Project CHANGES - Spoke 5

D2.2 – Technical report on the diagnostic methods applied to the chemical and microbiological degradation of different heritage materials– v1.2

Deliverable information

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No.	Name of Partner	Acronym	Role
1	University of Napoli Federico II	UNINA	Member
2	University of Catania	UNICT	Member
3	University of Bologna	UNIBO	Member
4	Consiglio Nazionale delle ricerche	CNR-ISPC CNR-SCITEC CNR-IAC	Spoke leader
5	Sapienza University of Rome	UNIROMA1	Member
6	Opificio delle Pietre Dure	OPD	Member

Executive Summary

The activity of this deliverable refers to the applications of chemical and microbiological diagnostic methods to the degradation of painted surfaces, stones, metals and written documents. Particularly, the project has focused mostly on the development of non-invasive, microinvasive and mathematical modeling to characterize/model the multicomponent (inorganic, organic, and biochemical) and multiphasic nature of work of arts of interest, and thus their degradation mechanisms with increased space and time resolution. Indeed, the experimental approach was combined with mathematical modeling dedicated to testing the mechanistic hypothesis with a predictive time-resolved approach, useful for preventive conservation strategies.

The research activity is the result of a collaborative effort of the Consortium involving both academic institutions (UNIBO, UNICT, UNINA, UNIROMA1) and research institution, such as CNR (ISPC, SCITEC, IAC) and the "Opificio delle Pietre Dure". The adopted approach is multidisciplinary, involving Biologists, Chemists, Engineers, Geologists, Mathematicians, Physicists along with Art Historians and Archaeologists.

The inorganic characterization integrates standard and innovative approaches, both elemental and molecular characterization, both macroscopic and microscopic investigations, studying different time scales. The research outcomes cover the mechanism of degradation of inorganic pigments (e.g. As_2S_3, HgS, $PbCO_3$), natural (e.g. marble, travertine and limestone) and artificial (e.g. mortars) stone materials, organic components (e.g. oil and paper), and biochemical components (e.g. collagen, milk and egg proteins) induced by chemical (e.g. oxygen, pH), physical (temperature and light) and microbiological factors

(bacteria and fungi).

The methodological protocols developed during the project have also been applied to several case studies including Museums (e.g. Museum of Capodimonte and Royal palace of Caserta), Archeaological sites (e.g. Holy Sepulcher and Cencelle) and monuments/edifices of the Italian historical built heritage (e.g. Baroque architecture of Catania).

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1. Introduction

This document describes the outcomes of the research activity carried out by the Consortium in Spoke 5 and Workpackage 2, on the diagnostics applied to degradation of works of art or of historical interest (deliverable D2.2). The document is intended strictly related to deliverable D2.1.

The present document first presents the state of the art and then the research outcomes on Analytical and aging protocols (Section 2) and outcomes on Case studies (Section 3). For easy reading we present, in sub-paragraphs, separate outcomes on paintings, stones, metals, and written documents (including works both on paper and on proteinaceous substrates). Section 4 reports the concluding remarks of the research activities on the four major artworks (paintings, stones, metals, written documents), summarizing the extent of

published articles and contributions to conferences, reporting the PE5 activity herein described. At the end of the document, both the general literature and the publications produced for the D2.2 are listed.

2. Analytical and aging protocols

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2.1.1 State of the art

From the chemical point of view, paintings are multilayered and heterogeneous systems composed of organic and inorganic components with amorphous or crystalline structures that modify their properties over time. Such transformations are typically prompted by different environmental factors, including light, humidity, temperature, air pollutants. It has been extensively documented that oxalates and carboxylates of metal ions (Casadio et al., 2019; Izzo et al., 2021; Rosi et al., 2019) and newly formed compounds arising from changes in the oxidation state of one or more elements constituting some inorganic or organo-metal pigments (Janssens et al., 2013; Miliani et al., 2018) are common alteration products of paint components. From the analytical point of view, the study of such complex processes is rendered more complicated by the fact that secondary compounds may form as layers and/or aggregates of limited size (generally below 100 µm) within heterogeneous paint matrixes. Thus, the combination of complementary and spatially resolved analytical methods is usually required, exploiting their ability to visualize chemical changes at multiple length scales (i.e., from the millimetric to the nanometric scale) both directly throughout the painting surface and across the

stratigraphy of minute paint samples (i.e., from both historical paintings and artificially aged paint mock-ups).

At the nano-/microscale level, the use of electron microscopy and synchrotron radiation (SR)-based X-ray methods [i.e., micro-X-ray fluorescence (μ-XRF) and X-ray absorption spectroscopy (XAS)] was successfully applied to gain specific information about changes of the oxidation state and/or coordination geometry of the absorbing element of some pigments both in the amorphous and crystalline form (Cotte et al., 2018; D'Acapito, 2022). Complementary information on the nature and distribution of crystalline secondary compounds of some pigments were obtained by integrating XAS with micro-X-ray diffraction (μ-XRD) mapping (Vanmeert et al., 2022). In selected cases, μ-XRD mapping was combined with micro-X-ray diffraction computed tomography (μ-XRD-CT) to visualize the inner distribution of crystalline components in minute historical lead-based paint samples, without physically cross-sectioning the material under investigation (Vanmeert et al. 2015; Gonzalez et al., 2020). Further insights into the chemical nature and stratigraphic distribution of organo-metallic compounds formed during alteration processes (such as metal-oxalates and metal-carboxylates) and changes in the optical properties of the paint were often achieved by combining the above-described X-ray methods with UV-VIS-NIR, micro-Raman and micro-IR spectroscopies (Monico et al., 2022; Pouyet et al., 2015; Vermeulen et al., 2018; Van Der Snickt et al., 2012; Monico et al., 2020).

