Reproducing bronze archaeological patinas through intentional burial: A comparison between short- and long-term interactions with soil

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A B S T R A C T

The reproduction of archaeological corrosion patinas is a key issue for the reliable validation of conservation materials before their use on cultural objects. In this study, bronze disks were intentionally buried for 15 years in the soil of the archaeological site of Tharros, both in laboratory and *in situ*, with the aim of reproducing corrosion patinas typical of archaeological artifacts to be used as representative surfaces for testing novel cleaning gels. The microstructural, microchemical and mineralogical features of the patinas were analyzed by a multianalytical approach, based on optical microscopy (OM), field emission scanning electron microscopy coupled with energy dispersive spectrometry (FE-SEM-EDS) and X-ray diffraction (XRD). The patinas developed in 15 years were compared with an archaeological bronze recovered from the same site after about two thousand years of burial (referred as short-term and long-term interaction, respectively). Results revealed a similar corrosion behavior, especially in terms of chemical composition and corrosion mechanisms. XRD detected the ubiquitous presence of cuprite, copper hydroxychlorides and terrigenous minerals, while OM and FE-SEM-EDS analyses of cross-sections evidenced similar patinas' stratigraphy, identifying decuprification as driving corrosion mechanism. However, some differences related to the type of local environment and to the time spent in soil were evidenced. In particular, patinas developed *in situ* are more heterogeneous and rougher, while the archaeological one is thicker and presents a major amount of cuprite, terrigenous deposits and uncommon corrosion compounds. Based on our findings, the disks buried *in situ* were selected and used as disposable substrates to study the cleaning effect of a novel polyvinyl alcohol (PVA)-based gel loaded with a chelating agent ($Na_2EDTA \cdot 2H_2O$). Results show that the gel is effective in removing disfiguring degradation compounds and preserving the stable and protective patina. Based on the conservation needs, the time of application can be properly tuned. It is worth noticing that after a few minutes the green corrosion products can be selectively removed. The EDS analysis performed on the gels after cleaning reveals that they are

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highly selective for the removal of copper(II) compounds rather than Cu(I) oxide or Cu(0) from bronze substrates.

1. Introduction

When archaeological bronze artifacts are recovered from the soil, their surfaces are often highly degraded due to long-term interactions with the surrounding environment. The degradation products layer (i.e., the patina) typically consists of a mixture of stratified mineral compounds, which can affect the chemico-physical stability and disfigure the artifact [1]. The degradation of metal objects is the result of electrochemical processes, which start from the metal surface and diffuse toward the core. Several factors influence the rate and the extent of corrosion under burial conditions [2–6]. The elemental composition and the microstructure of the metal substrate, as well as the presence of manufacturing defects, are commonly referred to as endogenous factors. The physico-chemical features of the soil, like porosity, pH, electrical conductivity, moisture content and chemical composition, are indicated as exogenous ones. In particular, acidic pH conditions and large amounts of water and oxygen can strongly increase the degradation rate. Severe corrosion phenomena occurring in bronze artifacts are also related to the presence of chloride ions into the soil [7–9]. Chlorides are in fact highly aggressive toward Cu-based alloys as they can penetrate into the porous patina's layers promoting the formation of the dangerous nantokite (CuCl), which is the first step toward bronze disease [10].

Mechanisms of patina formation are widely discussed in literature [11–14]. Metal elements from the alloy oxidize, in accordance with the electrochemical series of the standard potentials. Depending on the solubility and reactivity of the oxidized species, the metal cations can diffuse toward the ground or reprecipitate as mineral corrosion products. These can be stable and protect the bulk from a deeper corrosion (as copper hydroxycarbonates) or can further react once the external environmental conditions have changed (as copper chlorides).

After the finding and before exhibition inside museums, the surfaces of corroded objects must be carefully cleaned from the dangerous and disfiguring corrosion compounds, also to improve the esthetical pleasantness. Cleaning operations are traditionally carried out by invasive mechanical methods, based on the use of abrasive tools, or by drastic chemical procedures, like the solubilization of corrosion products with acid, basic or complexing solutions [1]. A complete control of these methods is not always achieved and irreversible damages, such as the complete removal of the stable patina layer (i.e., cuprite), can occur.

To overcome the drawbacks related to traditional cleaning methods, especially the uncontrolled spreading of solvents on the artifacts' surface and their environmental release by evaporation, novel conservation materials based on retentive matrices, able to avoid solvent dispersion and to confine the cleaning action to localized surface areas, were developed. These systems were successfully used for cleaning paintings [15,16], street art works [17], stone monuments [18] and paper substrates [19]. Some interesting results were also obtained for the cleaning of metal artifacts from corrosion compounds. Different existing gel typologies and dispersions were tested with several cleaning solutions and applied to remove corrosion layers from archaeological silver-plated copper alloy coins [20]. It was found that the best treatments to remove all the corrosion compounds above the silver plating were physical peelable gels (Agar or gellan gum), applied hot and containing 2–5% (w/w) of disodium EDTA. PVA-based peelable films able to adapt to rough surfaces were synthesized and applied to remove copper corrosion compounds from a bronze fountain [21] and a 16th century bronze pedestal [22]. For applications on brittle and mechanically weak corroded surfaces, where a peeling action could result too aggressive, pHEMA/PAA-based gels were developed and their ability to solubilize copper hydroxychlorides from an artificially aged bronze mock-up was proven [23]. These methods are very promising for the cleaning of archaeological bronze findings, especially those based on retentive gels, as the corrosion patinas of historical artifacts are usually very brittle. However, their validation on disposable substrates reproducing the mineral components, structure and roughness of archaeological corrosion patinas has still not been conducted. Tests on reference substrates are necessary before the application on real bronze artifacts.

In the literature there are several studies about the reproduction of patinated bronze substrates, but most of them are related to the development of patinas typically formed in an outdoor environment [24–31]. Artificial patination has been obtained by immersion treatments [24], by electrochemical methods [25], by exposure to aggressive species into a climatic chamber [26,28] and by reproducing rainfall in laboratory tests [29]. Natural patinas have also been obtained by a 16-year exposure of copper to different types of outdoor atmospheres (rural, urban, industrial and marine) [30] and by a prolonged stay (up to 29 years) in a site affected by industrial pollution [31]. Though successful, these methods induce the formation of smooth and homogeneous corrosion layers, mainly composed of copper sulfates, therefore too different from the mineralogical and structural complexity typical of archaeological patinas. Few attempts were made by burying bronze samples in natural soil to reproduce archaeological corroded surfaces [32,33]. Even if the treatment was quite short (up to 1 year), corrosion layers containing chlorine and terrigenous elements, typical of the burial context, developed. However, a chemical pretreatment was necessary to promote the growth of copper hydroxychlorides [32] and a complete characterization of the corrosion layers, including the structural, chemical and mineralogical investigations of both the surface features and cross-section, is missing. A procedure to realize archaeological bronze patinas, supported by a detailed investigation of the structural, chemical and mineralogical features, as well as the mechanisms of corrosion, would be of great interest to obtain reference samples representative of corrosion layers naturally grown on artifacts in archaeological burial contexts, especially in terms of surface roughness and structural heterogeneity.

