Rebuilding of the Burial Environment from the Chemical Biography of Archeological Copper-Based Artifacts

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ABSTRACT: The long-term interaction between Cu-based alloys and environmental species gives rise to the formation of different and sometimes unusual compounds (i.e., the patina) with distinctive chemical and structural features as a function of the peculiar characteristics of the context. In this paper, we describe some representative case studies concerning degraded bronze Roman valuable or common use objects, and we show that an attentive study at a microscale level, as for forensic analysis, allows one to understand the chemical processes that underlie the formation of the surface alteration products. The achieved information describe fragments of chemical life and disclose the complex chemical changes suffered by the artifacts, allowing one to write their chemical biography. This challenging approach expands the panorama of available information and demonstrates that it is possible to reconstruct the different modes through which the bronze surfaces and interfaces have interacted with environmental species, organic matter, and microorganisms, opening up a new possibility to describe complex environmental chemical stories, in certain cases interrelated.

INTRODUCTION

Cu-based alloys have played a crucial role in the development of human societies by contributing to the production of useful tools and fascinating works of art and by fueling the progress of ancient economy via their monetary use.1−3 With the passing of time, during the long-term exposure to the environment (burial soil, atmosphere, lake water, or seawater), the surface chemical composition and often also the bulk features of the Cu-based alloys have been substantially modified.4−9 Different types of reactions, in some case favored by microorganisms, have given rise to the formation of distinctive corrosion products and structures (i.e., the patina), sometimes unusual.10−12

The chemical and structural identification of the alteration products has been the subject of many studies for at least 180 years.1−3,13,14 The findings have revealed the formation of a wide panorama of copper, tin, lead, arsenic, antimony, and zinc compounds such as oxides, hydroxides, nitrates, chlorides, oxychlorides, carbonates, sulfates, sulfides, phosphates, and other complex compounds including organic salts to whose formation might have also contributed the microbially influenced corrosion phenomena.1−3,9−11 These pieces of information reveal that the formation of the patina and its chemical and structural features are largely influenced by the chemical composition and metallurgical features of the alloy as well as by the context characteristics.1−3 Indeed, the presence of the above-cited mineral classes clearly demonstrates the strong interaction among soil, atmosphere, or water components and Cu-based alloy elements, giving rise to the formation of mineral species that can form different structures via their accumulation or can be dissolved in the environment or chemically altered to form new minerals by reacting with environmental species.1−3,10,11

To describe thoroughly the structure and the chemical composition of the alteration products, some mechanisms have been proposed.1−3 These latter have been defined on the basis of detailed analytical studies suggesting the role of the ion migration phenomenon3 even if in some cases the corrosion behavior of archeological bronzes during soil or water burial has not always been properly understood as for some Cu-based artifacts retrieved from seawater or freshwater or for the arsenical bronzes.2 The current understanding is therefore sometimes limited, and these mechanisms could not be directly applicable to the formation of specific corrosion products.1,2

For these reasons, an attentive study of the chemical and structural features of the alteration products can throw new light on the environmental conditions suffered by the artifacts and disclose fragments of their chemical life, revealing the processes based on the interactions with environmental inorganic or organic species.1−3,10,11 Similar to the forensic investigation approach, the minute and systematic study of the patina’s chemical and structural features at a microscale level helps us gain further insight into the environmental contexts and to decipher in whole or in part what happened in the
course of time, enabling us to write a sort of a “chemical biography” of the artifact.

In this paper, we describe some representative patinas naturally grown on archeological objects found in Mediterranean sites characterized by different environmental conditions. The objects are both commonly used objects such as coins or small tools and important works of art such as the over-life-size Dancing Satyr statue and a fragment of an elephant statue, both retrieved from the Mediterranean Sea along the southwestern coast of Sicily (Italy).

As for the forensic analysis or the diagenetic process investigation, we demonstrate that an attentive study of the corrosion products allows us to achieve information otherwise impossible to obtain and to reconstruct the different modes through which the bronzes have interacted with environmental species, organic matter, and microorganisms, evidencing that the case studies tell us basically chemical stories, sometimes interrelated.

