

# Protecting archaeological collections in Capua Archaeological Museum (Italy): The importance of microclimatic monitoring and non-invasive diagnostic investigations

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## ABSTRACT

This study examines the importance of microclimatic monitoring and non-invasive diagnostic techniques in cultural heritage sites for the identification of critical environmental conditions and the development of appropriate conservation measures. In particular, the research focuses on the microclimate analysis in the 'Sala delle Madri' of the Archaeological Museum of Capua, Italy, which houses a collection of important Roman and Greek sculptures. The study reveals that the microclimatic conditions in the 'Sala delle Madri' are not constant throughout the monitored year and the environmental parameter are influenced by seasonal variations and natural phenomena. A preliminary diagnostic investigation has been performed on the sculptures located in this room to document the state of conservation of the sculptures and to plan a specific analytical protocol aimed to characterization of both original and restoration materials, verifying the influence of the microclimatic conditions, due to high temperatures and NO<sub>2</sub> levels. Moreover, X-ray fluorescence analysis (XRF) was performed on two archaeological coins to characterize the alloy composition and to document corrosion products and to understand degradation phenomena. This research highlights the necessity for the implementation of conservation measures to mitigate the negative impact of environmental conditions and prevent further damage to the archaeological findings displayed at Capua Museum. This study therefore contributes to the wider awareness of the importance of preserving cultural heritage and the role of monitoring systems in achieving this goal.

**Section:** RESEARCH PAPER

**Keywords:** microclimatic monitoring; cultural heritage sites; environmental conditions; conservation; custom monitoring; measurement

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## 1. INTRODUCTION

In recent years, there has been an increasing focus on monitoring microclimatic conditions in cultural heritage sites due to their impact on preservation [1], [2]. Scientific analyses have been conducted in this study on specific artworks from the Capua Museum to obtain important data for evaluating and documenting deterioration processes and past conservation treatments, examining the executive techniques employed, and

determining the composition of materials used in both the original and restored components. These investigations have the potential to aid in determining the age and origin of the artworks as well as in planning future conservation efforts. In this study, we performed non-invasive and non-destructive analyses on two different types of artifacts, tuff votive statues and archaeological coins (Figure 1), as follows:



Figure 1. Photographical documentation of the data acquisition phases performed on: a) two archaeological coins; b) two votive statues altered by historicized restorations.

- i) A monitoring campaign of the microclimate in the 'Sala delle Madri' of the Archaeological Museum of Capua, Italy, has been carried out. The room houses a collection of important Roman and Greek sculptures and has been identified as having potentially critical environmental conditions, including high temperature levels [3]-[6]. These are the so-called "Mothers" represented ex-voto for the granting of fertility to the goddess "Mater Matuta", an ancient Italic divinity of dawn and birth.

A comprehensive microclimatic monitoring system was installed, consisting of multiparametric sensors, to assess the environmental conditions inside the room. The data retrieved were correlated with the results of diagnostic investigations performed by non-invasive methodologies on the sculptures located in the room with the aim of documenting the state of conservation of original and restoration surface of the statues. The data have been collected over the period of eighteen months in order to reveal that the microclimatic conditions in the 'Sala delle Madri' their daily and seasonal variability throughout the year, and their inertia with respect to external climatic phenomena. Preliminary Visible Fluorescence induced by Ultraviolet source have been carried out to document the state of conservation of the sculptures in the room and to understanding the influence of microclimatic conditions, in particular any effect due to hygrothermal and chemical factors. Two votive statues that already showed conditions of advanced degradation have been selected. The monitoring campaign conducted in the 'Sala delle Madri' of the Archaeological Museum of Capua highlights the importance of microclimatic monitoring in cultural heritage sites for the identification of critical environmental conditions and the development of appropriate conservation measures [7]-[10].