Based on these considerations, we decided to perform an experimental study aimed at: I) the reproduction of bronze patinas similar to the real archaeological ones from burial sites in terms of mineralogical composition and structure; II) the characterization of their microchemical, microstructural and mineralogical features in comparison with those of an archaeological artifact; III) the

reconstruction of the mechanisms of patinas' formation depending on short- or long-time interactions with soil; IV) the implementation of preliminary cleaning treatments with a polyvinyl alcohol (PVA)-based gel loaded with a chelating agent ($Na_2EDTA \cdot 2H_2O$).

Namely, hydrogels made of PVA "twin-chain" polymer networks (TC-PNs) were adopted, as they represent new advanced tools with enhanced properties for the cleaning of works of art. The TC-PNs used in this study are prototypes identical to those previously developed and used for the cleaning of masterpieces such as paintings by Jackson Pollock and Pablo Picasso [34,35]. These networks are formed by two types of PVA that differ by the hydrolysis degree and the molecular weight (hence the name "twin-chain"). The addition of the lower molecular weight PVA induces changes in the porosity and mechanical behavior as compared to single-PVA gels, boosting the uptake and removal of soil from surfaces [34]. Overall, the PVA TC-PNs have been shown to provide adhesion to rough surfaces, controlled release of cleaning fluids, and thus safe removal of soil and aged coatings. In this study, the gels were uploaded with $Na_2EDTA \cdot 2H_2O$ and assessed for the first time for the selective removal of corrosion products on bronze substrates.

To produce disposable patinas, bronze disks with chemical features similar to those of archaeological artifacts were intentionally buried for 15 years in the soil of the Carthaginian-Roman site of Tharros (western Sardinian coast, Italy), both in laboratory and *in situ*. Due to its proximity to the sea, the site of Tharros is a highly corrosive environment. Once recovered from the soil (in laboratory and *in situ*), the patinas naturally grown on the bronze surfaces after 15 years of burial and the patina of a bronze artifact found in Tharros were fully characterized and compared using a multi-analytical approach, based on optical microscopy (OM), field emission scanning electron microscopy coupled with energy dispersive spectrometry (FE-SEM-EDS) and X-ray diffraction (XRD). The microchemical, microstructural and mineralogical information were then used to test the cleaning efficacy of the PVA-based gel on patinated bronze disks obtained after 15 years of *in situ* burial and used as reference substrates.

It is worth noting that the patinas considered in this work are unique materials to study the mechanisms of bronze corrosion in soil. The research time frame is usually short compared with that required for the development of naturally grown patinas. To the best of our knowledge, this is the first study that investigates and compares naturally grown bronze patinas after a short-term and a long-term interaction with soil, i.e., patinas developed in 15 years and over about two thousand years of burial, respectively.

2. Materials and methods

2.1. The soil of tharros

Tharros was an important Mediterranean city (Italy), founded by Phoenician people on the western Sardinian coast at the end of the VIII century BC. Over time, Carthaginians first and Romans later conquered the area, converting it into a prosperous colonial city. From the beginning of the V century AD, Tharros was gradually abandoned due to Vandalic raids. The site was recovered thanks to archaeological excavations, started during the XIX century and extensively carried out until the present days. A lot of Carthaginian and Roman artifacts, like metal coins, weapons, jewels, ceramics and decorative items have been found during excavations.

Due to the proximity to the sea, archaeological finds, especially metal objects, show very bad conservation conditions [36,37]. As evidenced by chemical analysis conducted on the Tharros' soil in the framework of the European Project EFESTUS (INCOME contract n° ICA3-CT-2002-10030) [38], large amounts of chlorine and smaller amounts of phosphorus are present in the soil. In addition, particle size distribution measurements designated it as a dangerous sandy loam. The presence of chloride ions, along with the access of oxygen and water promoted by sandy sediments, are factors that considerably enhance the corrosiveness of the environment. As a consequence, the bronze objects found in Tharros are extensively corroded [39,40].

For these reasons, the soil of Tharros was selected to perform intentional and heavy degrading burial treatments on bronze substrates.

2.2. Patinas naturally grown after short- and long-term interactions with soil

A bronze alloy was purposely produced to obtain microchemical and microstructural metallurgical features similar to those of the ancient metal artifacts [32]. To produce bronze disks, Cu, Sn and Pb granules were put in the right proportion into an electrically heated furnace at 1100 °C by using graphite crucibles, they were melted, solidified and rapidly cooled at room temperature in water. Ingots were cut to obtain disks with a diameter of 23 or 26 mm. The bronze disks were prepared with the following chemical composition: Cu 92.3%, Sn 7.5% and Pb 0.2% by weight.

The disks were used for the reproduction of archaeological corrosion patinas under burial conditions. The soil from the archaeological site of Tharros was sampled and put into distinct plastic containers in the laboratory, after being mixed with 4% (vol/vol) of NaCl. A bronze disk was inserted inside each container and left under the soil for 15 years. The soil was periodically irrigated with distilled water to simulate the action of rains. Down holes in the container let the water flow away and avoided stagnation. The patina developed with this procedure is referred to as PTh15_lab. Other disks were directly buried *in situ* in the archaeological site of Tharros at a depth of about 30 cm from the ground surface. After 15 years, they were extracted from the soil and brought to the laboratory for the analyses. This patina typology is referred to as PTh15_*insitu*. All the samples were gently cleaned with a brush and washed with distilled water to remove macroscopic soil deposits. In total, 22 disks were buried in the laboratory and 34 were buried at Tharros. For each of the two treatments, a representative patina was selected and described in the present work.

An archaeological artifact, found in the site of Tharros in the *cloaca* sewage system was included in the study. The estimated age of the object is about two thousand years, and it was extracted at around 1 m from the ground surface. The chemical composition of the alloy was determined by energy dispersive spectrometry (EDS) analysis carried out on the cross sectioned object in correspondence of

the uncorroded metal core. The results allowed us to classify the object as a classical bronze containing about Cu 92.5%, Sn 6.0% and Pb 1.5% by weight.

2.3. PVA-based gel and cleaning test

The PVA-based gel was prepared as previously reported by Mastrangelo et al. [34]. The water swollen gels were let exchange in a 5% (w/w) disodium ethylenediaminetetraacetate dihydrate (Na$_2$EDTA · 2H$_2$O) aqueous solution (adjusted to pH 11 with a sodium hydroxide 1 N solution) overnight at room temperature and atmospheric pressure.

Some of the bronze disks buried for 15 years in the archaeological site of Tharros were selected and used as disposable substrates to perform a preliminary cleaning test. The PVA-based gel, cut in small pieces ($1 \times 1 \times 0.2$ cm^3), was directly applied on the patinated surface for 10 min and then re-applied in a smaller area up to 90 min, checking the cleaning results every 10 min. During this time, the gel surface was covered with parafilm to avoid the evaporation of the fluid and the dehydration of the gel. After the cleaning operation, the disks surface was rinsed with distilled water and air-dried.