■ MATERIALS AND METHODS

Archeological Bronzes. The small objects were investigated in as-received conditions; in the case of large artifacts, small fragments were carefully sampled also to achieve cross-sectioned materials to investigate the structure of the corrosion product’s layer, bulk chemical composition, and metallurgical features. To prepare the cross sections, the small representative fragments were embedded in epoxy resin for 24 h and sectioned by using a diamond saw to preserve the micro-chemical structure and the surface features. Then, the sections were polished with silicon carbide papers until 1200 grit; the final polishing was performed with diamond pastes up to 0.1 μm.

Scanning Electron Microscopy–Energy-Dispersive X-ray Spectrometry (SEM–EDS) Analysis. The patinas were investigated by means of a scanning electron microscope (SEM) Cambridge Stereoscan 360 (Cambridge, U.K.) and a high-brilliance and high-resolution LEO Gemini 1530 (Zeiss, Germany) field emission scanning electron (FE-SEM) microscope. SEM and FE-SEM instruments were equipped with an INCA 250 and an INCA 450 (Oxford Instruments Analytical, U.K.) energy-dispersive X-ray spectrometer (EDS), respectively, and four-sector back-scattered electron (BSE) detectors. SEM micrograph images were recorded in both secondary electron (SE) and BSE modes at an acceleration voltage of 20 kV, whereas the FE-SEM images were recorded at different acceleration voltages from 1 to 20 kV to better disclose the micromorphological features of the bronze artifacts. Before the analysis, the surfaces of the objects and the cross-sectioned samples were coated with a thin layer of carbon or chromium to avoid charging effects.

X-ray Diffraction (XRD) Investigation. X-ray diffraction patterns were recorded directly on the artifacts or a small amount of powdered patina by a Siemens 5000 X-ray powder diffractometer with Ni-filtered Cu Kα radiation (λ = 0.154056 nm) by using the following experimental parameters: angular values between 10 and 90° in the additive mode, a step size of 0.05°, and a sampling time of 20 s. X-ray diffraction patterns were analyzed by using electronic databases and compared with the literature data.

Optical Microscopy (OM) Study. OM morphological investigations were performed by using Leica MZFLIII and Leica LAS multifocus stereo microscopes equipped with a digital camera (Leica DFC 320). The metallurgical features have been studied by means of a Leica MEF IV optical microscope equipped with a 420 Leica digital camera.

■ RESULTS AND DISCUSSION

Corrosion products are naturally formed on archeological and historical Cu-based alloys during the long-term chemical interaction between alloy elements and environmental species present in burial soil, seawater, lake marsh sediments, or the atmosphere. As a consequence of the corrosion phenomena, the surface and also the bulk chemical and structural features are changed (Figure 1), in certain cases substantially, producing a wide panorama of mineral species including carbonates, chlorides, sulfates, sulfides, oxides, and other, sometimes unusual, corrosion products. These latter can be differently structured (Figure S1) assuming various configurations, that is, the patina, sometimes well ordered and stratified or forming complex aggregations as more frequently observed.

The chemical nature and the structure of the corrosion products strictly depend on the alloys’ chemical composition and metallurgical features and, particularly, on the microenvironmental conditions experienced by the alloys. Similar to the approach adopted for the forensic analysis or the diagenetic process investigation, the microscope attentive study of the degradation products could provide the possibility of identifying which kind of environmentally driven chemical experiences the objects have lived through, in many cases for more than two thousand years, giving us the possibility of writing in whole or in part their chemical “biography”.

This approach could open new challenging possibilities to reconstruct the past environment and to figure out what happened from a chemical and a structural point of view to these witnesses of the ancient technology and creativity.

The case studies here presented have been selected from a large number of bronze archeological artifacts retrieved from the Mediterranean basin area that have been investigated to identify degradation agents and mechanisms and to select tailored and long-lasting strategies for their safe conservation and sustainable fruition.

The archeological bronze objects have been found in different sites and are mainly commonly used objects such as coins and small artifacts but may also include relevant artworks such as the fascinating Dancing Satyr statue and a fragment of an elephant statue retrieved from the Channel of Sicily (Italy).

The first case study describes the corrosion products naturally grown on a Roman coin (likely issued in the 2nd–3rd century AD) found during the periodic cleaning and dredging operations on the beds and banks of the Tiber river in the area of the Cloaca Maxima in Rome (Italy), which is one of the earliest sewage systems to convey surface runoff, to drain local marshes, and to remove the waste of one of the most populous cities of the ancient world.