- ii) X-ray fluorescence analysis (XRF) was performed on two archaeological coins to characterize the composition of the alloy, to document the alteration due to degradation products and to identify potential indicators that could provide valuable insights in archaeometric studies on coeval artifacts.
- iii) A study utilizing a digital optical microscope was carried out on multiple artworks. The primary objective was to record details such as the pictorial surface, archaeological patinas, and presence of restoration materials on the original surfaces. This analysis facilitated the examination of morphology of

the materials employed, as well as the presence of inclusions or overlapped layers on seemingly homogeneous surfaces, which are not perceptible to the naked eye.

In recent years, there has been a significant rise in the number of studies focusing on microclimate monitoring within museum environments, driven by the pressing need for preventive conservation of cultural heritage [11]-[14]. Despite this trend, the current state of the art is lacking in research that integrates environmental monitoring with archaeometric analyses on specific artifacts. Only a limited number of studies have explored the potential benefits of this combined approach [15]-[17].

The novelty of our study mainly lies in the introduction of a customized environmental monitoring system to address, for the first time, the air quality within the Capua Archaeological Museum. The multiparametric monitoring station was specifically designed to assess the needs of this museum setting. Furthermore, by combining microclimatic monitoring with X-ray fluorescence analysis (XRF) and digital optical microscopy on specific artifacts, we provide new insight into their deterioration mechanism and conservation needs. This approach not only enhances our understanding of material deterioration processes within museum settings, but also contributes to the development of more effective conservation strategies, thereby addressing a significant gap in the existing literature. Indeed, thanks to the design with a bottom-up approach of the long-term scheduled maintenance protocols, effective passive conservative measures can be applied starting from specific knowledge even for decentralized sites which generally do not have large economic resources available.

Consequently, our study underscores the importance of safeguarding cultural heritage and highlights the efficacy of customized monitoring systems and non-invasive diagnostic techniques in achieving this goal.

## 2. MATERIALS AND METHODS

### 2.1. Microclimate monitoring

For the project, a smart object has been designed and assembled for the non-invasive control of indoor environmental parameters of the site. Station is equipped with a microcontroller with custom firmware equipped with Bluetooth-Wi-Fi dual telecommunication channel and operating in Start-Go-Stop mode. The collected data are sent to a remote cloud and visualized through an application with a low-level analytics module. The monitoring station, shown in Figure 2, is equipped with a microcontroller, a multi-in-one air quality module integrating several sensors, including a laser dust sensor, an infrared carbon dioxide sensor, electrochemical sensors for formaldehyde, ozone, carbon monoxide, TVOC grade, and nitrogen dioxide, as well as temperature and humidity sensors. Additionally, electrochemical modules for hydrogen sulphide and sulphur dioxide monitoring are installed. A micro-fan inside the station is switched on for a pre-set time and frequency to have a balance with the environment to be monitored. Holes were made in the container to facilitate air exchange between the inside and outside of the station. During each sampling, the station acquired approximately 115 data points and provided four different types of values for each measuring point, including minimum, average, maximum, and the last acquisition. The monitoring station has several strengths. Firstly, it has small dimensions, which make it possible to install in areas where space is limited (Figure 2).



Figure 2. Multiparametric station.

Secondly, it is highly customizable, allowing the addition or removal of sensors depending on the type of monitoring to be carried out. This makes the station versatile since it can be adapted to different contexts and environmental conditions. By customizing the sensors, it is also possible to detect pollutants that might otherwise go unnoticed, providing even more accurate and comprehensive measurements. The ability to change the configuration of the station also makes it an efficient and economical option, as it can be adapted to different sites and purposes. The monitoring of temperature, humidity, CO<sub>2</sub>, NO<sub>2</sub>, formaldehyde and particulate matter in museum settings is crucial for the preservation of cultural property [18]. Changes in temperature and humidity directly affect the stability of materials, while NO<sub>2</sub> and formaldehyde can accelerate the degradation of artworks. CO<sub>2</sub> is an indicator of air quality and ventilation, critical for a healthy environment and prevention of other pollutants. Finally, particulate matter monitoring is essential to protect the surfaces of artworks from the accumulation of harmful dust.