The effect of the cleaning treatment was evaluated by comparing the surfaces' features of the patina before and after the test, using the stereo microscope and the electron scanning microscope described hereafter.
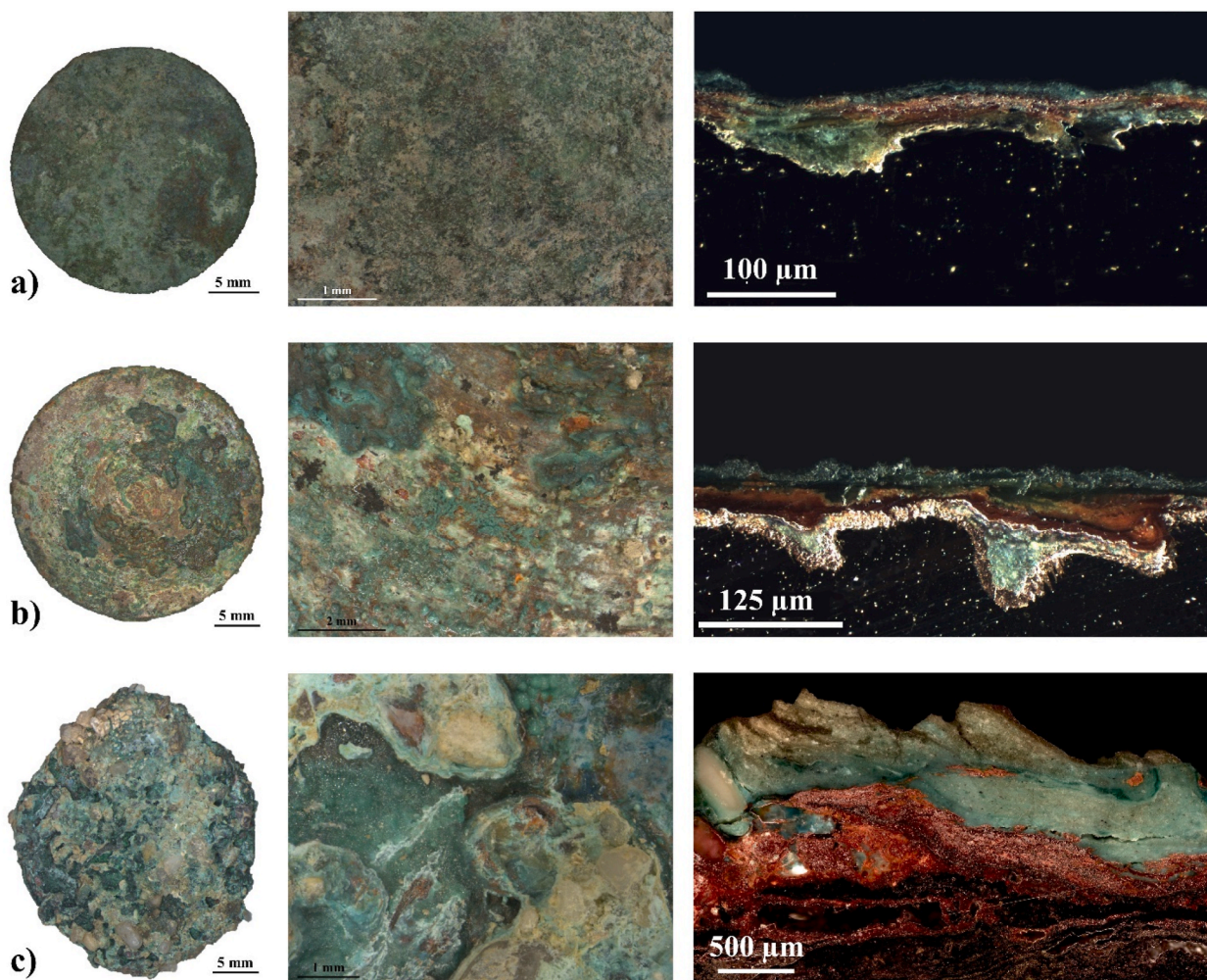

Fig. 1. Overall appearance, surface features and cross-sections of the three corroded objects. Optical images of the corrosion patinas developed on the bronze disks buried for 15 years inside the Tharros' soil in laboratory (a) and *in situ* (b) and of the archaeological patina (c). All the three surfaces appear highly degraded and covered by green corrosion compounds mixed with soil residues. Cross-section metallographic images show the stratigraphy of the corrosion layers. The young corrosion patinas are far less thick than the one developed during two thousand years of burial, but all are characterized by a similar stratigraphy. Red compounds, corresponding to cuprite crystals, developed over the metal core, while green corrosion products, consisting of copper(II) minerals, crystallized above the red ones. Differences are related to the extent of corrosion, which can be estimated by the amount of cuprite. The object that suffered long-term interactions with soil contains more copper(I) oxide than the samples buried for only 15 years.

Small gel pieces loaded with Na$_2$EDTA · 2H$_2$O were also applied for 100 min on a metal bronze surface, with a chemical composition equal to that reported in section 2.2 for the produced alloy, and on a pure cuprite patina. This was obtained by immersing the bronze alloy into a 15 mM Cu(NO$_3$)$_2$ · 2,5H$_2$O solution for 15 days at room temperature.

2.4. Microchemical, microstructural and mineralogical analyses

All the patinated materials considered in this study were firstly investigated by means of a Leica MZFLIII optical microscope and a Leica application suite (LAS) multifocus stereo microscope, both equipped with a digital camera (Leica DFC 320).

The structure and the chemical composition were investigated by a high-brilliance and high-spatial-resolution LEO Gemini 1530 (Zeiss, Germany) field emission scanning electron microscope, coupled by an energy dispersive X-ray spectrometer INCA 450 and four-sector back-scattered electron detectors. Images were all recorded in the back-scattered mode at different acceleration voltages from 1 to 20 kV. No sample metallization was performed before the investigation.

The mineralogical composition was studied by X-ray diffraction analysis conducted with a Bruker D8 focus diffractometer with Cu K_α radiation operating at 40 kV and 30 mA. Angular values between 10° and 65°, a step size of 0.025° and a sampling time of 2 s were used as experimental parameters. The X-ray diffraction patterns were acquired on the powders scratched from each sample and analyzed by electronic databases.

Cross sectioned samples were produced by using a diamond saw and by embedding the fragments in epoxy resin for 24 h. Sections were polished with silicon carbide papers until 1200 grit and diamond pastes up to 0.1 μm. Optical analyses of the cross sections were performed by a Leica MEF IV optical microscope equipped with a 420 Leica digital camera. Microchemical and microstructural analyses were performed by the FE-SEM-EDS equipment already described. Before the analyses, the surfaces were coated with a thin layer of carbon to avoid charging effects induced by the electron beam. Carbon layers were deposited by using a Bal-Tech SCD 500 apparatus equipped with a turbo pumping system for ultraclean preparations at a pressure of 5×10^{-3} mbar to produce a conductive film with a uniform thickness of about 1.0 nm.

3. Results and discussion

3.1. Characterization of corrosion patinas

The surface features of the patinas were first observed by optical microscopy and representative images are shown in Fig. 1a–c. Severe degradation processes occurred in all the three samples, resulting in the stratification of green corrosion products mixed with encrusted soil residues.

