

Characterisation of artificial patinas on bronze sculptures of the Carlo Bilotti Museum (Rome)

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Abstract Two bronze sculptures, *Ettore e Andromaca*, a reproduction of a plaster model by Giorgio de Chirico, and *Cardinale*, a cast made from an original by Giacomo Manzù, stand outside the Carlo Bilotti contemporary art museum in Villa Borghese park (Rome). The composition of the artificial brown patina present on the statues' surface, which was applied for aesthetic purposes, is unknown. This paper reports analysis carried out to identify the composition of the artificial patina and describe the corrosion products formed in outdoor conditions. Raman spectroscopy and scanning electron microscopy equipped with X-ray microanalysis were performed on sample fragments and powder scrapings taken from the bronze statues. X-ray powder diffraction was used whenever possible and subject to conservation priorities. Our data revealed, in the artificial brown patina, the formation of copper oxides (cuprite and tenorite) on the surface of both sculptures as possible result of oxidisation treatments performed with a blowtorch before the artificial patination process began. Furthermore, a copper nitrate (gerhardtite) was identified as an ingredient in the preparation applied to

the bronze surfaces. The green areas revealed the presence of corrosion products as copper sulphate hydroxide (brochantite) and copper sulphate-chloride (connellite), which form under acid rains conditions.

1 Introduction

Patination is an important final stage in the production process of a bronze artwork. It is the result of collaboration between the artist and the foundry where the quality of the finished surface depends both on its texture and on the application of coloured finishes [1].

Patinas can develop naturally on such objects over time, or they can be produced artificially by accelerating the natural process of corrosion with chemical treatments. In such cases, chemical reaction is controlled in order to achieve a stable corrosion process with the desired aesthetic effects [1, 2]. A variety of chemical patinas can be obtained by changing the composition of the patination solution or pastes (sulphides, nitrates, oxides, acetates, and chlorides) and/or through the application method (direct application, vapour colouring, immersion colouring, heat colouring, torch technique) [1, 3]. Different techniques and recipes are used to produce a wide variety of patina colours, ranging from black to reddish brown or green, and the surface can be given an opaque, semiopaque, or transparent finish [3].

Although understanding of the chemical nature of the products used in artificial patination can help to identify the production techniques and the best conservation approaches, few studies on the composition of artificial patinas are currently available [1, 4, 5]. Only a small portion of these researches refers to patinated artwork exhibited

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outdoors [6, 7]. Lately, several multidisciplinary approaches have been described in recent studies as being used to identify the composition of artificial patinas produced in the laboratory before being aged under controlled or urban conditions [7–13].

In this study, we characterised the artificial patinas used as a decorative technique on two bronze sculptures and their corrosion products formed in outdoor conditions (natural patina). The two bronze artworks are: *Ettore e Andromaca* and *Cardinale*, a reproduction and a cast of an original produced at the beginning of the twenty-first century by Giorgio de Chirico and Giacomo Manzù, respectively, and exhibited outdoors of the “Carlo Bilotti” contemporary art museum in Rome.

The artificial patina and the corrosion products on the bronze surfaces were characterised by combining Raman spectroscopy, X-ray powder diffraction (XRPD), and scanning electron microscopy (SEM) equipped with X-ray microanalysis (EDS).

2 Experimental

2.1 Site and bronze sculptures

The two bronze sculptures examined in this study are displayed in front of Villa Borghese’s ‘Aranciera’ (Fig. 1a), which currently houses the contemporary art museum named after Carlo Bilotti.

Ettore e Andromaca is a bronze sculpture, $230 \times 115 \times 77$ cm, and it is a reproduction of a plaster model made in 1986 and commissioned by the art collector Carlo Bilotti. This model was made from an original in glazed terracotta by Giorgio de Chirico. The copy was authorised by the wife Isabella de Chirico in order to respect the wish expressed by de Chirico himself that a monumental version be made of the terracotta sculpture. Two copies, numbered 00/00 and 0/0, were produced; the first was destined for the open-air museum “MAB” in Cosenza, Italy, and the second for the Bilotti Museum in Villa Borghese. Figure 1b shows the sculpture in its open-air location in 2006, where a homogenous dark-brown artificial patina can be seen covering the entire surface. In a photograph from ten years later (Fig. 1c), the surface of the statue appears drastically altered, with a bright green patina distributed unevenly across the surface. The most affected areas are on the side facing south-east, corresponding to the back of Andromaca, while the original dark-brown patina can still be seen on the opposite side (Fig. 2).