In this area, the soil of the riverbeds and banks contains stratified heterogeneous fluvial sediments including the materials picked up by the Tiber river and its tributaries along their ways. The sediments are composed of a complex
mixture of rotting organic matter, lithoid tuff, anthropic inorganic materials, mud, silt, lacustrine, and fluvial-palustrine sandy clay. These latter contain micalike minerals, chlorite, kaolinite, smectite, limestone gravel, and clayey and marine sands with quartz, feldspars, and calcite whose contents vary as a function of area and flooding events as evidenced by Bozzano et al.\textsuperscript{21–23} These works report some sediment compositions even though evidence of the lithological setting of the alluvial deposits of the Tiber river is still scarcely defined due to the lack of suitable outcrops and the large heterogeneity of the sediments.

The coin under study is almost completely coated with a bright sky-blue patina containing turquoise [\(\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8\cdot4(\text{H}_2\text{O})\)] (Figures 2 and S2), which is appreciated as an enchanting natural gemstone used since thousands of years to produce jewels and ornaments owing to its unique hue. As revealed by EDS and XRD results (Figures 2 and S2), cassiterite (SnO\(_2\)) and a small amount of Pb(IV)-based compounds are also present on the surface of the coin.

The presence of SnO\(_2\) is frequently observed on archeological bronzes, and it has been explained taking into account the process of Cu selective dissolution causing a Sn surface enrichment with its incorporation into the patina.\textsuperscript{1,3,18,24,25} This process often creates an outermost stable layer often pseudomorphically retaining the original morphology of the artifact. The formation of a SnO\(_2\) layer, identified also via X-ray photoelectron spectroscopy measurements,\textsuperscript{26,27} is related to both the environmental mobilities of Cu\(^{1+}\) and Cu\(^{2+}\) ions and to the stability of SnO\(_2\) over a wide range of pH values.

The presence of Pb(IV)-based compounds is related to the common use of a low-cost leaded bronze to produce coins.\textsuperscript{21} In this kind of alloy, the very scarce solubility of lead in the copper at room temperature and vice versa leads to the formation of small Pb aggregates,\textsuperscript{1,10,27,28} randomly scattered in the copper matrix, that are preferentially mineralized (galvanic coupling) and that participate in the formation of the patina as a function of the available environmental anions.\textsuperscript{1,8–10,18}

The presence of a complex copper phosphate is of great interest because, to the best of our knowledge, an archeological patina containing turquoise has been not yet been described in the literature.\textsuperscript{1,2} More generally, as pointed out by Scott,\textsuperscript{1,2} copper phosphates are rarely found as corrosion products except in characteristic environments, primarily in association with the presence of Pb.
with buried decomposing bones releasing phosphate anions\textsuperscript{10} and in arid climates.

Although the locus of finding of the coin, that is, the Cloaca Maxima area, is not arid, surely a consistent presence of phosphates in this area is conceivable due to the large amount of waste materials found here, including P-containing bones.

How was the formation of a hydrated copper-aluminum phosphate on the coin possible? The answer is, likely in a manner similar to that naturally occurring in the geological process. The turquoise gemstone is a secondary mineral generally formed in alluvial deposits by the percolation of acidic aqueous solutions during the weathering and oxidation of Cu-sulfide-bearing rocks with the incorporation of phosphorus from phosphate-containing waters or leached fluids that have interacted with phosphates as apatite, \(\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})\), with the contemporaneous presence of Al ions deriving from feldspatic rocks or clayey sediments.\textsuperscript{29,30}

The hypothesis that the weathering and the oxidation of Cu-sulfides were one of the chemical steps for the formation of a turquoise-containing patina is supported by the finding in the same area of some Roman coins almost completely coated by a smooth and adherent gold-like brilliant metal sulfide layer (Figures 3 and S3). The microchemical results reveal that their patina is mainly constituted by chalcopyrite crystals (CuFeS\textsubscript{2}) as revealed by XRD results and whose EDS analysis matches very well the theoretical stoichiometric elemental values for CuFeS\textsubscript{2}.

