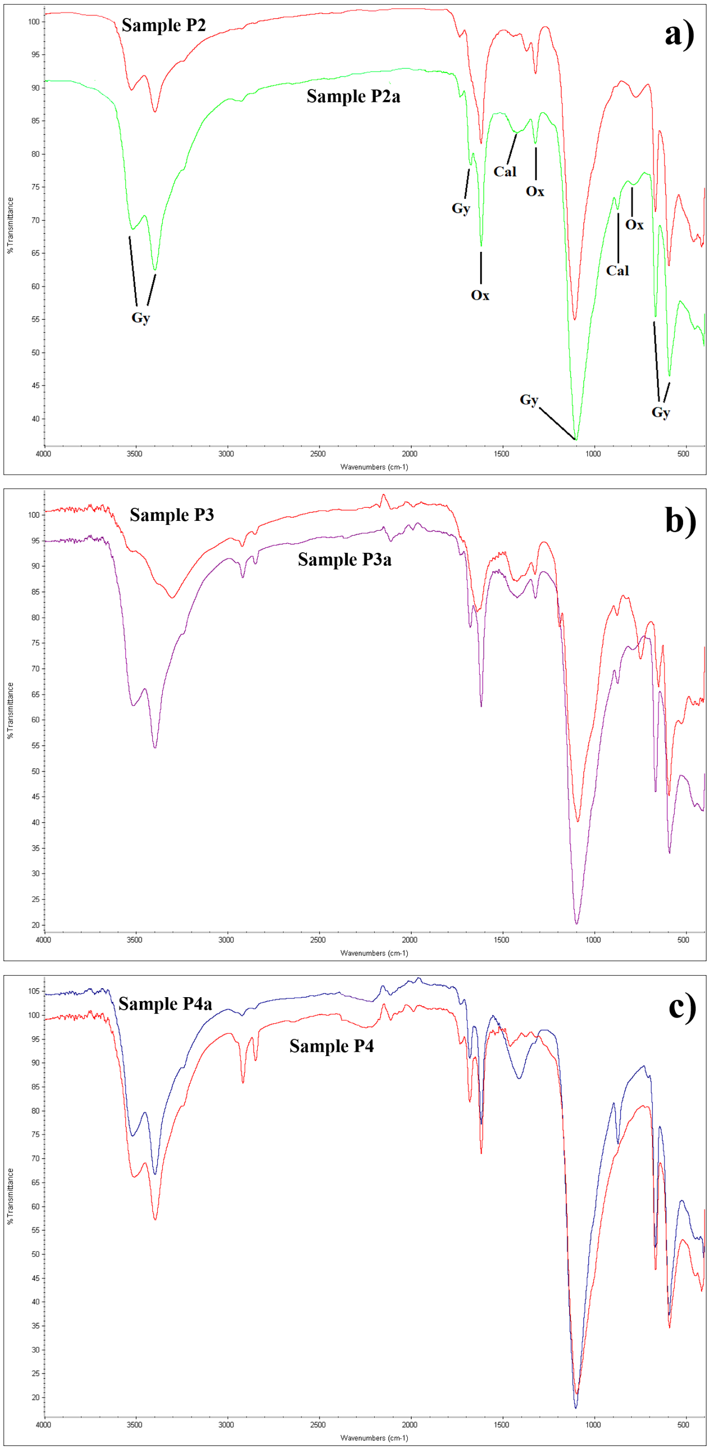


Figure 7

FT-IR spectra acquired on the shards before and after restoration: a) P2 and P2a; b) P3 and P3a; c) P4 and P4a