Below are the accuracies of the sensors at the station:

- PM:  $\pm 15 \mu\text{g}/\text{m}^3$  (when the concentration is  $\leq 100 \mu\text{g}/\text{m}^3$ );  $\pm 15 \%$  (when the concentration is  $> 100 \mu\text{g}/\text{m}^3$ )
- CO<sub>2</sub>:  $\pm 50 \text{ ppm} + 5 \%$  of the reading value
- CH<sub>2</sub>O:  $\pm 0.01 \text{ mg}/\text{m}^3$  (when concentration is  $\leq 0.2 \text{ mg}/\text{m}^3$ )  $\pm 20 \%$  reading value (when concentration is  $> 0.2 \text{ mg}/\text{m}^3$ )
- Temperature:  $\pm 0.5 \text{ }^\circ\text{C}$  (0-65  $^\circ\text{C}$ )
- Humidity:  $\pm 3 \%$  RH.

## 2.2. Non-invasive *in situ* analyses

Non-invasive diagnostic investigations were conducted on two tuff votive statues selected for complexity of their surfaces, including areas with restorations. Extended sections of the statues have been altered by the presence of plaster, which



Figure 3. Two tuff statues involved in the preliminary diagnostic investigation.



Figure 4. XRF analysis conducted on the two archaeological coins selected for this study and characterized by the typical patinas of copper alloy artifacts.

replicates facial features and other details, affecting the original surfaces. These historicized restorations have been intentionally left in place to document the conservation history of the collection. In the first step of this study, Visible fluorescence induced by Ultraviolet source (UVF) imaging was carried out to map the various materials on the surfaces of the statues depicting the "Madri". We focused on two statues exhibited in room VIII, which had undergone incorrect past restorations (Figure 3).

The observations and documentation were carried out to accurately locate the restoration areas and record their state of conservation. Additionally, our aim was to identify any residues of organic and/or inorganic materials from prior restorations and/or foreign substances applied to the original layers. The use of digital optical microscopy allowed for the observation and documentation of any restoration materials applied directly to the original surfaces, thus allowing us to identify their morphology and uniformity/homogeneity, including the presence of inclusions on apparently homogeneous surfaces that may not be visible to the naked eye.

Furthermore, X-ray fluorescence was employed on two archaeological coins kept in the Museum in order to perform a non-invasive analysis to identify their chemical composition (Figure 4) and to understand any alteration due to environmental conditions.

The portable XRF spectrometer used for the multi-elemental analysis of the alloy of archeological coins consists of the X-ray tube (Mini-X - Amptek) equipped with a Rhodium (Rh) target and operating at a maximum working voltage of 40 kV and maximum current 0.2 mA. The detection of the characteristic X-Ray radiation emitted by the sample is as a function of the energy (Energy Dispersive: ED-XRF) and allowed by a Silicon Drift Detector system (X-123 SDD – Amptek) with 125 - 140 eV FWHM at 5.9 keV Mn K $\alpha$  line Energy resolution (depending on peaking time and temperature), collimator 1 or 2 mm. The detection range of energy is from 1 keV to 40 keV, with a maximum rate of counts up to  $5.6 \times 10^5$  cps. The primary beam is positioned perpendicular to the sample, while the detector is positioned at 40 degrees with respect to the primary beam. A