Observed at higher magnifications, some minor differences emerged. The patina developed in the laboratory is quite flat and homogenous, while the one grown *in situ* for 15 years is characterized by a rough and heterogeneous surface, with widespread cracks revealing underlying orange or white layers. Terrigenous inclusions are diffused, as well as black and arborescent micrometric compounds. The archaeological find appears likewise rough and heterogeneous. Green and brown compounds form thick encrustations and embed terrigenous pebbles into the patina.

The microchemical and microstructural features of each surface were investigated by FE-SEM-EDS analysis and the micrographs acquired on the most representative areas of each patina are shown in Figures S1-3. Although developed for different periods of time, the surface of all the three patinas is characterized by significant amounts of Cu, Cl and O suggesting the presence of copper hydroxychlorides. In some areas these developed as euhedral micro-granular crystals with well-formed faces (Figure S4). Terrigenous elements like Si, Ca, Fe, Al, K, Mg were ubiquitously detected. They indicate the inclusion of loam into the patinas and are strictly

Table 1
Mineralogical composition of the three corrosion patinas detected by X-ray diffraction analysis. Copper hydroxychlorides and cuprite are ubiquitous corrosion compounds, along with quartz inclusions from the soil. Schoenfliesite (MgSn(OH)$_6$) was found for the first time inside patinas developed in burial conditions.

	Patina PTh15_lab (15 years of burial in the Tharros' soil in the laboratory)	Patina PTh15_insitu (15 years of soil burial in Tharros)	Archaeological patina (two thousand years of burial in Tharros)
Cuprite Cu$_2$O	*	*	*
Atacamite Cu$_2$Cl(OH)$_3$	*	*	*
Botallackite Cu$_2$Cl(OH)$_3$		*	
Clinoatacamite Cu$_2$Cl(OH)$_3$	*	*	
Malachite Cu$_2$(CO$_3$)(OH)$_2$			*
Schoenfliesite MgSn(OH)$_6$	*	*	
Quartz SiO$_2$	*	*	*
Calcite Ca(CO$_3$)	*	*	*
Microcline K(AlSi$_3$O$_8$)		*	

related to the burial environment.

Some differences between the recent and the ancient patinas however emerged. Tin was detected only on the surface of the patinas buried for 15 years, whereas it was not found on the surface of the archaeological object. The element is present in correspondence of the flat areas, as evidenced by Figure S1, or under the Cu and Cl compounds, as reported in Figure S2. Here, the tin compounds developed as a smooth and brittle layer that was cracked and partially detached, revealing the presence of underlying copper oxide.

Moreover, small amounts of Cu and S, most likely in the form of copper sulfides, were found only on the surface of patina PTh15_insitu (Figure S5). As previously observed, they are characterized by an arborescent growth, made up by the aggregation of nanometric crystals [41]. Phosphorus-containing compounds were instead detected as rounded aggregates only above the surface of the archaeological find (Figure S3). Also some differences in the amount of terrigenous elements have been observed. The patina of the disks buried for 15 years contains smaller percentages of Al, Si and Ca than the archaeological sample. Though the EDS analyses were acquired on spot areas, they can be considered representative of the general composition of the corrosion patinas. The higher content in the terrigenous elements is attributed to the prolonged interaction with the soil suffered by the archaeological sample and for this reason it was identified as a time-dependent feature of natural patinas.

In order to obtain information about the mineralogical composition of each patina, XRD investigations were performed (Figure S6). X-ray diffraction analysis revealed that the corrosion products developed during short-term burial are those that typically grow during long-term interactions between Cu-based alloys and soils [42–48]. As reported in Table 1, they consist of corrosion products of the alloying elements (as copper oxide, copper hydroxychlorides polymorphs, copper hydroxycarbonate and tin hydroxide) and compounds coming from the soil (as silicates and calcium carbonate).

Among the copper hydroxychlorides polymorphs, atacamite was detected in all the three samples, while botallackite was found only in patina PTh15_insitu. As reported in previous studies, this polymorph is the rarest of the naturally occurring ones [49]. It crystallizes first, but rapidly converts into the more stable atacamite or clinoatacamite.

Copper(I) oxide, namely cuprite, was also ubiquitous, as it forms in the very first step of bronze corrosion, while copper carbonate, namely malachite, was found only in the archaeological object. It is reported that the transition from cuprite to malachite is very difficult to replicate in the laboratory [1]. The formation of the copper hydroxycarbonates could be affected by environmental conditions or time-dependent factors. Some works based on Surface Enhanced Raman Spectroscopy also report that copper surfaces exposed to different aqueous media acquire an oxygenated shallow layer whose structure may involve the presence of adsorbed oxygen atoms [50], OH groups [51], or a mixture of them. Similar Raman spectroscopy results were obtained on bronze corrosion patinas, especially at the interface between the metal alloy and the crystalline cuprite layer [52–54]. It was concluded that a native oxygenated passive layer was a primary corrosion patina on the metal surface [53]. Based on the analytical techniques used in the present study, different Cu(I) oxidized forms cannot be discriminated but their formation cannot be rule out.

A tin and magnesium hydroxide, namely schoenfliesite, was detected inside the patinas A and B. This is the first time that schoenfliesite has been found in bronzes buried in soil. Its formation was in fact reported only for bronze objects under coastal sediments or marine environments [55–57]. The mineral is the result of the oxidation of tin and of its reaction with Mg coming from the soil.

Terrigenous residues are always present, mostly consisting of quartz, calcite and silicate minerals, while no Cu and S compounds, nor phosphorus-containing minerals, were detected.

3.2. Mechanisms of corrosion processes

To obtain information about the stratigraphy of the corrosion products and to better understand the mechanisms of patinas' formation, the samples were sectioned and investigated by OM and by FE-SEM-EDS. Metallographic images representative of each
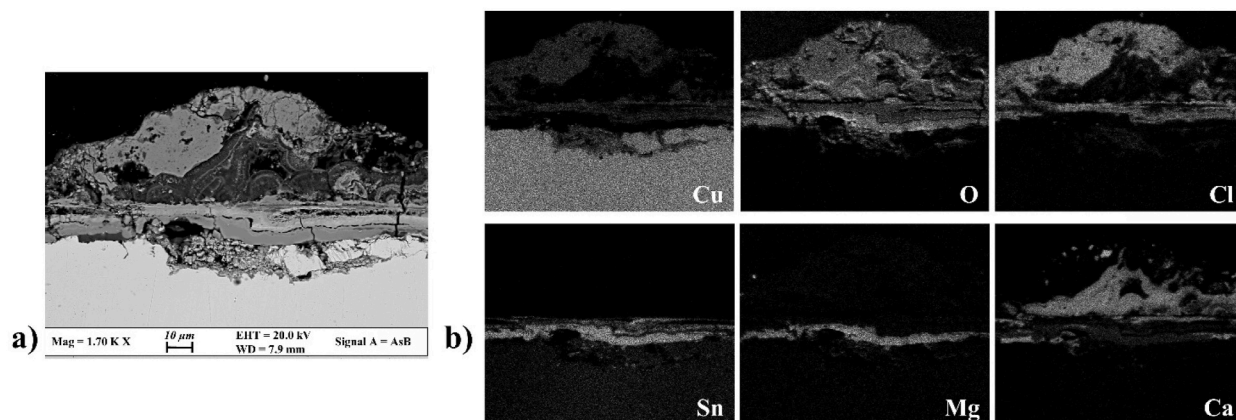

Fig. 2. Cross-section of the patina developed over 15 years of burial inside the Tharros soil in the laboratory. FE-SEM image (a) and relative X-ray maps (b) revealed the stratigraphy of the patina and the chemical composition of each layer. Copper hydroxychlorides and calcium carbonate crystallized over a layer of schoenfliesite.

patina are shown in Fig. 1a–c, while representative FE-SEM images and EDS maps are shown in Fig. 2a,b, 3a,b and 4a,b.