The formation of a copper or copper-iron sulfide on a buried bronze object reveals the metabolic activity of sulfidogenic and nonpathogenic microorganisms\textsuperscript{10,11,31,32} that is, the sulfate-reducing bacteria (SRBs). These latter transform in corroding H\textsubscript{2}S the sulfate species present in an anaerobic humus-rich soil with decomposing organic matter thus giving rise to a degradation process defined as microbially influenced corrosion (MIC).\textsuperscript{31,32} This latter process produces a biofilm capable of modifying drastically the microenvironment, forming copper sulfides or chalcopyrite (CuFeS\textsubscript{2}). It is worth noting that the presence of chalcopyrite has been rarely detected on archeological bronzes almost always retrieved from lake or river sediments.\textsuperscript{8,32} Less rarely, copper sulfides such as covellite (CuS), digenite, (Cu\textsubscript{5}S\textsubscript{9}), chalcocite (Cu\textsubscript{2}S), or djurleite (Cu\textsubscript{1.96}S) have been found on bronze objects buried in seawater or in lake sediments probably due to different local microenvironmental conditions.\textsuperscript{8,32}

The inclusion of Fe\textsuperscript{3+} ions in the sulfide corrosion product is not related to the chemical composition of the coin alloy, which does not consistently contain Fe, but is related to Fe-containing compounds locally available in the surrounding microenvironment as Fe-corroding masses.\textsuperscript{10,11} In a soil rich in organic matter and in an almost oxygen-free environment, copper ions from the coin, hydrogen sulfide produced by SRBs, and Fe\textsuperscript{3+} ions, likely from contiguous corroding iron objects, can coprecipitate on the bronze object as a uniform layer of chalcopyrite as in this case study.

Although the mechanism by which the CuFeS\textsubscript{2} was formed on the Roman copper-based coins is not exactly known,\textsuperscript{8,31,32} the presence of a brilliant and well-crystallized chalcopyrite layer, whose thickness ranges from 80 to 110 \(\mu\)m, suggests that the local microenvironmental conditions remained constantly favorable for the chalcopyrite formation up to the present days.
Some of these CuFeS₂-patinated coins remained under these pristine anaerobic conditions until their discovery, but some others could have been removed from the primary burial context likely by a wastewater stream or a flood, thus changing their local environmental conditions that become oxidizing, giving rise to a topotactic transformation.² As a consequence of this variation, the resulting oxidized product reacting with environmental phosphate anions and Al³⁺ from the burial soil has formed the turquoise mineral.

The presence of a low amount of sulfur and iron in the turquoise-containing patina, revealed by EDS spectrum A (Figure S2), can be interpreted as a survival presence or a relic of the primary sulfide, thus confirming the above-described hypothesis of turquoise formation. It is worth noting that a similar reaction has been proposed as one possible cause for the formation of brochantite on archeological objects during burial caused by the oxidation of the copper sulfides previously grown on the artifact,¹⁰ under an anaerobic, waterlogged burial environment.

Another finding that supports the proposed mechanisms is the large presence of reactive phosphate anions in the soil of the Cloaca Maxima area as documented by the discovery in the same site of some leaded-bronze objects coated by a pale green-bluish patina whose main component is pyromorphite [(PbCl)Pb₄(PO₄)₃] (Figure 4). This latter corrosion product is formed from the long-term interaction between the lead of the bronze objects and the phosphate-containing soil produced by the decay of organic matter, likely from the dissolution of bones during burial.

Pyromorphite has been in fact observed on leaded-bronze objects found at Tharros (Sardinia, Italy) in an area where a large number of fragments of decomposing sheep bones was present.¹⁰ It is worth pointing out that the patina of these bronzes contains only a small amount of copper likely due to the more relevant preferential corrosion of the less noble lead dispersed in the copper matrix. Copper phosphates like libethenite [Cu₃(PO₄)₂(OH)] or corretite [Cu₃(PO₄)(OH)₃] could be also formed on lead-free bronze artifacts always associated with decomposing buried bones and other organic or inorganic P-containing materials.²

The three above-described case studies describe specific bronze corrosion products, that is, turquoise [Cu₄Al₆(PO₄)₄(OH)₈·4(H₂O)], chalcopyrite (CuFeS₂), and pyromorphite [(PbCl)Pb₄(PO₄)₃], and disclose some possible chemical interrelated vicissitudes suffered by the archeological bronzes during their long-term burial.