At the macro scale level, complementary knowledge into some of the above-described paint alteration phenomena were obtained by integrating the micro-

analytical data obtained from paint samples with non-invasive measurements (from the IR to the X-ray range) gathered with portable instruments (Rosi et al., 2019; Monico et al., 2020; Gonzalez et al., 2023; Simoen et al., 2019; De Meyer, 2019). Recent advances in the non-invasive analysis performed in situ, directly on paintings, have focused on the use of various imaging techniques to monitor the transformation of paint materials (Rosi et al., 2019, Monico et al., 2015). Mobile macro-X-ray fluorescence (MA-XRF), macro-X-ray diffraction (MA-XRD) and confocal X-ray fluorescence (CXRF) have been increasingly used for the mapping of elemental and crystalline phases, respectively, providing insight into the distribution of original materials and degradation products in painted artworks (Romano et al., 2016, Simoen et al., 2019, ; Vanmeert et al., 2018).

Very little is known about the reciprocal interactions between the inorganic pigments and the proteinaceous binders, and their impact on paint aging under variable environmental conditions (Elert et al., 2018).

A LiP-MS-based approach (Schopper et al., 2017), new to cultural heritage studies, was optimized to explore how pigments influence the 3D structure of protein binders, identifying regions affected by pigment-binder interactions.

Moreover, further improvements of a microinvasive diagnostic kit for protein analysis towards spatially resolved imaging of artwork surfaces and sectional analysis, utilizing MALDI-Imaging technology, are in progress. This innovative tool, initially developed with a cellulose acetate sheet functionalized with trypsin (Cicatiello et al., 2018; Ntasi et al., 2021), enables the direct digestion of proteins in situ on painted surfaces without the need for any physical sampling from the artwork. The resulting digested peptides can be analyzed

using traditional MS or MS/MS techniques to identify the proteins.

The activity performed within WP2 focuses on the study of naturally and artificially aged paint mock-ups to develop a multi-method and multi-scale approach for monitoring and studying the key degradation factors (see deliverable 2.1 for details) and characterizing the secondary compounds arising from the transformation of pigments, binding media, and pigment-binder interactions.

2.1.2 Analytical protocols for the degradation of selected pigments

2.1.2.1. Methods

CNR-ISPC. The integration of 2D MA-XRF for elemental mapping and 2D MA-XRD for analyzing crystalline phases distributions will enable the identification of both original materials and degradation products in paint mock-ups and historical objects (see paragraphs 2.1.2.2 and 3.1 for details and also the deliverable 2.1). Additionally, 3D CXRF mapping has been used to detect mechanical degradation, such as protrusion or delamination, across the paint layers. These mobile, non-invasive methods provide micrometric resolution for in situ analysis. Laboratory-based XANES and EXAFS at XRAYLab of CNR-ISPC will explore the chemical environment and oxidation states of pigments, with validation from synchrotron experiments. The analytical protocol is mainly realized by using the mobile instrumentation developed and available for applications at the XRAYLab.

- MA-XRF Imaging: This mobile technique uses real-time technology for

fast scanning of paintings over an area of 120 x 90 cm² in one scanning session. It provides elemental distribution images of the pigment materials on the painted surface on the fly, with a lateral resolution down to 50 µm. The main component of the device is the spectrometric head, which utilizes a Rh-anode primary X-ray source focused by a polycapillary, along with a 3D array of six SDD detectors operating in parallel, allowing chemical sensitivity in the range of 0.6 cps/ng·cm², rivalling the sensitivity of XRF beamlines operated with a single detector in synchrotron facilities.

- MA-XRD Imaging: The device allows scanning operation over an area of 50x50 cm², providing crystal phase distribution images of paintings. It consists of a Cu-anode source focused with a polycapillary, with a spot size of 186 µm, and a Si-strip detector with 1280 strips (50 µm x 8 mm size), allowing recording of the diffraction pattern in one shot, with a dwell time of about 3 seconds. The device operates over a Bragg region of approximately 30° (2θ) with an angular resolution of about 0.2° (2θ). Irradiation and detection angles are both 10°. During the activity, the system will be updated by installing new 2D detectors (1024 x 1024 Si pixels in hybrid technology) and a new high-brilliance monochromatic Cu source to further improve angular resolution and diffraction pattern intensity. XRD data in reflection geometry will be compared with those obtained from the same samples using a transmission setup already operated at XRAYLab, which works with a high-brilliance monochromatic Ag source and a 2D pixelated detector, aiming to probe the full depth of the samples.
- 3D CXRF mapping: This mobile device is used to perform 3D elemental

mapping of layered materials. It is based on a Mo-anode source focused with primary optics at a 7 µm spot size and an SDD detector coupled with a secondary optic with a 10 µm spot size. The system operates in a 45°-45° geometry. The two foci create a confocal (quasi) spherical volume of approximately 10 µm diameter, used for 3D rastering of the samples over its thickness.

- XANES/EXAFS: These techniques are widely used at synchrotron facilities for the compositional analysis of samples, providing detailed insights into the electronic structure and coordination environment of the absorbing atom. The recently installed hiXAS device at XRAYLab enables XANES and EXAFS measurements in the 4 to 13 keV range. At the present, scientific activity consists in validating the use of this device in pigment investigation.

CNR-SCITEC, UNIBO. A combination of complementary techniques, including electronic and vibrational spectroscopies (UV-VIS-NIR, FT-IR and µ-Raman), and X-ray-based methods with laboratory sources and synchrotron radiation (µ-XRF, XAS and XRD/µ-XRD), was applied to monitor the chemical changes induced by the exposure to controlled conditions of lighting and relative humidity in copper-arsenite, arsenic sulfide and cadmium sulfide pigments in oil paints (see par 2.1.2.2 for details). By following up previous studies (Monico et al., 2022; Vermeulen et al., 2018; Broers et al., 2023), the effect of other binders on the reactivity of arsenic sulfide-based pigments (i.e., commercial orpiment and realgar), was evaluated by preparing an additional set of samples using Arabic gum. UV-VIS-NIR reflectance spectroscopy and colorimetry were