Cardinale was a gift from the collector Carlo Bilotti to the museum, and it is one of eight casts made in 2004 from a 1965 original by Giacomo Manzù. The statue depicts a slim stylised figure, with an overall pyramid-like shape. It



Fig. 1 a Location of the sculptures: the circle indicates the position of *Ettore e Andromaca*, the square that of the *Cardinale*. b, c *Ettore e Andromaca* in 2006 and 2016, respectively. d, e *Cardinale* in 2006 and 2016, respectively

was first placed outside the museum in 2006, with its front side facing north-west. From the beginning, the sculpture presented an uneven surface with a brown to leaden green patina (Fig. 1d). Today its front side is predominantly covered with a brown patina, apart from a green patina on the lower right side, while the back has mostly become green (Fig. 1e).

Due to the high artistic value of the two bronze statues, the number and size of the samples were restricted.

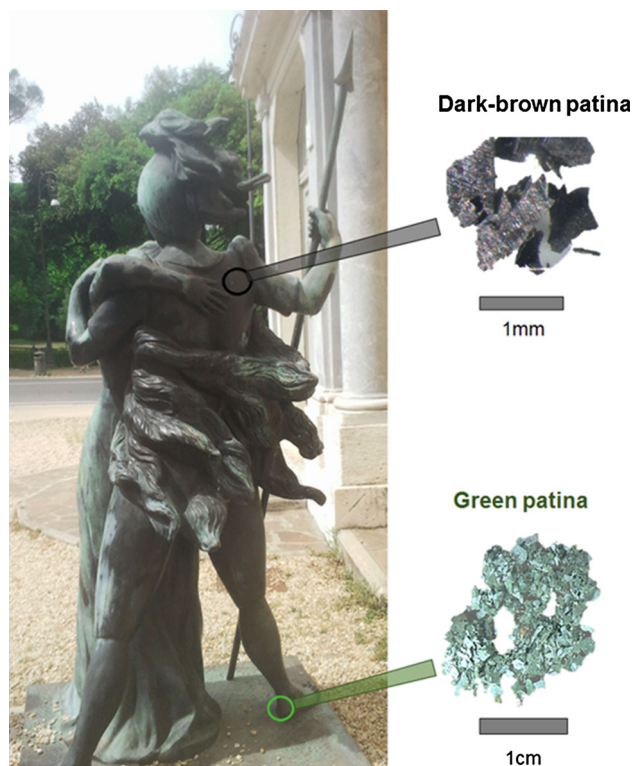


Fig. 2 Back of the bronze sculpture *Ettore e Andromaca* and the two sample areas

Specifically, two patina samples were taken from *Ettore and Andromaca*: one from the dark-brown patina and one from the green. Each sample fragment was a few millimetres in size and about 30 micron in thickness. The dark-brown patina sample was taken from the area of Ettore's right shoulder blade, while the green patina was taken from his shinbone (Fig. 2). The removal of fragments from *Cardinale* was forbidden for conservation reasons, and we therefore scraped a small quantity of powder from the brown and green surfaces to the rear of the statue (Fig. 3).

All samples were photographed using an Olympus SZX16 stereomicroscope, and digital pictures were taken with a Color View II (Soft Imaging System GmbH, Münster, Germany) digital camera coupled to Cell^B software.

2.2 Raman spectroscopy

Raman measurements were performed on both sides of the fragment in order to identify the molecular composition of the artificial and natural patina.

Raman spectra were acquired by using a Labram Micro-Raman spectrometer by Horiba, equipped with a He-Ne laser source at 632.8 nm (nominal output power 18 mW).