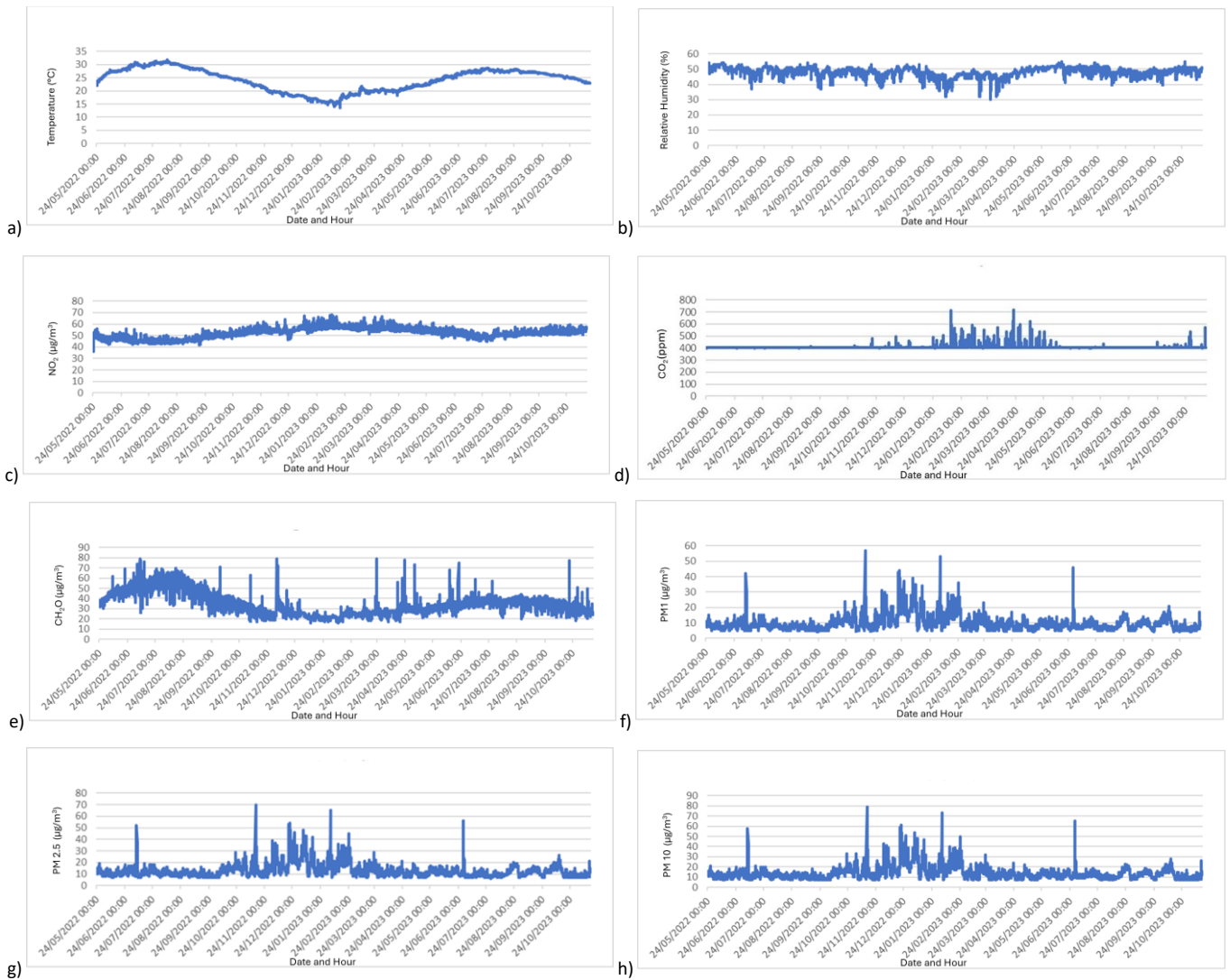


Figure 5. From top to bottom: a) Temperature (°C); b) Relative Humidity (%); c) NO<sub>2</sub> (µg/m<sup>3</sup>); d) CO<sub>2</sub> (ppm); e) CH<sub>2</sub>O (µg/m<sup>3</sup>); f) PM1 (µg/m<sup>3</sup>); g) PM2.5 (µg/m<sup>3</sup>); h) PM10 (µg/m<sup>3</sup>) trends.

dedicated control software allows to administrate measurements and acquisitions. For the analysis, the following measurement parameters are set in order to ensure a good spectral signal and to optimize the signal-to-noise ratio (SNR): voltage 35 kV, current 80 µA, acquisition time 60 seconds per area, working distance 1 cm.