The patinas developed in only 15 years of burial are quite thin with respect the archaeological one, even if that grown *in situ* is slightly thicker (Fig. 1a and b). They are composed by different corrosion layers. Starting from the metal core, the first stratum of patina PTh15_lab is characterized by the presence of Sn, Mg and O and by the absence of Cu (Fig. 2a and b). It consists of schoenfliesite crystals, according to the previous XRD analysis. The compound was also found inside patina PTh15_*insitu*, above an inner layer containing Cu and O and consisting of cuprite crystals (Fig. 3a and b). In this case, schoenfliesite developed following two different morphologies: as a flat microcrystalline stratum delimiting the surface's original edges and as rounded nanometric compounds. Few percentages of Mn were detected in correspondence of the rounded phases as it can enter in the schoenfliesite crystal-structure (Figure S7). This mineral belongs in fact to the double hydroxyperovskites, which include wickmanite, $MnSn(OH)_6$ [55,58]. Extensive solid solution exists between schoenfliesite and wickmanite under low-temperature conditions [59]. The formation of Mn-bearing schoenfliesite containing small amounts of Mn, like those observed in this study, is thus highly likely.

Above the schoenfliesite, a layer containing Cu, Cl and O and corresponding to atacamite and its polymorphs, developed in both the two samples. The copper hydroxychlorides are mixed with terrigenous compounds coming from the soil and containing Si and Ca.

The archaeological patina is very thick and mainly characterized by red cuprite layers (Fig. 1c). Anyway, similarities were found with the previous two samples. Copper is present almost all over the section and its content decreased from the metal core to the external patina (Fig. 4a and b). It combines with oxygen to form cuprite crystals and with chlorine and oxygen in the outermost stratum forming copper hydroxychlorides. Tin is absent in the external corrosion compounds, but it is concentrated in the inner layer at the interface with the metal core and in association with oxygen. Embedded soil deposits, mainly consisting of quartz and silicates, are present among the copper corrosion products. A complete mineralization of the object did not occur since a metal core is still present. However, the surface original edges are not well recognizable as they appear rippled by the occurrence of long-term corrosion reactions.

Some additional features were detected for the real archaeological find. Between the cuprite and atacamite layers, there is a thick stratum where Cu is associated with S. Due to the absence of oxygen in that area, it can be assumed that copper sulfides developed. Phosphorus was also found into the inner corrosion layers along with Ca, Pb and Cl (Figure S8). Since XRD analysis did not detect any phosphorus-containing compound, the presence of hydroxylapatite ($Ca_5(PO_4)_3OH$) and pyromorphite ($Pb_5(PO_4)_3Cl$) can only be inferred by the chemical information provided by FE-SEM-EDS [57]. It is worth mentioning that the presence of generally rare phosphorus corrosion compounds, like pyromorphite, has been observed in the patina formed on the bronze objects found at Tharros [60].

Despite the different thickness observed for the three samples, the interaction with soil led to similar corrosion patterns for both short- and long-term grown patinas. As already evidenced, the copper content in the corrosion layers is lower with respect to that of the original alloy composition. At the same time, the areas at the interface with the metal core are enriched in tin. The mechanism of copper depletion from its alloys is known as copper leaching or decuprification [12,61,62]. Once the element oxidizes, it rapidly turns into copper(I) oxide (cuprite), and with continued oxidizing conditions, it converts into Cu^{2+} cations [63]. These ions then dissolve and migrate toward the soil. Here, they partially diffuse toward the surrounding environment and partially react with the available anions, precipitating on the surface as copper(II) corrosion products. Atacamite and malachite were in fact detected in the outermost patinas' layers of all the three samples. During the crystallization, they embedded terrigenous elements and soil residues, such as quartz pebbles and calcite.

Conversely, when tin oxidized, it converts into Sn^{4+} ions and precipitates as a mixture of stable oxides and hydroxides. It replaces the voids left by the copper dissolution, starting from the surface toward the core. Although it is frequently reported in the literature that these compounds are stable in a wide range of pH and electric potential [8,13,64], they are also very brittle. As evidenced in this study, the tin hydroxide layers easily fracture, leaving the underlying alloy exposed to the aggressive environment. Oxygen can thus
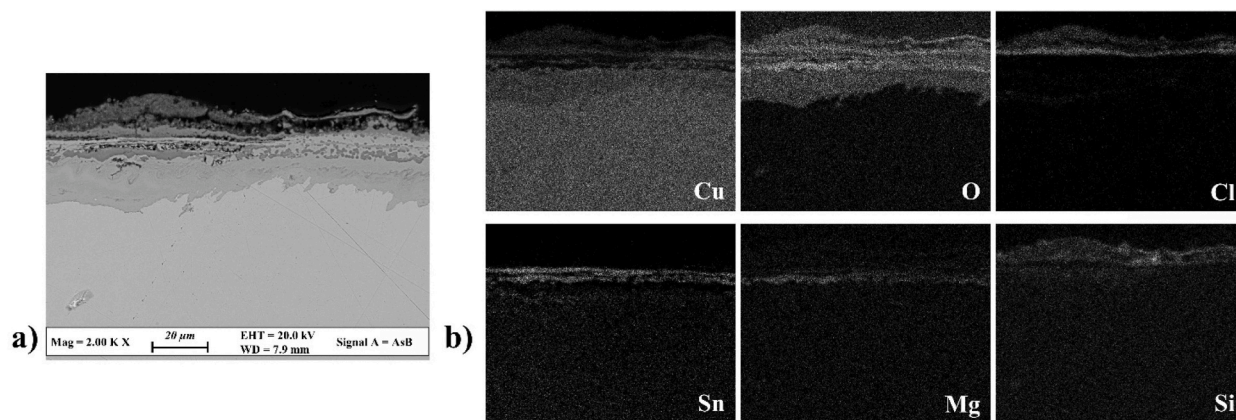