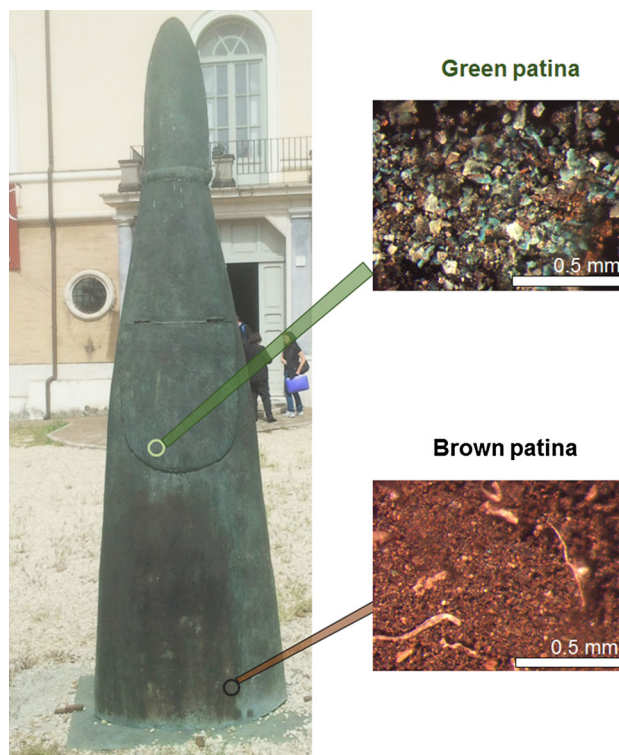


Fig. 3 Back of the sculpture *Cardinale* and the two sample areas

The illumination and collecting optics of the system consist in a microscope in confocal configuration. The system achieves the high contrast required for the rejection of the elastically scattered component by an edge filter. The backscattered light is dispersed by a 1800 line/mm grating, and the Raman signal is detected by a Peltier cooled ($-70\text{ }^{\circ}\text{C}$) 1024×256 pixel CCD detector. Nominal spectral resolution is about 1 cm^{-1} . In order to avoid sample degradation, neutral filters were used to reduce the laser power on the samples. Spectral acquisitions in the range $100\text{--}3600\text{ cm}^{-1}$ were performed with $50\times$ and $100\times$ objectives, depending on the response and structure of the individual sample. On each sampled point, we collected three accumulations, 50 s each, in order to avoid degradation while collecting enough statistics. Origin software was employed for pre-treatment analysis, such as baseline correction, normalisation, and smoothing.

2.3 Scanning electron microscope equipped with X-ray microanalysis (SEM/EDS)

The sample fragment both of "*Ettore and Andromaca*" and small quantity of powder of "*Cardinale*" sculptures were placed on conventional Al stubs and observed with an XL30 SEM microscope (FEI Company, Eindhoven, The

Netherlands) with backscattered electron detectors, equipped with an energy-dispersive spectrometer (EDS analysis) at LIME (Roma Tre University). Samples were placed in the vacuum chamber and backscattered electron (BSE) images were acquired, in order to analyse the elemental distribution of the samples, with an accelerating voltage of 20 kV and a working distance of 11 mm. In order to identify the elemental composition and distribution of the points of interest, an EDS energy-dispersive X-ray fluorescence spectrometer was used for microanalysis on samples using an accelerating voltage of 20 kV, a filament current of 1.80 A, an emission current of 20 μ A, an aperture current of 300 nA, and a working distance of 11 mm. In these conditions, the detection limit for the elemental composition is about 0.1 wt%. The analysis on each sample was performed on single points, hereafter referred to a “spots” and on extended areas ($40 \times 40 \mu\text{m}^2$), in order to

average out small compositional differences between different points of the sample.

2.4 Powder X-ray diffraction (XRPD)

XRPD analysis was applied on the powders of the “Ettore and Andromaca” sculptures in order to characterise the mineralogical composition of the two different patinas.

X-ray analyses were performed using a Scintag X1 diffractometer under $\text{CuK}\alpha 1$ radiation ($\lambda = 1.54055 \text{ \AA}$, 40 mA, 45 kV), fixed divergence slits, and a Peltier cooled Si(Li) detector (resolution $<200 \text{ eV}$). A divergent slit width of 2 mm and a scatter-slit width of 4 mm have been employed for the incoming beam; a receiving slit width of 0.5 mm and scatter-slit width of 0.2 mm have been used for the diffracted beam. Data have been collected in step-scan mode: 2° – 70° 2θ range, step-size 0.05° 2θ , counting time 3 s/step.