### 3. RESULTS

#### 3.1. Microclimate monitoring

The microclimate monitoring data were collected over an eighteen-months period, from May 2022 to November 2023.

It should be noted that before June 2023, the room did not have any mechanism for air conditioning the indoor air.

The data showed that the temperature inside the room ranged from 31.8 °C in August 2022 to 13.5 °C in February 2023 showing that the environmental conditions inside the room prove to be particularly critical during the summer and winter months. The relative humidity (RH) ranged from 30 % in March 2023 to 55 % in October 2023. The concentration levels of various atmospheric pollutants, including CO<sub>2</sub> (401-717 ppm), NO<sub>2</sub> (36.0-68.2 µg/m<sup>3</sup>), CH<sub>2</sub>O (16-79 µg/m<sup>3</sup>), PM1

(4-57 µg/m<sup>3</sup>), PM2.5 (6-70 µg/m<sup>3</sup>), and PM10 (7-79 µg/m<sup>3</sup>) were recorded at different levels throughout the year (Figure 5).

An accurate statistical analysis of the collected data was carried out following UNI standards [19]-[21]. The results were compared with the normative standards related to museum environmental parameters.

The statistical analysis showed that the hygrothermal values recorded are not within the limits suggested by the standard (especially in the summer and winter months) for some periods.

It is observed that as temperatures drop, NO<sub>2</sub> levels tend to rise. This phenomenon suggests a higher concentration of air pollutants during colder months, a condition that, if not properly managed, can accelerate the degradation processes of exposed materials. The marked negative correlation between these two parameters (-0.82) highlights the need for targeted mitigation strategies during winter periods.

At the same time, a positive correlation was found between formaldehyde (CH<sub>2</sub>O) and temperature. This phenomenon could potentially be due to the increased release of volatile organic compounds from materials and furnishings inside the museum during the warm months.

As for particulate matter, a slightly greater increase was identified in the cold months. This could be attributed to lower



Figure 6. UV Fluorescence images: bluish-white areas indicate the historicized restorations.

particle dispersion due to reduced ventilation activities and increased indoor emissions [22], [23]. The presence of particulate matter in greater quantities during the cold months emphasizes the need to maintain constant cleanliness and implement effective filtration systems. No particular critical issues related to CO<sub>2</sub> are found.

### 3.2. Non-invasive diagnostic investigations

#### 3.2.1. Visible fluorescence induced by Ultraviolet source (UVF)

The non-invasive diagnostic investigations clearly identified differences between the mortar integrations and the original tuff surface, which were affected by environmental conditions. This resulted in widespread alterations and detachments, caused by the varying behaviours of the original materials and the mortar integrations in response to daily and seasonal changes in temperature and humidity.

In particular, the fluorescence images seen under ultraviolet light reveal how the original stone surfaces on the faces and other features of the Mothers were extensively altered by the integrations. The restoration part appears characterized by a bluish-white fluorescence under the UV light, whilst the original surfaces do not show characteristic fluorescence, but instead appear as dark areas.

Additionally, UVF imaging showed that residues from past treatments were present on the surface, making it vulnerable to environmental damage like the accumulation of atmospheric particles, microorganisms, and salts, which can result in additional deterioration (Figure 6).

#### 3.2.2. Digital Optical Microscopy

The use of digital optical microscopy enabled the detailed observation and documentation of the restored surfaces and original tuff. This diagnostic information helped identify the morphology and uniformity that was not apparent to the naked eye (Figure 7a-b). Additionally, the optical microscope documentation showed evidence of a potential preparation layer associated with an original polychrome feature on the original surface (Figure 7c).

The initial UVF and MO mapping data will help identifying sampling areas for further analysis of the materials detected through infrared spectroscopy, ion chromatography, and XRD.

This next phase of research will focus on identifying degradation products caused by environmental factors, as well as assessing how historic integrations impact the preservation of the original tuff surfaces.