Fig. 3. Cross-section of the patina developed over 15 years of soil burial in the site of Tharros. FE-SEM image (a) and relative X-ray maps (b) revealed the stratigraphy of the patina and the chemical composition of each layer. Copper hydroxychlorides, mixed with silicate species, developed over the schoenfliesite layer.
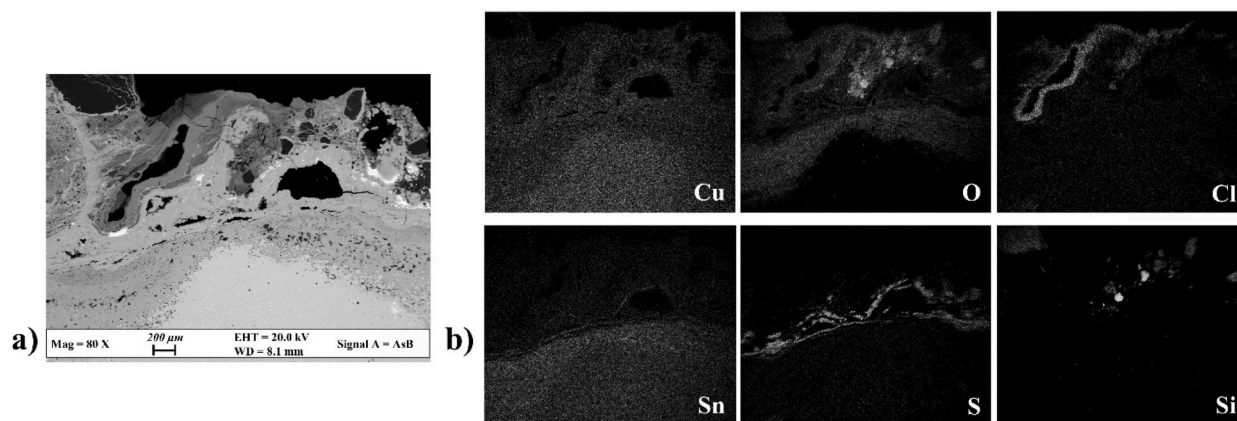
Fig. 4. Cross-section of the patina developed over about two thousand years of burial in the soil of Tharros. FE-SEM image (a) and relative X-ray maps (b) revealed the stratigraphy of the patina and the chemical composition of each layer. Copper hydroxychlorides and silicate species developed above a layer enriched in Cu and S and depleted in O. Tin oxides are present under the external corrosion layers at the interface with the metal core mixed with cuprite crystals.

penetrate toward the core and oxidize the metal copper, which in turn converts into cuprite (Figure S2).

It is possible that a similar mechanism of failure of the tin corrosion compounds occurred for the archaeological find. As pointed out by the X-ray maps of Fig. 4b, tin is present in the core of the patina as oxides (or hydroxides) dispersed in a cuprite matrix [65]. A flat layer of tin compounds, similar to those observed for the young patinas, may have developed starting from the first years of burial. With time, this layer could be cracked and aggressive species coming from the environment could have reached the underlying metal alloy. In this way, the corrosion process re-activated, as well as the copper oxidation and depletion, resulting in the patina's growth toward the core and in the extensive consuming and rippling of the surface. The failure of the patina layer followed by the resumption of the corrosion processes in the archaeological sample is also evidenced by an alteration in the patina stratigraphy (Figure S9). In some areas, the green copper compounds were found in the middle of the red layer, probably as a result of a local cuprite conversion into Cu (II) corrosion products. More specifically, a fracture in the patina could have favored the exposure of the internal Cu(I) oxide to the external aggressive environment, enabling the oxygen and chlorine penetration and thus inducing further corrosion reactions up to the metallic core. The extent of corrosion cannot be estimated by the amount of hydroxychlorides, but the overall composition of degradation products has to be taken into account. Since corrosion usually starts with the formation of cuprite, it is worth noting that the long-term interactions with soil induce the growth of thick layers of copper(I) oxide, such as those detected in the archaeological patina (Fig. 1c).

Lead converted into corrosion products only in the case of the archaeological patina. This fact can be attributed to the smaller amount of Pb in the original alloy composition of the artificial samples and to its rapid oxidation and diffusion toward the soil [66].

Environmental conditions highly affected the typology of corrosion products developed on the three bronze objects, determining the composition and stratigraphy of each patina [67]. The presence of copper sulfides on the patinas developed *in situ* at Tharros suggested the establishment of anaerobic conditions during the burial and the occurrence of biochemical corrosion. Copper sulfides are indeed related to the presence of sulfate reducing bacteria (SRB) inside the loam. During their metabolic activities, these microorganisms reduce the sulfate ions present inside the soil into hydrogen sulfide (H_2S), establishing a micro-environment with local reducing conditions [60]. Copper reacted with the aggressive acid and precipitated as copper sulfide on the surface of the bronze objects [60,68]. However, conditions may change through time and return to oxidizing. This happened in the environment where the archaeological patina was buried for about two thousand years. The alternation of sulfur- and oxygen-enriched layers (Fig. 4a and b) reflects a change in the surrounding local conditions, which at some point returned aerobic, promoting the formation of copper oxide, hydroxychlorides and carbonates above the sulfide layers.

The occurrence of phosphorus-containing compounds in the archaeological patina can also be related to the environment where it developed. Archaeologists found the object inside the remains of a sewage system (*cloaca*) in the site of Tharros. As already reported [57], this type of environment can contain waste residues, such as decomposing bones. Moreover, a lot of partially roasted bones were found in the site of Tharros [39]. Phosphorus-containing compounds are thus the result of the interaction between the elements coming from the alloy and the phosphate anions, which dissolved into the percolating water from the biological remains in the soil. It has also to be pointed out that the burial treatment, which was significantly longer for the archaeological sample, could have played a major role in the formation of peculiar corrosion products, such as the thick layer of sulfides and the phosphorus-containing compounds. Moreover, a possible effect of the different burial depth cannot be ruled out.

3.3. Preliminary cleaning test

One of the patinas developed in 15 years of soil burial in the site of Tharros was selected for a preliminary cleaning treatment. A PVA-based gel, loaded with a 5% (w/w) aqueous solution of $Na_2EDTA \cdot 2H_2O$, was applied on the patina's surface for different times.

The aim was to gradually remove the degrading corrosion products (such as copper hydroxychlorides) and the terrigenous encrustations. The incorporation of a chelating agent solution into the gel is necessary to gradually solubilize the corrosion patina and transport it into the gel matrix. $Na_2EDTA \cdot 2H_2O$ was chosen as it is typically employed by conservators to remove corrosion layers [1].

The use of gels in conservation practices is advantageous because these systems overcome some crucial limitations related to the common restoration operations with classical solvent thickeners that are hard to remove and prone to leave residues [69]. Moreover, the gels can gradually remove corrosion products in a controlled way as opposed to non-confined cleaning fluids [23,70]. In particular, the PVA TC-PNs were selected for this study given their ability to adapt homogeneously to rough surfaces providing time-effective and controlled removal of unwanted layers. The presence of the lower molecular weight PVA in the gel network yields gels that are mechanically compliant and exhibit an interconnected, disordered sponge-like porous networks [34], while single-PVA gels produced with similar freeze-thaw synthetic processes have hexagonally packed channel-like pores. These differences favor the removal of soil and solubilized/detached patinas by the TC-PNs and their uptake into these gels.