Table 1 Results of EDS qualitative microanalyses “Ettore e Andromaca”

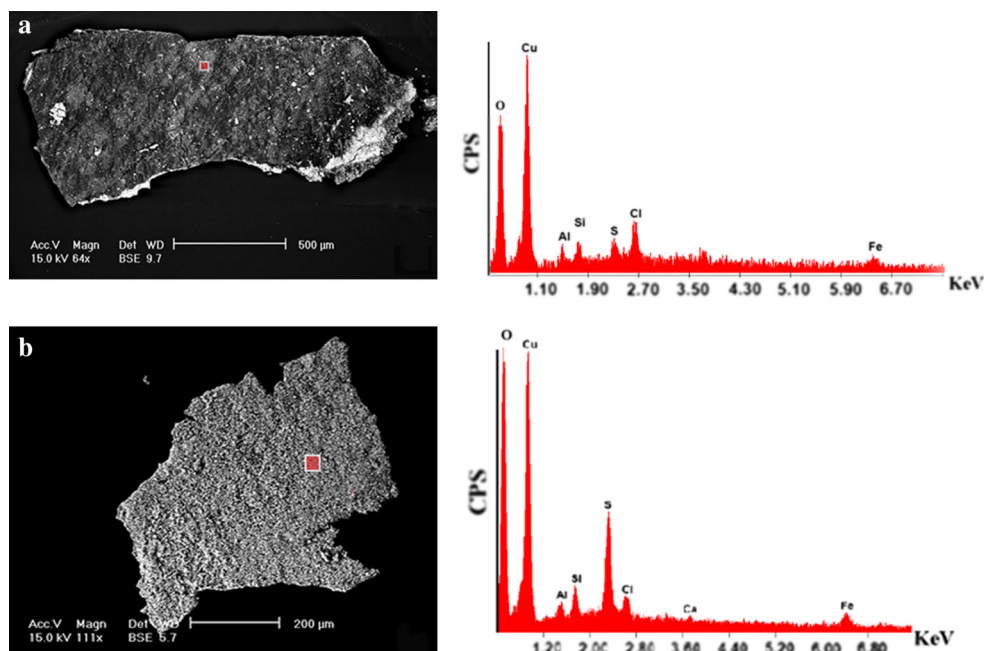
Sample	Elemental composition
Dark-brown patina	
Spot 1	O, Cu , Si, S, Ca, Fe
Area 1	O, Cu , Al, Si, S, Cl, Fe
Area 2	N, O, C, Cu , Si, Cl, Fe
Green patina	
Spot 1	O, Cu, S , Cl, Fe
Area 1	O, Cu , Al, Si, S, Cl, Ca, Fe

3 Results and discussion

3.1 Patina on the Ettore e Andromaca bronze statue

The results of the SEM–EDS analysis of the patinas, carried out at different “spots” and on different areas of the two samples, are reported in Table 1, where elements with higher concentrations are highlighted in bold. The presence of N in the dark-brown samples could suggest a nitrate-based artificial patina. We noted a higher sulphur content in the green patina than in the dark-brown one (see Fig. 4).

Fig. 4 SEM–BSE image and elemental EDS spectrum of Ettore e Andromaca statue **a** of the dark-brown sample and **b** of the green sample in correspondence of the area highlighted in red on the SEM image