used to follow the chromatic alteration of the paint surface with increasing aging time; FT-IR and Raman spectroscopies were instead employed to characterize the composition of the original paint and the newly formed degradation compounds, such as metal-soaps, metal-oxalates, arsenic (V)-containing compounds and sulfates. XAS measurements at S K-, Cu K- and As K-edges (both in single point and mapping analysis modes), often combined with SR μ-XRF mapping, allowed the visualization and analysis of changes in the oxidation states of sulfur, arsenic and copper at the surface and throughout the stratigraphy of both unaged and aged paint mock-ups. SR XRD gave insights into the nature of crystalline degradation compounds. Notably, SR μ-XRF/XAS investigations were performed at the BM23 (Mathon et al., 2015), ID21 (Cotte et al., 2017), BM08 (D'Acapito et al., 2019) of the European Synchrotron Radiation Facility (ESRF)-EBS (Grenoble, France) via submission and approval of proposal that were 100% funded by ESRF (data to be published soon). SR XRD measurements were carried out instead at beamlines ID13 and ID22 of ESRF through access to the Historical Materials ESRF-BAG (Cotte et al., 2022) and at the Deutsches Elektronen-Synchrotron (DESY)-P06 beamline.

All data obtained from the photoaging treatments of cadmium sulfide yellow paints have been exploited to develop and optimize a mathematical model to predict the degradation pathways of this class of pigments (see deliverable 2.1 for details). A selection of datasets will also contribute to the development of open-access databases for the Heritage Science community within the PNNR H2IOSC project, the *"Humanities and Cultural Heritage Italian Open Science Cloud"*, specifically within the *"Scientific Digital Hub For Painting Collections"*

(WP7, Task 6.7).

2.1.2.2. Aging protocols and preparation of paint mock-ups

CNR-ISPC. Artificial aging conditions for the study of degradation processes were carefully selected (Table 1). The duration of an aging cycle may range from one week to several months, depending on the material's response. To determine the optimal cycle length, weekly monitoring is conducted using MA-XRD and µ-XRF imaging. The acquired data are processed and analyzed using in-house developed software and compared with those from reference samples that have not been subjected to artificial aging. An extensive selection of inorganic pigments combined with different binders were chosen, to have a representative study of the mainly pictorial techniques used over time. In particular, lead-based pigments, smalt, semiconductor pigments, copper-based pigments, and arsenic-based pigments mixed with linseed oil, egg tempera, or arabic gum (75:25 weight ratio) were applied on glass slides with controlled thickness (100–500 µm).

Table 1 Ageing conditions of XRAYLab' mockups

Dryer 1 & 2 (dark, T 25°C, RH 94%, pH 9, KNO_3)	HgS gum, oil, egg **Mix** As_2S_3+ $PbCO_3$, As_2S_3 + idrocer, As_2S_3+ biacca, smalt + idrocer, smalt + $PbCO_3$ **Stratigraphy** As_2s_3 + idrocer, As_2S_3 + $PbCO_3$, Smalt + Idrocer, Smalt + $PbCO_3$ Cu-based pigments oil, Smalt **Stratigraphy** Smalt + Idrocer, Smalt + $PbCO_3$
Dryer 3 & 4 (dark, T 40°C, RH 89%, pH 9, KNO_3)	As_2S_3 egg, gum, HgS gum, As4s4 gum, **Mix** Pb_3O_4 + ZnO **Stratigraphy** Pb_3O_4 + ZnO, Cu-based pigments oil
Dryer 5 (dark, T 25°C, RH 81%, pH 5, $(NH_4)_2SO_4$)	Arsenic sulphides oil, gum, egg **Stratigraphy** Orpiment + $PbCO_3$ egg

VIS light (2700K), pure LED, 188000 LUX VIS light (6500K) pure LED, 28500 LUX UV light	Semiconductor pigments (arsenic sulphide, HgS, Pb_3O_4)
Climatic Chamber (KBF LQC by BINDER) • Solar light, T 25°C, RH 40% (6 months) • Solar light, T 58°C, RH 70% (6months) • Aging cycle (Total time: 3 months) 1.2 hours Solar light, T 10°C, RH 70% 2.2 hours solar light, T 20°C, RH 40% 3.2 hours solar light, T 50°C, RH 10%	Arsenic sulphides oil, gum, egg, $PbCO_3$ gum, egg **Stratigraphy** As_2S_3 + EB gum, As_2S_3 + EB egg, As_2S_3 + $PbCO_3$ gum, As_2S_3 + $PbCO_3$ egg **Mix** $PbCO_3$+ As_2S_3

CNR-SCITEC, UNIBO. Paint mock-ups were prepared by mixing pigment powders with cold-pressed linseed oil (Zecchi), with a 4:1 weight ratio. After having dissolved four parts of Arabic gum (Kremer Pigmente GmbH & Co) in 1 part of water, arsenic sulfide pigments were mixed with the binder in a 1:1 weight ratio. Such mixtures were then applied on polycarbonate slides (up to ca. 2×1 cm2 area). All paint mock-ups were left to dry in the dark under ambient temperature and humidity conditions from 10 days (for Arabic gum samples) up to 2 months (for oil paints) since they were touch dry. To analyze the paint stratigraphy, a small fragment of each paint cut into slices of 10-30 µm thickness, using a microtome. Except for cadmium yellow paints, a small fragment of each sample was embedded in resin before cutting.

Three aging treatments were carried out to assess separately the effect of UVA-visible light, relative humidity (RH≈95%) and the combined influence of both light and humidity on the chemical stability of the paint (see deliverable 2.1 for further details about the results). The photochemical aging was performed

inside a home-made chamber equipped with a 300 W "ozone free" Cermax xenon lamp at RH≈35% at ca. 35 °C. A Pyrex glass filter has been placed between the paint mock-ups and the lamp to cut wavelengths shorter than 320 nm, thus simulating indoor lighting conditions. Samples were exposed to radiant energy per area values up to ≈1-2×10^6 W·h/m^2. The aging under high moisture conditions was carried out inside a sealed vessel in the absence of light at 40 °C up to 150 days. Inside the vessel, the humidity was kept at RH≈95% using distilled water. The combined effect of light and humidity was performed by placing a selection of the prepared mock-ups in the home-made chamber inside a sealed glass with distilled water to ensure RH≈95%. A mock-up for each paint was stored in darkness at ambient temperature and relative humidity as a control sample.