#### 3.2.3. XRF analysis

The XRF analysis of metallic artifacts allows for qualitative, and, under certain circumstances, quantitative examination of the

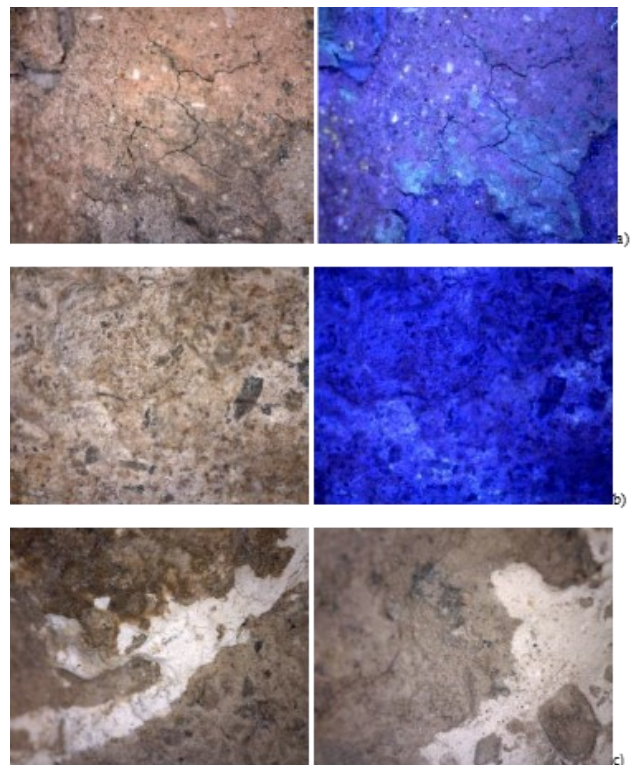


Figure 7. Digital optical microscope Vis and UV images (50 x) on: a) mortar constituting the sculptured surfaces integration due to past restoration work; b) original tuff surfaces; c) supposed traces of a preparation layer of an original pictorial layer.

chemical elements present in the alloy, as well as any surface elements or patinas resulting from ongoing or previous corrosion processes [24].

It is important to highlight that the composition of the patina, which forms as a result of corrosion or dissolution of alloy elements or interaction with the surrounding environment (such as soil, marine or river water, and atmospheric conditions), can impact the accurate quantitative identification of the alloy components [25].

XRF spectra acquired on two coins under investigation, verifying respectively the presence of copper, tin, lead, zinc, and trace amounts of calcium and iron (Figure 8) and gold, silver, and

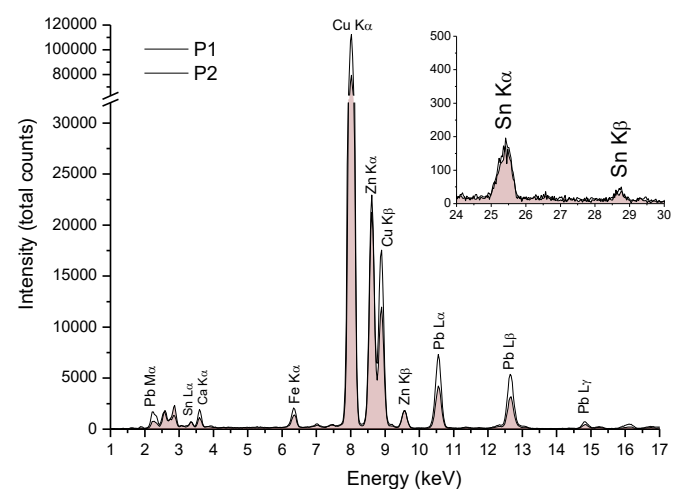


Figure 8. XRF spectra acquired on both faces of the bronze coin. The identified chemical elements are Copper, Tin, Lead, Zinc, and trace amounts of Calcium and Iron.