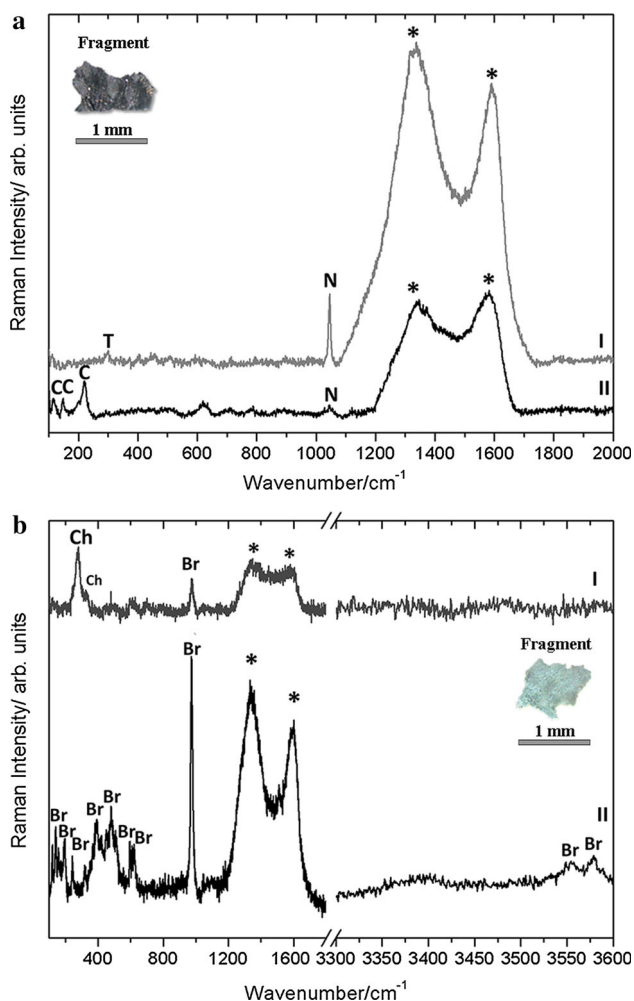


Fig. 5 Raman spectra of patinas on *Ettore e Andromaca*. **a** Two representative spectra of the black-brown sample. Label *C* marks band of cuprite, *N* copper nitrate, *T* tenorite, and *asterisk* marks amorphous carbon; **b** Raman spectra of the green sample. Label *Br* marks band of brochantite, *Ch* chalcocite and *asterisk* amorphous carbon

Several Raman spectra were then performed at different points of the fragments, and XRPD analysis was applied where necessary in order to obtain more information.

For the dark-brown patina, the Raman spectra (two representative examples are shown in Fig. 5a) showed bands at 117, 148, 220 cm^{-1} characteristic for cuprite (Cu_2O) and a band at 297 cm^{-1} due to tenorite (CuO). Cuprite and tenorite can grow on the bronze both by exposure to moist air and by blowtorch method [14]. The pre-treatment by torch was the most common method in the patination process in the nineteenth century for large bronze sculptures, and it is still used. In the torch technique, the metal, before treated with the patination solution, undergoes to a reducing flame where no oxidation reaction occurs. Then, upon removal from the reducing flame, the hot metal can react with O_2 and H_2O from the

environment resulting in the formation of an oxide film (often cuprite) on the surface [7, 11, 15, 16]. For this reason, we suggest that the presence of copper oxides in these samples is likely due to the oxidising treatment made with a blowtorch on the surface of the statue before applying the artificial patina.

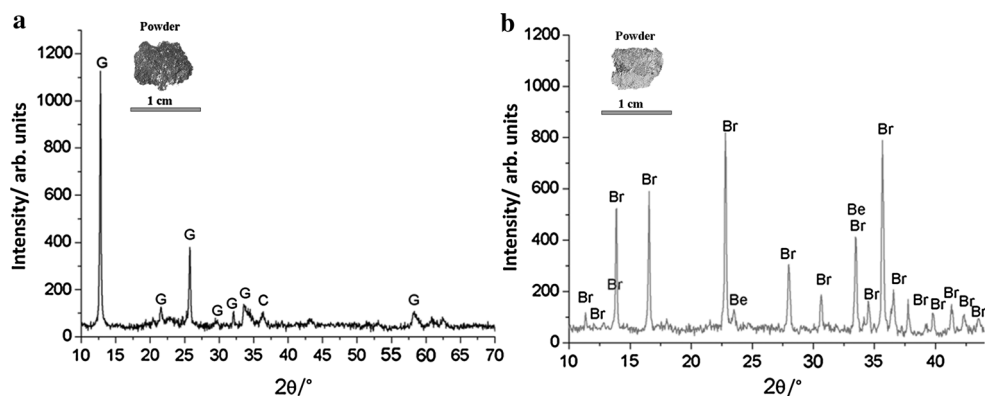
Additionally, all spectra revealed a strong Raman band at 1047 cm^{-1} , attributed to the NO_3^- symmetric stretching mode (Fig. 5a). This Raman spectrum suggests the presence of copper hydroxyl nitrate, an ingredient frequently used in many artificial patina recipes [3, 9, 11, 17]. Usually, artificial patinas based on copper nitrate are composed by two minerals gerhardite and rouaite [7–9, 18]. These minerals are polymorphs with the formula $\text{Cu}_2\text{NO}_3(\text{OH})_3$, gerhardite is a naturally occurring copper nitrate mineral in the orthorhombic system, and rouaite is in the monoclinic system [18, 19].