These examples evidence that different microenvironments can be identified in the same area by attentive investigations that can reveal the complex interaction between the artifact and the surrounding microcontext, the consequence of which is the formation of different distinctive mineral species.

More specifically, the formation of turquoise, chalcopyrite, and pyromorphite can be related to the presence of a large amount of available phosphorus in the archeological context from a sewage system and of sulfide anions produced by SRB bacteria in an almost oxygen-free environment, thus confirming in some way what was written in 1605 AD by Yuan Hongdao, a Chinese poet of the Ming Dynasty (1568–1610 AD), “bronzes that have been in the soil a long time are deeply impregnated with the essence of the earth”.²³⁴

Another example of the interaction between the burial environment and a bronze artwork is provided by the microchemical results achieved from the study of the patina grown on the Dancing Satyr, an over-life-size statue of a nude satyr in a whirling pace of dance in honor of the god Dionysus. This statue was retrieved by fishermen about 20 years back from the seawater of the Channel of Sicily (Italy) at a presumed depth of about 500 m, where it was arduous to identify the environmental conditions.³³

The Dancing Satyr in as-received conditions showed large areas characterized by a dark-brown patina whose cross-sectioned chemical structure is shown by an SEM image and EDS elemental chemical maps (Figure 5). These latter highlight the presence, among other elements, also of a thin layer of vanadium, tin, and magnesium under an external thick layer containing iron. The presence of vanadium could appear unusual and has surely an environmental provenance being absent even in minute traces in the bronze alloy. Furthermore, V cannot be precipitated from metal-corroding masses surrounding the bronze statue because this element is absent in the alloys used in ancient times;³⁶–³⁸ then, the possible provenance could be only geochemical or biological.¹³,¹³

The first hypothesis can be ruled out because vanadium has been found in the patina of some bronze artifacts retrieved from other underwater Italian areas of Sardinia and Sicily (Figure 6) as well as along the Croatian coast, being observed also on the Appoxiomenos statue.³⁹,⁴⁰
The second hypothesis is more convincing because V has been found in numerous marine organisms as chromagen proteins and active centers of enzymes and has an important role in different biological systems as in the blood cells of tunicates like the ascidians or immobile marine invertebrates permanently attached to rocks or other substrates. These latter are colonizing microorganisms that feed by filtering seawater and accumulate vanadium in the blood to a very high level with respect to the surrounding seawater (1–30 mg/L) even though the reason of this unusual ability remains a biological mystery.

The presence of vanadium in the patina can be explained by the long-term colonization by ascidians on the surface of the bronze statue and its accumulation as a consequence of their life cycles. At the moment of their death, the decay process of the organic matter releases V that can be partially incorporated by the bronze corrosion products likely as a mixed oxide with lead. The significant colonization by microorganisms onto the surface of the Dacing Satyr is supported by the presence of many fossilized relics embedded into the patina (Figure S4).

The presence of unexpected elements in the patina reveals the capture not only of anions from the environment but also of metal ions as a result of the chemical interaction with the alloying elements as demonstrated by the presence of the schoenfliesite [MgSn(OH)₆] in the patina of the Dancing Satyr or other bronze artifacts retrieved from the Mediterranean Sea as shown by XRD results (Figure S5). Schoenfliesite is produced by the interaction between the Sn cations from the corroding bronze and Mg²⁺ from the marine environment that gives rise to the formation of a mixed hydroxide.

Other interesting information about the chemical life of an object can be provided by the attentive analysis of the outermost layers. For example, the presence of the ferruginous thick layer on the dark-brown patina of the Dancing Satyr (Figure 7) can be related to a drastic variation of the microenvironmental chemical conditions. This change caused the deposition of iron species, the curbed formation of schoenfliesite, and a significant reduction of feeding for the ascidians, thus hindering their growth and multiplication. One possible hypothesis could be the restriction of water circulation around the statue and a high local concentration of iron ions provoked by neighboring corroding masses that cause the deposition of an iron oxide-hydroxide layer. Likely, the Dancing Satyr statue was initially placed on the wood deck of the ship; then, some centuries later as a consequence of the wood decomposition and structure collapse, the statue sank into the ship’s hold where it was exposed to different microenvironmental conditions more biologically hostile where iron masses were corroding. This hypothesis is...
supported by observing in details the corrosion products grown on the hair of the Dancing Satyr that discloses the cellular wood structure likely of the ship’s deck that has survived the deterioration being in contact with the copper biocidal corrosion products (Figure 7).