In Fig. 5a and b, optical images of the surface before and after the cleaning are shown, while in Fig. 6a and b FE-SEM images and EDS analysis, acquired on representative areas of the patina, are displayed. After only 10 min of application, the gel removed all the rough encrustations, leaving a flat surface and preserving the underlying stable cuprite layer, with results that are highly desirable for metal conservators. It also preserved the green appearance of the patina, often appreciated for its ancient allure. FE-SEM-EDS analysis acquired after 10 min of treatment revealed a significant decrease of the Cl content, as well as of the terrigenous elements (Ca, Si, Al, P, Fe).

To achieve deeper cleaning, the time of application of the gels can be properly tuned, gradually raising the duration of the treatment, thus removing the corrosion products to a greater extent. FE-SEM-EDS analysis confirmed the deeper removal of the dangerous copper hydroxychlorides and revealed an enrichment in tin corrosion compounds on the cleaned surface.

In order to better understand the behavior of the gel system toward different types of bronze substrates, an additional test was performed. The chemical composition of the gel after 100 min of application on another *PTh15_insitu* patina was analyzed by EDS and compared to that of the gel applied on a pure cuprite layer and on the bare bronze surface. The EDS analyses were performed on representative areas of each gel surface that was in contact with the substrates and the results are reported in Table 2. The composition of the as prepared gel was also evaluated for the sake of comparison. The amount of copper found for gel system is significant when this is applied on the patina composed of Cu(II) compounds, being about 5.8%. In the case of the gel applied on the pure Cu(I) oxide and on the bronze surface, only minor percentages of the element were detected in few areas. The gel can also capture the metal cations related to the soil (Si, Al, Fe, Mg, K, Ca) and the tin compounds developed on the buried sample, thus confirming the removal of the terrigenous and corrosion products. Optical images of Fig. 7a–d shows the cuprite and the *PTh15_insitu* patina appearance before and after 100 min application of the gel. No visual changes related to copper oxide dissolution were evidenced in the pure cuprite sample, whereas the green copper(II) compounds were clearly removed by the gel. These findings evidenced that PVA-based TC-PNs loaded with $Na_2EDTA \cdot 2H_2O$ have a major affinity toward Cu(II) compounds rather than Cu(I) oxide or Cu(0) surfaces. The cleaning action provided by this system can thus be considered highly selective. Even in cases where the cuprite layer is highly inhomogeneous, the majority of the layer is unaffected by the gel even in prolonged applications (Figure S10).

Finally, it is worth noting that the cleaned sample has been stored and monitored at room atmospheric conditions for about one year after the treatment. The surface does not present any signs of aesthetic alteration nor adverse effects related to the cleaning.

4. Conclusions

Bronze substrates were intentionally buried in the soil of the archaeological site of Tharros (Western Sardinia coast, Italy), both in the laboratory and *in situ*, in order to create patinas that are really representative of archaeological objects. After 15 years of burial, they were unearthed, and the corrosion patinas were analyzed and compared with that of a real archaeological bronze recovered in the
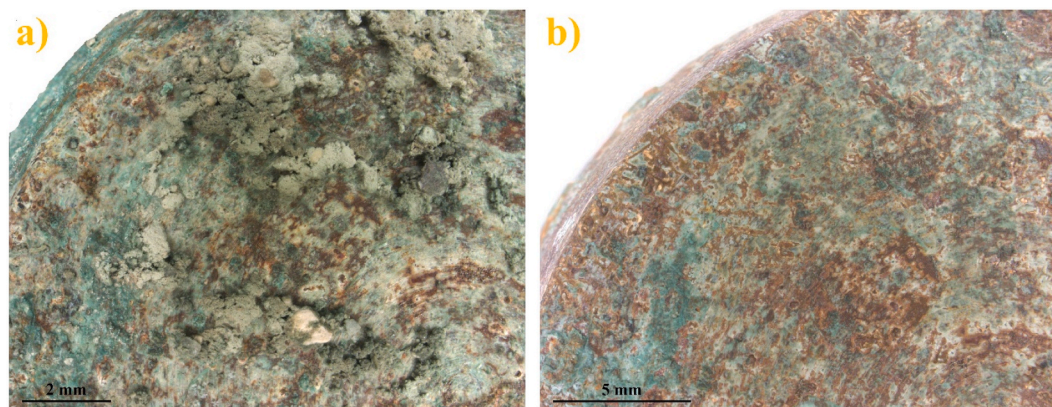

Fig. 5. Surface's features before and after the cleaning test. Surface before (a) and after (b) 10 min of application of the PVA-based gel loaded with 5% $Na_2EDTA \cdot 2H_2O$. The cleaning was effective in removing all the rough and disfiguring encrustations.

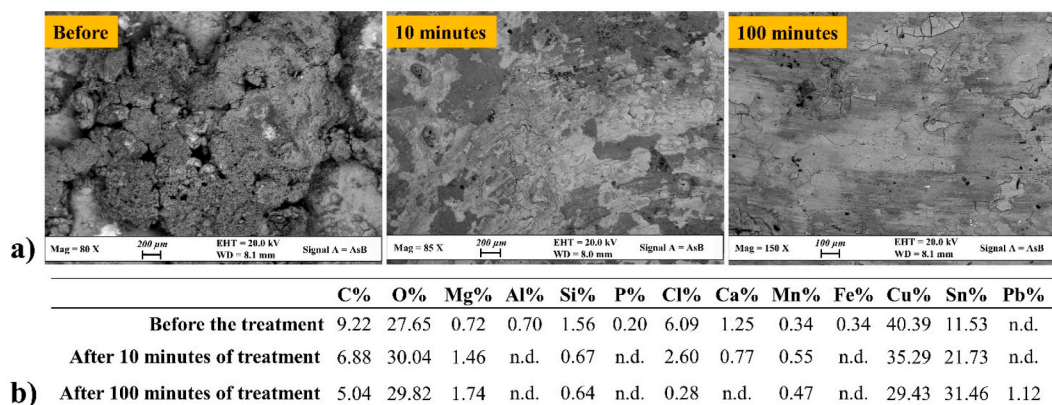|	C%	O%	Mg%	Al%	Si%	P%	Cl%	Ca%	Mn%	Fe%	Cu%	Sn%	Pb%
Before the treatment	9.22	27.65	0.72	0.70	1.56	0.20	6.09	1.25	0.34	0.34	40.39	11.53	n.d.
After 10 minutes of treatment	6.88	30.04	1.46	n.d.	0.67	n.d.	2.60	0.77	0.55	n.d.	35.29	21.73	n.d.
After 100 minutes of treatment	5.04	29.82	1.74	n.d.	0.64	n.d.	0.28	n.d.	0.47	n.d.	29.43	31.46	1.12

Fig. 6. Surface's morphology and chemical composition of the patina before and after the cleaning treatment. FE-SEM images (a), acquired on representative areas of the patina before and after different times of gel application, reveal a gradual flattening of the surface, while EDS analysis (b) shows a progressive decrease of the Cl and terrigenous elements content (results in weight%, n.d. = not detected). After 100 min of cleaning treatment, the surface was enriched in Sn corrosion compounds.