Unfortunately, due to the small number of bands present in the spectra and to the overlapping of the NO_3^- asymmetric stretching mode with the broad bands at 1328 and 1589 cm^{-1} , which can be ascribed to amorphous carbon-based substances, it is not possible to distinguish between the two polymorphs by Raman spectroscopy alone. For this reason, XRPD measurements were taken to complement the Raman spectroscopy. The XRD pattern of the dark-black patina shows well-resolved peaks at about 12.8° ($d = 6.91 \text{ \AA}$), 21.53° ($d = 4.12 \text{ \AA}$), 25.80° ($d = 3.45 \text{ \AA}$), 32.04° ($d = 2.79 \text{ \AA}$), 33.63° ($d = 2.66 \text{ \AA}$), 58.12° ($d = 1.58 \text{ \AA}$) characteristic of gerhardite (well-matched with the gerhardite pattern from ICDD PDF 00-014-0687) (Fig. 6a) [9]. In addition, we noticed peaks at 36.41° ($d = 2.46 \text{ \AA}$), 43.05° ($d = 2.09 \text{ \AA}$) and 60.99° ($d = 1.53 \text{ \AA}$) consistent with the presence of cuprite (well-matched with the cuprite pattern from ICDD PDF 00-005-0667).

In the literature, copper nitrate is reported as an ingredient used to obtain an artificial patina with a green hue [1, 3, 11]. However, copper nitrate was sometimes used in the preparation of brown patinas to obtain a homogenous surface, with the subsequent addition of other ingredients to provide the brown colouration.

The high content of sulphur and copper revealed in the green patina by EDS analysis suggests the presence of a copper sulphate (Fig. 4b), and this was confirmed by Raman analysis. In fact, in Fig. 5b the Raman bands at 120, 140, 156, 170, 193, 242, 317, 417, 450, 480, 594, 609, 3550, 3577 cm^{-1} show the presence of brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) [7, 20–22]. The presence of this compound was confirmed by the powder XRD patterns (Fig. 6b) (well-matched with the brochantite pattern from ICDD PDF 00-043-1458) and is indicative of the pH conditions of the environment [7, 20, 23]. As reported by Frost [18], brochantite is stable at pH values between 4 and 6, while antlerite ($\text{Cu}_3\text{SO}_4(\text{OH})_4$) is stable at lower pH values (<4).

Fig. 6 XRD patterns of patinas on *Ettore e Andromaca*. **a** XRD pattern of the black-brown sample. Label *G* marks lines of gerhardtite, *C* of cuprite; **b** XRD pattern of the green sample. Label *Br* marks lines of brochantite and *Be* of bernalite



Chalcanthite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) is in a stable phase under conditions of higher acidity.

In agreement with Kosec et al. [7], the acidity of rain water in an urban atmosphere (pH 5) favours the formation of brochantite more than other polymorphs. Interestingly, the distribution of incidental rainfall in Rome is at its highest on surfaces exposed to the south and to the south-east [24], corresponding to the side of the sculpture most affected by the green patina, containing brochantite.

Moreover, Raman bands at 274 and 328 cm^{-1} (Fig. 5b I) suggest the presence of copper sulphide chalcocite (Cu_2S). This may be due to the polluted atmospheres containing hydrogen sulphide [14] or may form during the production of the artificial patina in reductive atmosphere [7, 11].

Interestingly, the XRD results show the presence of bernalite [$\text{Fe}(\text{OH})_3$] (Fig. 6b), probably due to dissolved iron resulting from the presence of a ferric compound in wet conditions and with specific pH values [25]. The presence of bernalite and the EDS detection of Cl and Fe in all samples (Table 1) could suggest a patination treatment by using a recipe based on ferric chloride (FeCl_3) solutions, which are often stippled onto the heated metal surface in order to obtain a dark artificial patina [3, 13]. However, no evidence of the presence of ferric chloride was found by Raman spectroscopy. This is, in fact, very difficult to detect, being thermodynamically unstable in its anhydrous form [26].