2.1.3 Analytical protocol for proteomic analysis of proteinaceous binders

Proteins are routinely identified by MALDI-TOF or LC-MS/MS of tryptic digests of protein-containing samples, with various proteomic approaches depending on the research aims. Bottom-up proteomics combined to ad-hoc bioinformatic software (Mascot, MaxQuant, Proteome Discoverer, Peaks) is used for the identification of the protein content, for the determination of the species, and for the semi-quantitative evaluation of the covalent modifications present. Alternative proteomics approach such as Limited Proteolysis coupled to tandem MS (LiP-MS) is used to specifically evaluate structural changes

eventually correlated to protein-ligand interactions or different conditions/treatments applied to samples.

2.2 Stones

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2.2.1 State of the art

2.2.1.1 Natural stones

Natural stones, widely used in cultural heritage, are subjected to complex degradation processes which alter the physical, chemical, and aesthetic properties of the stone, threatening its longevity and historical value (Sesana et al.,2021).

Fourier-transform infrared spectroscopy (FTIR) has emerged as a key analytical tool for studying the chemical changes induced in natural stones by environmental degradation (Theophanides et al., 2018). A promising advancement is the integration with Principal Component Analysis (PCA), which enhances the interpretation of spectral data (Medeghini et al., 2016), recognizing minimal variations in chemical composition thus providing a detailed understanding of degradation patterns.

Raman spectroscopy can efficiently monitor chemical and physical transformations of stones due to weathering and to thermal treatment (Rossi et al., 2022).

2.2.1.2 Mortars

Mortars, like any other natural and artificial stone materials, are subject to atmospheric weathering agents which affect their durability, i.e. their ability to withstand physical and chemical degradation processes in full compliance of their design functionality.

Notoriously, the durability of mortars is strongly influenced by a number of

factors including: a) the local environmental conditions; b) the ingredients used for the mortar preparation (e.g., binder, aggregates and water) and the relative proportions, which also influence the pore network as well as the physical-mechanical properties of the mortar; and c) on-site construction practices (Papayianni & Hughes, 2018). Regarding the testing methodologies to estimate mortar durability, the most commonly used include: water absorption by capillarity and total immersion, wetting-drying cycles, freeze-thaw cycles, drying shrinkage, sulfate attack and salt crystallization test (Borges et al., 2014; Baptista Junior et al., 2024).

2.2.2 Analytical protocols

2.2.2.1 Natural stones

In order to individuate a diagnostic method for the evaluation of the degradation of geomaterials of cultural heritage interest, two different materials have been selected. Specifically, stone parallelepipeds, obtained from slabs of white marble and travertine from quarries have been prepared and then analyzed by attenuated total reflectance (FTIR-ATR), µTransmission (µ-FTIR), and external reflection (ER-FTIR) (Brunello et al., 2019; Izzo et al., 2020; La Russa et al., 2009).

Then, statistical analysis of the spectra was applied to characterize the degradation products and to identify possible correlations between different samples.

Raman spectroscopy was also adopted to study weathering effects typical of

rupestral painted walls, where both pigments and stones undergo to potential degradation, involving oxalates formation and iron oxide conversion.

Protocols of microplastics biomonintoring via lichens and *Pittosporus tobira* (Capozzi et al. 2023; Capozzi etal 2024) or in seawater (Rossi etal 2025) were also developed for future investigation of the potential microplastics effect on the deterioration of sculpture.

2.2.2.2 Mortars

The study of the mortar degradation has been divided in two distinct phases: 1) the first one has been devoted to the mineralogical-petrographic and chemical characterization of mortars from the historical built heritage and *in situ* observation of their decay forms; 2) the second step has regarded the realization of mortar replicas in the laboratory by using the ancient recipes and their subsequent characterization and aging tests.

In particular, with regard to the characterization of ancient mortars, the following investigations were carried out: a) petrographic analysis by means of polarized optical microscope on thin sections in order to highlight the compositional and textural features of mortars; b) X-ray diffraction analysis to determine the mineralogical composition; c) chemical investigations through X-ray fluorescence spectrometry (XRF) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS).

The artificial mortar specimens have been prepared by mixing binders and aggregates of different nature in specific proportions and specific conditions of

temperature and relative humidity during the curing process. The following investigations were conducted on the specimens: a) petrographic analyses on thin sections; b) mineralogical analyses (XRD); c) micro-chemical SEM-EDS analysis through the acquisition of high-resolution maps and quantification of the hydraulic index through an innovative GIS-based image processing approach; d) porosimetric analysis by means of mercury intrusion porosimetry (MIP); e) hydric tests (water absorption by capillarity and total immersion).

2.2.2.3 Mathematical modelling

A mathematical model for the capillary water absorption and permeability properties of historic lime-based mortars from the built heritage of Catania (Sicily) has been developed. The validation of the mathematical model was carried out successfully by comparing the experimental retention curve with the one obtained by the simulation algorithm (Bretti & Belfiore, 2024).

Moreover, the water absorption properties of marble, travertine and wakestone samples has been also investigated. Firstly, a preliminary study on measurements has been done and numerical algorithms have been developed in order to smooth data and reduce the noise eventually due to instrumental error. Then, the calibration of model parameters for the different porous materials has been carried out by comparing the quantity of water absorbed obtained by the simulation algorithm against the quantity of water absorbed found experimentally.