Table 2
Chemical composition of the gels after application on different bronze substrates. Results of EDS analyses showing the elemental composition of the gel systems as prepared and after 100 min of application on the metal bronze surface, on a pure cuprite layer and on the green patina developed in 15 years at Tharros (results in weight%, n.d. = not detected). The Cu content in the gel was significantly higher after the cleaning of the green patina, thus proving the selectivity of the gel system toward Cu(II) compounds. The gel was also effective in solubilizing Sn ions and terrigenous elements.

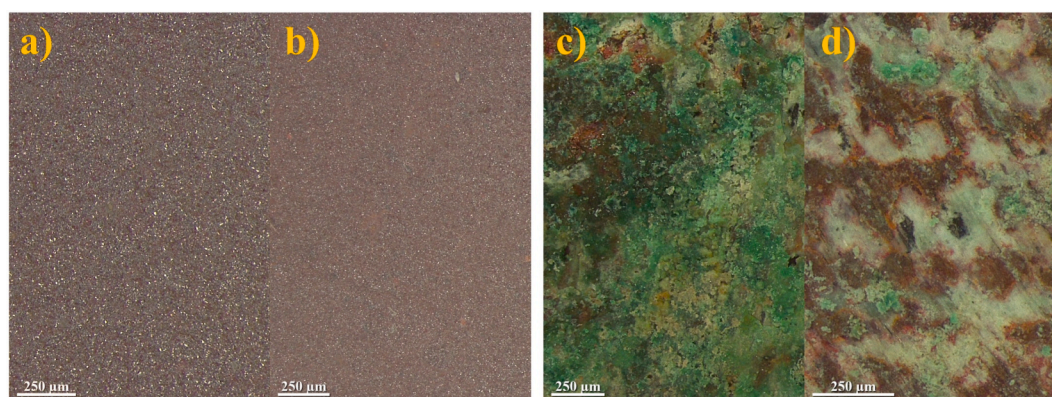|	C	O	Na	Si	Cu	Sn	Al	Fe	Mg	K	Ca	Cl	P
Gel	56.1	38.1	5.3	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Gel applied on the bronze alloy	57.5	37.1	4.7	0.6	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Gel applied on the cuprite	54.6	38.4	6.0	0.3	0.3	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Gel applied on the green corrosion patina (PTh15_insitu)	28.7	37.9	8.1	7.9	5.8	3.9	3.2	2.3	0.6	0.9	0.3	0.3	0.1

Fig. 7. Surface features of different bronze substrates before and after the cleaning treatment. Optical images show the appearance of the pure cuprite layer before (a) and after (b) 100 min of application of the PVA-based gel and the appearance of the PTh15_insitu patina before (c) and after (d) the same cleaning treatment.

same site. To the best of our knowledge, this is the first study on bronze patinas formed after more than one year of intentional burial, considering both in laboratory and *in situ* treatment in the same soil.

A multianalytical approach, based on OM, FE-SEM-EDS and XRD analyses, was used for this investigation. All the patinas appeared highly corroded and covered by green compounds and soil residues, although those buried *in situ* are rougher and more heterogeneous with respect to that treated in laboratory. Atacamite was ubiquitously detected, confirming the aggressiveness of the chloride ions largely present in the soil of Tharros. Cuprite, quartz and calcite were also detected in all the samples, whereas malachite only in the archaeological one. Schoenfliesite ($MgSn(OH)_6$) was found for the first time inside patinas developed during burial in soil.

The analysis of the three cross sections revealed some additional features and allowed us to rebuild the mechanism of patinas' formation under burial conditions. The patinas developed in only 15 years have features characteristic of those grown over long-term

burial in real archaeological soils. The external surfaces are composed of copper(II) compounds, like copper hydroxychlorides, and embed pebbles and soil residues (quartz, silicates and calcite). Under this layer, copper(I) corrosion products (cuprite) and tin oxides developed. Decuprification processes occurred for both short- and long-term grown patinas, as well as the replacement of copper vacancies by tin compounds.

The presence of copper sulfides in the patinas grown *in situ*, and of phosphates in that of the real archaeological find pointed out that the local environments surrounding the buried objects strongly affected the typology of corrosion products. Copper sulfides are related to the presence of sulfate reducing bacteria into the soil, which create an anaerobic micro-environment during their metabolic activities. Phosphates suggest the presence of decomposing bones into the ground and are characteristic of the *cloaca* context where the archaeological object was retrieved.

The thickness of the patina and the amount of cuprite and terrigenous elements were identified in this study as time-dependent features. The object that suffered two thousand years of burial underwent corrosion processes to a larger extent than the bronzes left inside the soil for only 15 years, resulting in the development of thicker corrosion layers with a higher content of Al, Si and Ca, and of a major amount of red copper(I) oxide.

The intentional burial of bronze substrates in soil, both in laboratory and *in situ*, successfully induced the development of corrosion patinas on the bronze surfaces. These patinas present most of the structural, chemical and mineralogical features typical of corrosion layers formed during thousands of years of soil burial. Some peculiarities of archaeological find are the presence of uncommon alteration compounds, including phosphates and large amounts of sulfides, the greater patina thickness and the extensive rippling of the inner corrosion layers, that can be mainly attributed to the long-term interaction with soil. Therefore, the internationally reproduced patinas show structural, chemical and mineralogical features that are similar, even if not totally identical, to the archaeological find, thus can be considered representative. Based on these considerations, the young patinas grown in Tharros for 15 years were selected as a disposable substrate to perform preliminary cleaning treatments with a "twin-chain" PVA-based gel. The gel, loaded with $Na_2EDTA \cdot 2H_2O$ was applied on the surface of the patina for different times. After 10 min of treatment, it was effective in gradually removing the disfiguring rough encrustations and the chloride species, leaving the surface flat and preserving the green appearance. The stable compounds, such as the cuprite layer and the tin corrosion products, were also preserved. By properly varying the time of application, the cleaning properties of the gel can be easily tuned. Cleaning treatments up to 100 min were performed on the green patina grown in Tharros for 15 years, on pure red cuprite and on bare bronze alloy. The results clearly show that the PVA-based TC-PNs gels loaded with $Na_2EDTA \cdot 2H_2O$ preferentially dissolve copper from Cu(II) compounds rather than Cu(I) oxide or Cu(0) surfaces. This system thus provides a highly selective, as well as gradual cleaning action.

Overall, the intentional burial was successfully used to promote the formation of bronze patinas with surface features similar to those found in archaeological objects. Fifteen years of burial allowed to obtain representative disposable substrates that were used to perform preliminary cleaning treatments. Our findings revealed that PVA-based gels can be used to gradually remove unwanted corrosion products, preserving the stable species, and represent thus highly promising tools for application in cultural heritage conservation.

Author contribution statement

Francesca Boccaccini: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Elena Messina; Ferdinando Bosi: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Cristina Riccucci; Marianna Pascucci; Teresa Guaragnone: Performed the experiments; Analyzed and interpreted the data.

David Chelazzi; Piero Baglioni; Gabriel Maria Ingo; Gabriella Di Carlo: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Data availability statement

Data will be made available on request.

Fundings

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e19626.

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