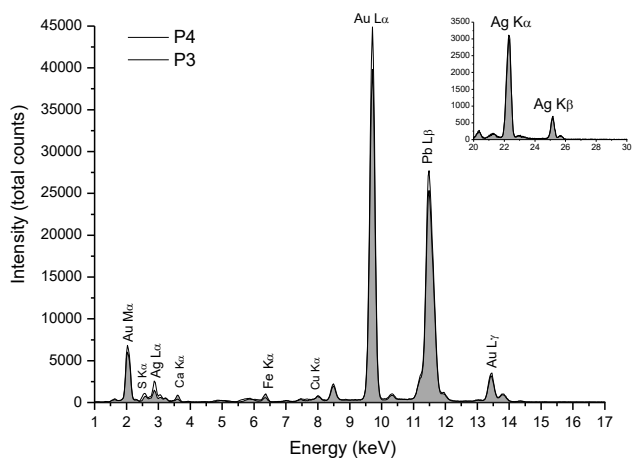


Figure 9. XRF spectra acquired on both faces of the golden coin. The identified chemical elements are Gold, Silver, and trace amounts of Sulphur, Calcium and Iron.

trace amounts of sulphur, calcium and iron (Figure 9). The sulphur could correlate the black patina formation observed on surface of the Au-Ag coin due to the formation of silver sulphides (Figure 10).

Moreover, Figure 11 displays microscopy images of the surfaces of the Cu-Sn-Zn alloy coins, documenting alterations due to the typical products of the copper corrosion. The examination of the patinas on bronze artifacts is a topic of significant interest for both conservation and archaeometric purposes [26].

When copper-based alloy artifacts deteriorate, a patina layer forms on the surface due to the presence of alteration products. The composition and thickness of this patina layer are influenced not only by the original alloy composition but also by the environmental conditions in which the corrosive process occurred. Unlike the rusting of iron-based alloys, the patina is often seen as a desirable feature that can enhance the value of copper-based alloy artifacts. For instance, outdoor bronze artifacts are intentionally coated with patina to improve their aesthetic appearance.

Copper patinas, indeed, are generally regarded as aesthetical features, and much of the use of copper in architecture and sculpture, in ancient times as today, is based on patina being formed. Once established, the patina tends to be extremely stable and to become a permanent part of the archaeological or artistic surface, also acquiring a conservative function for the work of art. Any significant change in these patinas, which can occur under some conditions, is thus generally detrimental [27]. Any change could represent a signal for the possible formation of alteration products which are not stable and dangerous for the bulk alloy constituting the artefact of historical-artistic interest.

The most prevalent alteration products of copper include (1) oxides (such as cuprite:  $\text{Cu}_2\text{O}$ , with a dark red hue); (2) sulphides (like chalcocite:  $\text{Cu}_2\text{S}$ , and covellite:  $\text{CuS}$ , predominantly found in urban atmosphere); (3) basic sulphates (e.g. brochantite:  $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ , antlerite:  $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ ); (4) chlorides/hydroxychlorides (such as atacamite:  $\text{Cu}_2\text{Cl}(\text{OH})_3$ , capable of penetrating deep into the patina); (5) basic green-blue carbonates (like malachite  $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ , azurite:  $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ); (5) and oxalates with varying degrees of hydration  $\text{Cu}(\text{COO})_2 \cdot n\text{H}_2\text{O}$  [26]-[28].

In particular, the copper chlorides/hydroxychlorides, that appear as light green, powdery and voluminous deposits are a



Figure 10. Microscopies of the golden coin revealed abrasions and damage, as well as the formation of corrosion products of the metals present in the alloy (likely silver sulphides and copper oxides).



Figure 11. The microscopy on the bronze coin reveals a first reddish-brown layer that is commonly attributed to the formation of copper oxides (cuprite), upon which greenish-blue layers of copper compounds (chlorides or carbonates) subsequently started to grow due to the conservative conditions to which the artifact has been exposed.

signal of active corrosion (called “bronze disease”). Previous studies have individuated different thresholds for the start of the cuprous chloride reaction: 42–46 %, 40–50 %, and 63 %. The

varying results from available scientific studies of bronze disease mean that evaluating risk is difficult, but all the studies suggest that below a RH of 42 % active corrosion is unlikely, and above 68 % RH the risk of outbreaks of bronze disease increase [29].