2.2.3 Aging protocols

2.2.3.1 Natural stones

Marble and travertine samples were aged at open environment and left without any protection to atmospheric agents. They have been analysed monthly, to evaluate variation in their infrared signal response. Currently, the natural aging time of the samples is 10 months. Moreover, stone samples underwent accelerated aging tests by salt crystallization (UNI EN 12370:2020) to simulate the action of air pollution. Specifically, the samples underwent fifteen 2 h-cycles at 20°C of total immersion in a 14% $Na_2SO_4 \times 10H_2O$ solution and subsequent drying for 16 h at 105°C. After the 15th cycle, the samples were placed in deionized water for 24 h to dissolve any sodium sulphate retained in pores and fissures of mortars, then rinsed with running water, put in the oven and weighed to obtain the final mass (M_f) compared to the initial dry mass (M_d). The results were expressed as percentage weight loss (ΔM%).

2.2.3.2 Mortars

The artificial mortars underwent accelerated aging tests to simulate in laboratory the degradation processes to which the mortars are subject when exposed in outdoor environment. In particular, the resistance of mortar samples to salt crystallization and their behavior when exposed to sulfur dioxide (SO_2) attack were tested.

The salt crystallization test was carried out according to the UNI EN 12370 (2020) recommendation. After the salt crystallization test, MIP analysis was

carried out on the degraded samples to investigate the modifications undergone by the pore structure.

The aging test by sulfur dioxide (SO_2) was carried out to simulate the action of natural (volcanic) and anthropic air pollution. The procedure carried out is the one followed by Fioretti (2016). A hermetically resealable vacuum bell, connected to a vacuum pump on one side and to a conical flask on the other through silicone tubes and closing valves. The test samples were placed on a perforated grid, in the lower hemisphere of the bell. Then, 100 ml of sodium sulphite dissolved in water was introduced into the bottom of the bell through a thin glass funnel. The vacuum pump, previously connected to the bell by means of a small tube, was then operated and, once the vacuum was reached, it was turned off. At that time, 110 ml of hydrochloric acid dissolved in the distilled water was introduced by a small tube connecting it to the bell. When the transfer of the solution was completed, the connecting valve with the flask was closed to prevent air from entering. At the end of this operation, the production of sulfur dioxide took place, so giving start to the exposure of the samples, which were kept in the system saturated with SO_2 for 30 days. To investigate any physical and compositional changes occurred on the surface of the samples at the end of the SO_2 treatment, colorimetric analysis, mineralogical and morphological/chemical investigations were carried out.

2.2.3.3 Mathematical modelling

A mathematical tool for the prediction of damage due to repeated cycles of salt

crystallization on both mortars and natural stones (marble, travertine and wakestone) is going to be developed.

2.3 Metals

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2.3.1 State of the art

Sulphurisation due to atmospheric hydrogen sulphide (H_2S) and organic sulphur compounds is well known as the primary cause of tarnishing of silver objects. The most widespread prevention strategies used to protect silver cultural heritage from tarnishing involve the application of polymeric coatings (Molina et al., 2023 and references therein). The thickness of the coating layer

is a crucial parameter to consider when analysing its protection effectiveness. Previous studies investigated the effects of artificial aging due to H_2S exposure of silver treated with different types of lacquer coatings (Grissom et al., 2013; Guidera et al., 2024), but did not explore, in detail, the relationships between thickness and protection effectiveness. Measuring coating thickness and establishing a quantitative correlation with the progression of sulphurisation processes are essential for understanding protective performance, enabling a comparative evaluation of different products under identical conditions. XRF scanning has proven particularly effective for the acquisition of polymeric coating thickness maps (Porcinai & Ferretti, 2018; Porcinai & Heginbotham, 2021).

This project aims to establish a method for correlating the colour alteration of silver surfaces after accelerated aging tests through exposure to H_2S with the thickness of the protective coatings.

2.3.2 Analytical protocols

2.3.2.1 Silver coupons preparation

Sterling silver 20 mm x 20 mm wide and 0.8 mm thick coupons are polished with 1200 and 2500 mesh sandpapers and grinded with pumice sand to obtain a matte finish. The mock-ups are treated with different protective products prepared as solutions with different concentrations. 120 µl of solution is applied with the drop-casting technique on the overall surface of each specimen to realize an uneven distribution of the polymeric film resulting in

different thickness values. Back and lateral sides are sealed by brushing the same solution as the front side. Uncoated silver coupons are prepared as controls. Unsupported films of protectives are also prepared to check the colour steadiness of the polymers upon exposure to H_2S.

The tests conducted thus far are based on the acrylic Paraloid® B72, supplied by CTS (Italy), and the nitrocellulose lacquer Zapon®, supplied by Lechler (Italy), using butyl acetate and ethyl acetate, respectively, as solvent media.

2.3.2.2 Measurement of the thickness of the polymeric film

1) Gravimetric method: a precision analytical balance with five decimal digits is used to measure the polymer mass deposited on each mock-up.

2) Eddy Current (EC) measurements: they are performed with a portable coating thickness gauge Leptoskop 2042 (Karl Deutsch-D), with a 5 mm diameter. An internal standard for non-ferrous alloys is used to calibrate the instrument zero. Accuracy is assessed on certified calibration foils. Ten measurements are carried out in the central area of each mock-up.

3) Micro-XRF scanning measurement: they are performed using Bruker M6 Jetstream, equipped with a Rh X-ray tube at 30 W and two 60 mm^2 SDD detectors. No filters are used for the primary radiation. The scans are acquired with a 100 µm spot size on the overall area of the mock-ups. A 40 kV tube voltage and a 700 µA current, with a dwell time of 1 second/pixel, are used to optimize the maximum intensity of Ag L lines signal. Mylar® PET foils with certified thickness are used to build an empirical calibration curve for thickness XRF measurements. A correction factor for the mass attenuation coefficient

values is applied accounting for taking into account the hardening of the primary beam.

2.3.2.3 Evaluation of the effects of aging

1) Visual observation: the surfaces of the mock-ups are observed by means of a stereomicroscope Leica M205C with LED illuminating source.

2) Colorimetry: colorimetric measurements are carried out using a Konica Minolta CM-26dG portable colorimeter, with 8 mm aperture size. For each specimen, ten measurements are taken at the centre of the sample. Polymer-only test samples are placed on a standard white slide for colour measurement. Data are expressed in L*, a*, b* coordinates in the CIELAB colour space (CIE 1976), calculated for a standard D65 illuminant, 10° viewing angle and with specular component included (SCI).