Amorphous carbon spectral fingerprints (1328 and 1589 cm^{-1}) were detected in all samples (Fig. 5). This could be due to environmental pollution or to the production technique used to obtain a brown hue. Bronze artworks were, in fact, sometimes subjected to gentle heating during the application of red ochre, chrome yellow, or carbon black pigments.

3.2 Patina on the Cardinale bronze statue

Both patina samples were scraped from the back of the *Cardinale* statue, and elements constituting the bronze alloy (Cu, Sn, Pb, Zn) were detected in the EDS test results

Table 2 Results of EDS qualitative microanalyses *Cardinale*

Sample	Elemental composition
Brown patina	
Spot 1	O, Cu, Al, Si, S, Sn, Zn
Area 1	O, Cu, Si, Pb, Cl
Area 2	O, Cu, Al, Si, Pb, Cl, Ca, Fe, Zn
Green patina	
Area 1	O, Cu, Mg, Al, Si, S, Cl, Ca, Fe
Area 2	O, Cu, Al, Si, S, Pb, Cl, Ca, Zn
Area 3	O, Cu, Mg, Al, Si, S, Cl, Ca, Zn

(see Table 2). The EDS analysis also showed a higher sulphur and chlorine content in the green patina than in the brown one (Fig. 1S).

The Raman bands acquired from the brown patina revealed the presence of cuprite (Cu_2O) with bands at 117, 148 and 220 cm^{-1} (Fig. 7a I), whereas the bands at 274 and 328 cm^{-1} are due to traces of copper sulphide (Cu_2S) (Fig. 7a II), highlighting the presence of the brown artificial patina used by the foundry [7, 11, 26].

The Raman band at 1047 cm^{-1} could be signatures of copper nitrate (gerhardtite or rouaite) (Fig. 7a III) [9]. As mentioned above, it would have been necessary to carry out an XRPD analysis of the patina in order to distinguish between the two polymorphs. Unfortunately, this was not feasible with our equipment, due to the little amount of powder (<0.5 mg). We also detected the presence of calcite (CaCO_3), but it would be necessary to carry out further analysis to assign the origin of this compound to the casting technique or to environmental residues or degradation.

The Raman spectra of the green patina revealed the presence of anatase (TiO_2), with bands at 142, 394, 516, and 635 cm^{-1} (Fig. 7b I). This is one of the three mineral forms of titanium oxide, the other two being the more common rutile and the rare brookite. Anatase is a common constituent of many soils, sediments, and clays [27]. By an informal conversation with the founder, we deduced that the anatase presence on the statue may be due to the