Patinas may also contain silica particles, carbon particles derived from atmospheric particulates, and organic substances from paints or waxes applied for preservation treatments. Red and green patinas, associated with the presence of oxides or copper carbonates, are typically considered to hold historical and artistic significance, and are therefore preserved. Conversely, green patinas containing chlorides, which lead to cyclic corrosion reactions, or black and scaly crusts that disfigure artifacts, necessitate removal. Therefore, the analysis of composition and chemical structure of the corrosion patina can provide valuable information regarding the state of conservation of the artifact. This assessment is crucial for conservation and restoration efforts and can offer insights into the chemical composition of samples, production techniques, environmental conditions, and type of soil in which the artifacts were buried. The corrosion process of bronze is often attributed to the structural and dynamic properties of copper, but recent studies suggest that alloy elements may also play a significant role in either inhibiting or accelerating corrosion processes.

Lead, for example, plays a critical role in the corrosion mechanism as it tends to form intergranular islands during the solidification process of the alloy, creating preferential surfaces for degradation [27]. Additionally, migration processes of elements or ions along the thickness of the alloy, may lead to a concentration gradient in the corroded layer. This is evidenced by the significant increase in lead concentration in the corrosion coating, surpassing values found in the bulk alloy by up to four times. The presence of tin enhances the alloy's resistance to the formation of corrosion patinas. However, the enrichment of tin, due to its high stability, is also closely tied to decuprification processes.

#### 4. CONCLUSIONS

The study highlights the importance of microclimate monitoring in cultural heritage sites to identify crucial environmental conditions and create suitable conservation strategies. The monitoring system set up in the 'Sala delle Madri' uncovered fluctuations in microclimatic conditions within the room over the course of eighteen months, with particularly concerning environmental conditions detected during the summertime and winter months. The environmental measures were accurately analysed and compared to UNI standards, showing that certain values were not within the ideal ranges. As a result, further interventions are required to improve the environmental conditions in the 'Sala delle Madri' in order to properly preserve the sculptures.

The preliminary non-invasive investigations performed on the sculptures in the 'Sala delle Madri' showed that their conservative state was greatly impacted by microclimatic conditions. This was evident through encrustation, incoherent deposits, detachments, and alterations that affected the interface between the original surface and the integrated historicized mortar. The identification of constituent material and of the newly formed products will help assess and plan the necessary interventions to prevent the degradation of the original compounds. This phenomenon could be accelerated by chemical or physical interaction, under unfavourable environmental

conditions, with the altered restoration materials found on the two analysed statues.

The importance of maintaining ongoing monitoring of artwork and environmental conditions in museums is highlighted in this research. A significant advancement in research is the introduction of the microclimatic monitoring system employed in this study. The system's compact design makes it ideal for use in limited spaces and can be customized to suit the monitoring requirements of specific environments. The capability to detect critical environmental conditions that could jeopardize the preservation of cultural heritage sites, allows for the implementation of suitable conservation methods to prevent damage. Its customizable and versatile features make it a cost-effective and efficient choice for monitoring microclimatic conditions in cultural heritage sites.

Moreover, XRF analysis performed on two archaeological coins allowed us to characterize the alloy composition and to document the alteration products and localize any instable patina correlated to recorded environmental condition. Additional quantitative compositional analyses will be however necessary to determine the percentage composition of the chemical elements present in the alloy of the analysed coins. This will allow for more detailed correlations with coeval production methods and comparison with the expected production timeframe, based on a dating hypothesis established through archaeological and stylistic analysis of the two coins.

The findings of this study may contribute to the development of future conservation strategies aimed at mitigating the negative impact of environmental conditions on cultural heritage, ensuring their conservation for future generations.

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