3) Imaging analysis: photographic documentation under visible (VIS) and ultraviolet (UV) radiation is acquired with a Nikon D800 camera, equipped with a full-frame 36.3 Megapixel CMOS sensor (36 mm × 24 mm) and modified by removal of the athermic filter. Illumination for VIS images is provided by Godox D300 Pro flashes. Two filters — a Hot Mirror filter and a 710 nm pass filter — are used for photography. Standard targets are included in the setup (for illumination compensation and calibration in the UV-NIR range). Light reflections are minimized by moving light sources at varied angles around the samples. Captured images are processed with Pickshine software to remove reflections (Miccoli & Melis, 2013). For UV fluorescence imaging, a Tristandard MADATEC target is incorporated. The coupons are illuminated with MADATEC

LED CR500 UV lights and the camera is fitted with Hot Mirror and T*UV Zeiss filters.

2.3.3 Aging protocols

The accelerated ageing tests are conducted in different steps of exposure to H_2S, each with a duration varying between two and four days. For each step, the coated silver coupons and the polymer-only specimens are put inside a 22-liter glass container. A beaker with 50 ml of 1M HCl solution, heated to 45°C, is placed at the centre of the container and different amounts of BaS are poured into the solution to produce H_2S, in order to obtain a peak concentration comprised between 3.0 and 11.0 ppm in different steps. The total duration of the test can reach about 40 days. The H_2S concentration is monitored with a long-operating continuous detector based on a diffusion sensor (Riken Keiki HS-04) logging the H_2S concentration every five minutes.

2.4 Written documents

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2.4.1. State of the art

In this project we have performed research activities on several substrates (paper and proteinaceous materials) used for written and printed documents, and for photograph.

2.4.1.1. Ink

Ink represents a complex mixture composed of pigments suspended in a liquid carrier with binders and other additives [Pines, 1931]. A chronology of ink history is sketched in Figure 2.4.1:

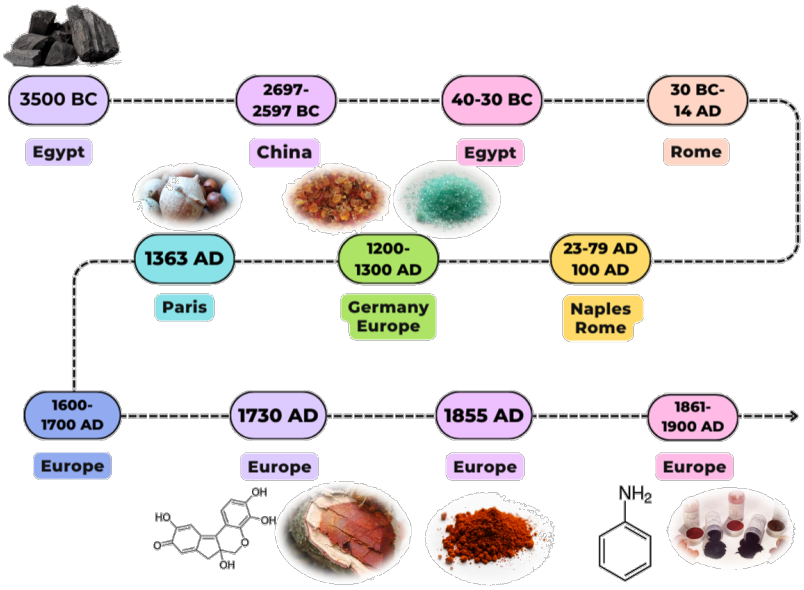

Figure 2.4.1. Schematic chronology of inks

Ancient scribes formulated the inks using carbon black suspended in an aqueous solution of gum, that had a role in keeping the fine carbon particles in suspension and thickening the writing fluid for easier application. In medieval times, iron gall ink gradually replaced carbon black ink. The first reference to an iron gall ink comes from the 11th century *Encyclopaedia of Christian arts* written by a monk named Theophilus who first described a method of preparation of this ink. Iron gall ink was the first to be obtained by a chemical reaction and despite the variability of its method of preparation, the historical recipes contain three main components: an extract of gall nuts, an iron salt and a binder. The chemistry of the preparation of iron-gall inks involves enzyme tannase that releases gallic acid and glucose through the catalytic hydrolysis of tannic acid found in the gall nuts extract. Then, when iron (II) is added it leads

to the formation of an iron gallate complex, then oxidized by dioxygen in the atmosphere to an iron (III) pyrogallate complex which is black in color (Hidalgo et al., 2018) Although literature on iron gall ink is quite rich, there is a limited literature regarding inks created by deliberately mixing charcoal with tannin extracts or iron gall ink, herein called *C-IGI* based mixed inks.

Recipes were collected for many different inks, including iron gall inks (IGI) and carbon-based inks (CbI). Their mechanism of degradation are affected by several parameters, including pH, light, microrganisms temperature. Several times mixed IGI-CbI were reported but very little is known on their recipe and degradation mechanism (Melo et al., 2022).

2.4.1.2 Paper

Paper is a common support for written documents, photographs and drawings. The microbiological effect on the paper is a complex interplay of microenvironmental conditions (temperature, humidity, light), chemical composition of the paper, and microbiological population. The microbiota is mainly composed by bacteria and fungi, with these latter responsible of the most dramatic changes in paper texture and strength. Indeed, they are able to produce extracellular enzymes, such as cellulase, xylanase, pectinase, and to produce and excrete pigments and organic acids. Monitoring and early detection of these biodeteriogens is essential to implement conservation strategies. Despite the high specificity and sensitivity of traditional approaches, they are time-consuming and expensive, and they need specific laboratory

equipment, which may not be suitable for real-time, on-site assessments. Moreover, the threshold of biodeteriogens concentration (CFU) over which the damage is perceptible by eye is still not completely clear. Indeed, no rules have been established until now for the limit of bacteria and fungi potentially dangerous for the material. Thus, there is the necessity of sensitive but not too specific methods to identify a wider range of fungi and bacteria potentially dangerous for the material.