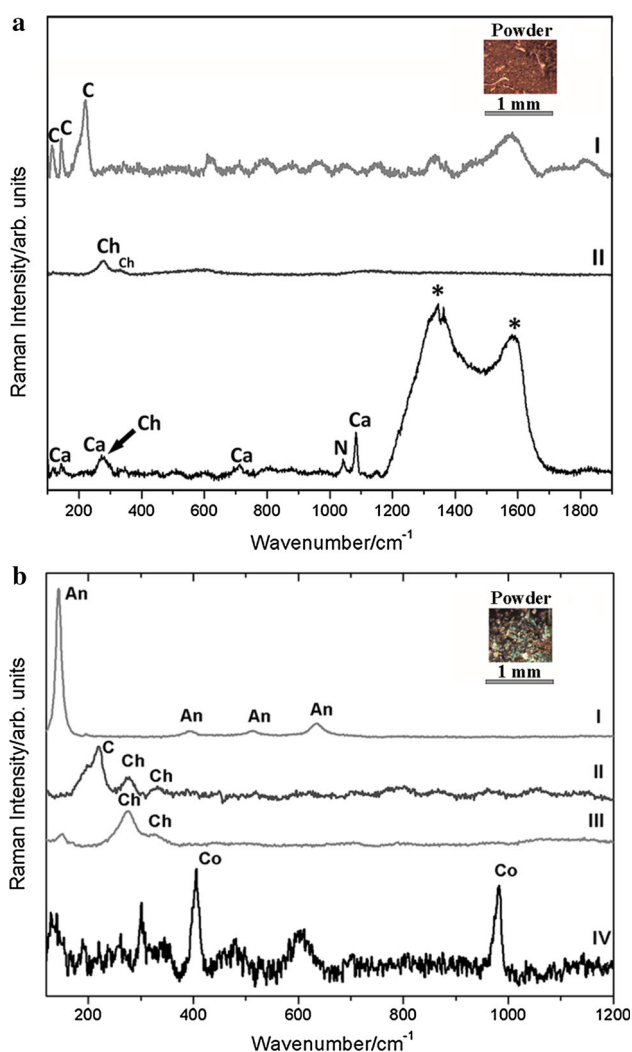


Fig. 7 Raman spectra of patinas on *Cardinale*. **a** Three representative spectra of the brown sample. Label *C* marks band of cuprite, *Ch* chalcocite, *N* copper nitrate, *Ca* calcite, and *asterisk* marks amorphous carbon; **b** Raman spectra of the green sample. Label *An* marks band of anatase, *C* cuprite, *Ch* chalcocite, and *Co* connellite. Connellite spectrum was normalised to the strongest peak of anatase in order to avoid excessive intensity differences

presence of residual traces of the clay used in the lost wax casting technique, or to environmental pollution. The presence of cuprite and copper sulphide was also detected in these samples (Fig. 7b II, III).

Lastly, the Raman spectrum in the light-blue areas visible at the microscope on the sample (Fig. 7b IV) revealed an intense band at 984 cm^{-1} , assigned to the sulphate SO symmetric stretching mode, and a strong band at 404 cm^{-1} , attributed to CuO stretching vibrations [28]. These bands could in principle be attributed to a complex basic copper (II) chloride sulphate, known as connellite $[\text{Cu}_3\text{Cl}_6(\text{SO}_4)_2(\text{OH})_{62}\cdot 12\text{H}_2\text{O}]$, or to buttgenschite $[\text{Cu}_3\text{Cl}_6(\text{NO}_3)_4(\text{OH})_{62}\cdot 12\text{H}_2\text{O}]$ [17, 20, 26]. However, the absence of the band at around 1050 cm^{-1} , characteristic of

NO group, suggests the presence of connellite. This is a blue crystalline copper chlorosulphate: it is generally classified as a bronze disease [14]. It is often associated with cuprite, gerhardtite, and malachite [29]. Pollard et al. [30] report that copper trihydroxychlorides can be replaced by other insoluble mineral species such as brochantite and connellite, when even small quantities of sulphate and chloride ions are present in an aqueous solution. Connellite is stable within a pH range of between 5 and 8 [14].

4 Conclusions

A multidisciplinary investigation was carried out on the artificial and on corrosion products formed in outdoor conditions (natural patina) of two bronze sculptures located in front of the Carlo Bilotti contemporary art museum in the Villa Borghese park (Rome). SEM/EDS analyses were carried out, and Raman spectra were collected at several points of the samples. Where necessary, XRD investigations were used to complement the results of EDS and Raman analysis.

The artificial brown patina covering the back of the bronze sculpture, *Ettore ed Andromaca*, is due mostly to the development on the surface of cuprite (Cu_2O), and, to a lesser extent, tenorite (CuO), as a result of the original patination process. Copper nitrate (gerhardtite), commonly used in the preparation of bronze surfaces before patination, was also detected.

The green patina, found mainly on the back of *Andromaca*, is composed of brochantite $[\text{Cu}_4\text{SO}_4(\text{OH})_6]$, bernalite $[\text{Fe}(\text{OH})_3]$, and copper sulphide (Cu_2S), as a result of the corrosion products formed in outdoor conditions (natural patina). The formation of brochantite is favoured at pH values similar to those of acid rain (pH 5). In fact, the areas most exposed to incidental rainfall (south and south-east sides) are those most affected by the green patina.

The artificial brown patina on *Cardinale* has a similar composition, with an oxide layer in the form of cuprite (Cu_2O), followed by copper sulphide (Cu_2S) and a nitrate. The main corrosion product found in the green patina is connellite $[\text{Cu}_{19}\text{Cl}_4(\text{SO}_4)(\text{OH})_{32}\cdot 3(\text{H}_2\text{O})]$, another mineral that forms under acid rain conditions.

Naturally, it would be desirable to perform more tests on the patinas of both statues, and examine more areas where alteration has taken place. But, as explained above, this was not permitted due to conservation concerns. Nonetheless, the results obtained are fundamental for subsequent comparisons of the statues.

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