These findings reveal that the interaction of the bronze artifact with the surrounding microenvironment can include also the chemical−physical incorporation of inorganic species capturing soil minerals or organic matter such as insects, textiles, feathers, wood, bones, and leather whose structure and morphology can be preserved in some way as a consequence of their mineralization.2,19

Due to the biocidal character of copper ions, the organic natural or man-made materials can be preserved or most frequently can be pseudomorphically replaced. A highlighting example is shown by the surface of a bronze Carthaginian coin (Figures 8 and S6) placed on a human body buried in a grave at Ras Zebib (Tunisia 3rd century BC). The coin was placed inside a garment at the chest height, and the textile material (wool) was replaced by the copper corrosion products participating in a pseudomorphic substitution likely during the initial corrosion period of burial, thus forming a negative cast of the fibers.2,19,49

As in this case study, the careful investigation of the micromorphological details allows one to reveal the presence of embedded organic materials, sometimes fossilized, or their imprint, allowing the identification of the textile nature and of the fibers’ size besides providing valuable information, otherwise difficult to obtain, about the twisting process to form the textile.

Finally, we point out that the detailed micro- and nanochemical and morphological information can be useful to investigate in details the material nature of ancient works of art50 and also can be used to select the most appropriate procedures for conservation. These latter can utilize innovative materials and approaches based on the emerging nanotechnologies that are under study also for bronze conservation after having been already successfully used to contrast the degradation of other classes of artworks.51−53

■ CONCLUSIONS

The surface of archeological Cu-based alloy artifacts found in different contexts has been investigated by adopting an attentive approach aimed at identifying the ancient environmental conditions experienced over time by the objects.

The results highlight the relevance of the minute microchemical and morphological investigations of the corrosion products grown on archeological bronzes during their long-term burial too often wholly ignored in their scientific study.1−3,11,19,49

The case studies here described emphasize how the interaction between alloy elements and environmental chemical species, microorganisms, and materials can change the surface and subsurface chemical and structural features in many different ways that can be revealed by detailed investigations carried out at a microscale.

The results can greatly extend and supplement the possibilities presently afforded for example by Pourbaix’s diagrams that represent only the possible presence of a stable phase as a function of the electrochemical potential and the pH values in an aqueous system, but which are also highly influenced by the presence of certain reactive species such as chloride ions. Moreover, particular burial corrosive environ-
ments can be disclosed in details, thus contributing to explain the formation of unusual mineral phases.

According to this approach, the microscale study of the interaction products should be carefully performed prior to cleaning and conservation procedures, thus contributing to identifying the ancient environmental conditions and their eventual changes over time and to decipher what had taken place on the surface of the cultural heritage artifacts.

Finally, it is worth pointing out that this approach could be of interest to a large number of researchers of different disciplines including materials science, chemistry, environment, and geology, stimulating new tailored research, and it could provide the opportunity to write, in whole or in part, a sort of a chemical biography of these fascinating witnesses of human art, creativity, and technology.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomeg.a9b00569.

Micrographs of cross-sectioned patinas naturally grown on bronze archeological objects; SEM and EDS spectra of the surface of the Roman coin with a blue patina containing turquoise; SEM and EDS spectra of a Roman coin whose patina is composed by chalcoprite (CuFeS₂); BSE–SEM image of a fossilized marine microorganism embedded in the patina; XRD pattern of a patina containing schoenite [MgSn(OH)₆]; OM and SEM images of wool fibers pseudomorphically replaced by Cu corrosion products (PDF)

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G.M.I. designed the research; G.M.I. and C.R. performed the research; G.M.I., G.G., C.G., G.D.C., M.A., and C.R. analyzed the data; and G.M.I. wrote the paper.

Notes

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