To develop sound methods of paper preservation we have collected, isolated and maintained in culture 23 fungal strains from Italian Libraries and Archives. These strains will be used to develop tests on paper muckups that will be specifically designed. More detailed investigations are currently underway to assess the extent of microbiological degradation in three libraries identified by the Soprintendenza Archivistica e Libraria of Campania (Italy) as a part of the PNRR-PE project CHANGES, Spoke 5 (WP2).

2.4.1.3 Parchment and silk

Parchment and silk are integral components of cultural heritage but, like all materials, they are susceptible to deterioration. Due to their fragile nature, non-invasive techniques are essential for detecting degradation markers. Consequently, an in-depth evaluation of the effects of ion beam techniques on these materials, employing non-invasive spectroscopic methods, is critical. This type of approach can elucidate the extent of degradation and structural alterations resulting from varying proton beam dosages and aid in generating

chemical maps of the degradation markers.

2.4.2 Analytical protocols

2.4.2.1 Ink

The workplan involves mostly preliminary optical microscopy, followed by potentially non-invasive vibrational spectroscopies (FTIR and Raman spectrsocopies) and microinvasive chromatographic techniques coupled with mass-spectrometry (GC-MS). Elemental investigation has been conducted via SEM-EDS. Regarding written documents, this analytical approach can be employed to discover the ink recipe and the ink/paper degradation mechanisms, related to the presence of both carbon and iron gall in the composition of mixed inks.

GC-MS. A multi-step extraction protocol was performed to recover the organic components and then separate them into the three main classes of biomolecules. To separate the polar component (saccharides and proteins) from the non-polar ones (lipids and terpenoid acids), a liquid-liquid extraction was conducted, enabling the separation of the lighter, non-polar fraction. Lipids contained in the isolated apolar fraction undergo a transesterification reaction and were analysed as fatty acids methyl esters (FAMEs), rendering them analysable by GC-MS. Sugars were analysed as monosaccharides mixtures as they are more volatile and suitable for GC-MS analysis.

2.4.2.2 Paper

Fungi identification. For the identification of fungi growing on paper sterile swabs were used to collect samples from books and other works of art that showed obvious signs of fungal contamination. Subsequent isolation of different strains was carried out using different culture media, including PDA, MALT, YES, CYA and CD, followed by molecular identification using ITS markers (ITS4-5), Bt2a (β-tubulin) and CMD5 (calmodulin).

Immunosensor. A detailed investigation of biodeteriogens on paper was conducted aiming to identify the main issues, with fungi being identified as the primary target of interest. Then, to identify the best immunochemical approach, fungi were "classified" based on the main problems they cause, and a thorough search for commercially available antibodies suitable for our purpose began. Cellulase was the selected enzyme, due to the problems related to its activity. Standard cellulase isolated from *Thricoderma reesei* and specific antibody were ordered for preliminary tests related to the identification of microorganisms on paper.

2.4.2.3 Parchment and silk

A set of parchment and silk samples was exposed to proton beam irradiation at varying doses, ranging from 0.125 to 20 μC/cm², delivered by ATOMKI. The samples were subsequently analyzed using Micro Fourier Transform Infrared Spectroscopy mapping (μ-FTIR) with the iN10 FTIR microscope in mapping mode, covering the mid-infrared (mid-IR) and near-infrared (NIR) regions (7000–675 cm^{-1}).

Principal Component Analysis (PCA) and brushing techniques were employed to reduce data dimensionality and extract the most relevant variables associated with changes in the chemical structure induced by irradiation.

The analysis revealed that μ-FTIR mapping in the Near-Infrared (NIR) region effectively identifies modifications caused by proton beam irradiation. These insights are valuable in understanding the vulnerability of parchment and silk to ion beam analysis (IBA), thereby helping to define safe analytical conditions for such investigations.

2.4.3 Aging protocols

2.4.3.1 Ink

The Mockup composition was chosen according to literature and to our cases studies (see below): 60% $FeSO_4$ + 20% Gallic acid+ 20% Carbon.

IGI precipitate was prepared according to Ponce et al. (2016), the rest of the components were commercial ones. In order to discriminate the contribution of Carbon component and IGI components, both these inks were studied as well, along with the mixed ink. A set of ink mockups at increasing compositional complexity have been prepared, combining iron sulphate, amorphous carbon, gallic acid and ligands (Arabic gum or linseed oil). The thermal and microbiological aging in ongoing for substrate-free mockups (Alberico etal 2025). During the last year we expect to explore also the potential action of the substrate (paper and/or parchment) on ink aging.

2.4.3.2 Paper

Paper ageing is mainly the result of two competing reactions, one oxygen-dependent (atmospheric oxidation) and the other oxygen-independent. Ageing depends also on intrinsic characteristics of paper, but the accelerating effect of elevated temperatures on the rate of paper ageing has been early recognized. Moreover, the recognition of the

effects of moisture and the need to simulate natural ageing as much as possible led to some standardized protocols. As ageing procedure, we used the protocol ISO 5630-3. Moist heat treatment was performed at 80ºC and 65% RH.

3. Applications to case studies

3.1 Paintings

The microinvasive diagnostic that, by using a cellulose acetate sheet functionalized with trypsin, enables the direct digestion of proteins *in situ* on painted surfaces without the need for any physical sampling from the artwork, was successfully applied to five areas of the altarpiece San Francesco, currently under restoration at the Museo di Capodimonte. This analysis identified the protein binders used by the unknown artist, providing useful information to guide the restoration process.

3.1.1. Results from applying the analytical protocol are presented below. The investigations were conducted on both real artifacts and artificially aged mock-ups, the latter detailed in D2.1.

As part of a MOLAB campaign at the Egyptian Museum in Turin, we conducted MA-XRD, macro- and micro-XRF scans of the "Book of the Dead" of Kha. The scans focused mainly on areas exhibiting a noticeable glittering effect on the surface of the painted vignette, particularly in orpiment painted area. As in the case of the mock-ups (see deliverable D2.1), a significant presence of sulfur aggregates was detected not spatially correlated to arsenic, which rather appeared to be diffuse, as shown in Figure 3.1.1

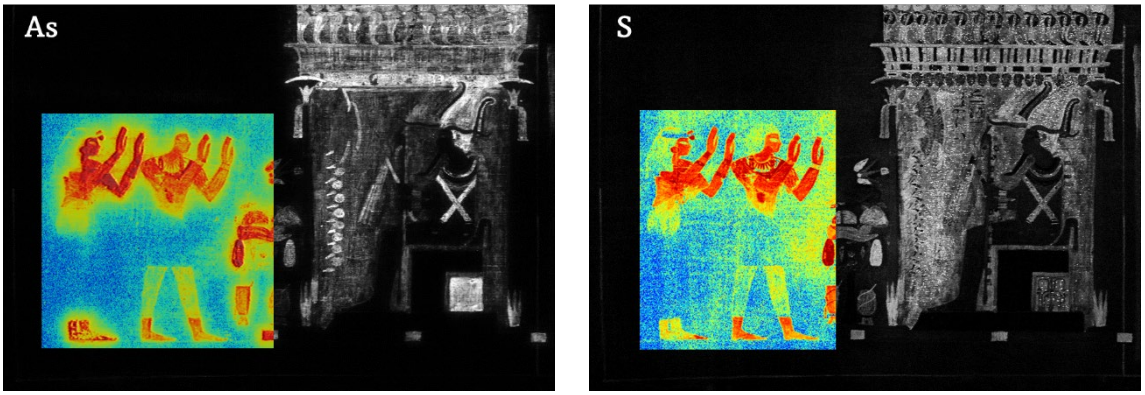

Figure 3.1.1 As and S spatial distribution maps. As diffusion is evidenced. S spatial distribution map features the loss of ornamental details and formation of sulfur aggregates.

Lead white, or ceruse, was one of the most widely used white pigments in classical European painting, from antiquity until its ban in the 20th century due to its toxicity. Although relatively stable, lead white is known to darken over time, especially in frescoes. Plattnerite (β-PbO_2), a black-brown mineral, has often been identified as responsible for this darkening. X-ray diffraction (XRPD) is commonly employed to analyse crystal structures, typically on samples or mock-ups. However, within the MOLAB project, in situ XRD measurements were successfully conducted in the Benedictine convent of St. John in Müstair, Switzerland. This in situ application enabled the identification of plattnerite in darkened areas Fig. 3.1.2.

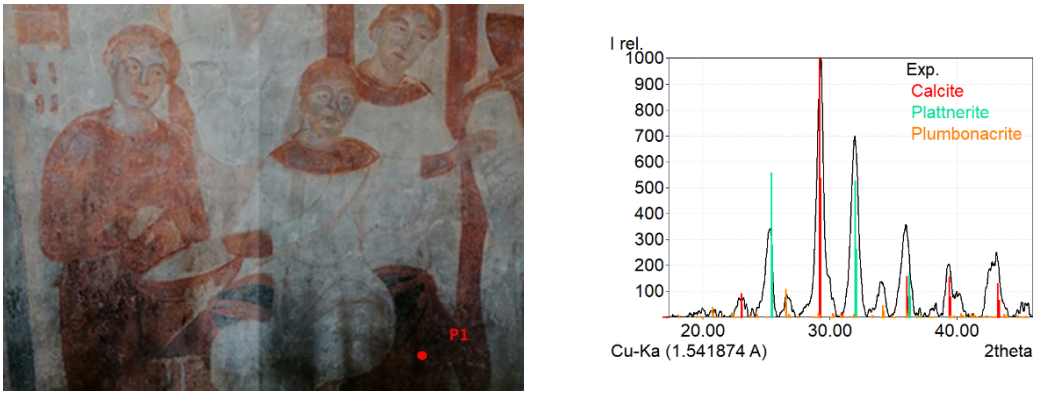

Figure 3.1.2 XRPD pattern acquired on black areas in situ at the Benedectine Convent of St. John in Mustair

3.2 Stones

3.2.1 Natural stones

IR spectroscopy has been applied to various geomaterials from archaological and architectural sites to monitor the degradation processes which can occur. Specifically, marbles from the archaeological site of the Holy Sepulchre are being analyzed to define a monitoring procedure of the degradation processes.

3.2.2 Mortars

The diagnostic approach above mentioned has been applied to historic lime-based mortars from the Baroque built heritage of Catania. These mortars are characterized by two different volcanic aggregates peculiar of the Etna territory, namely *azolo* and *ghiara*. The minero-petrographic and physical characterization of the mortars and the aging tests of laboratory replicas highlighted the different textural features of the two aggregates which lead to final products with unlike technological performances and diverse response to

decay processes. Additionally, mortars from the archaeological site of Cencelle have been also analyzed.

A minero-petrographic, chemical and microbiological analysis was carried out on the sculpture "Real Infante Carlo Tito di Borbone", recently attributed to Giuseppe Sanmartino. A combination of microscopic, spectroscopic, chromatographic characterization along with the isolation of the microbial population was adopted to evaluate the conservation state of the sculpture. The stone composition was characterized and both biodeterioration and traces of previous restoration were detected (Cappelletti etal 2023). Particularly, the isolate identified as *Sarcoladium subulatum* is reported for the first time as colonizer of marble work of art.

3.3 Written documents

3.3.1. Vanvitellian Ink

Raman micro-spectroscopy on Vanvitellian letters allowed to identify the inorganic composition of the inks. The molecular characterization resulted in a mixture of a) amorphous carbon, b) iron and other sulphates, with peaks around 986 cm^{-1} (green trace in Figure 3A) and c) the orgametallic species related to iron-gallotannates (1490 cm-1 and 1424 cm^{-1}, 500-600 cm^{-1}, blue trace in Figure 3.3.1) (Bicchieri et al., 2008).

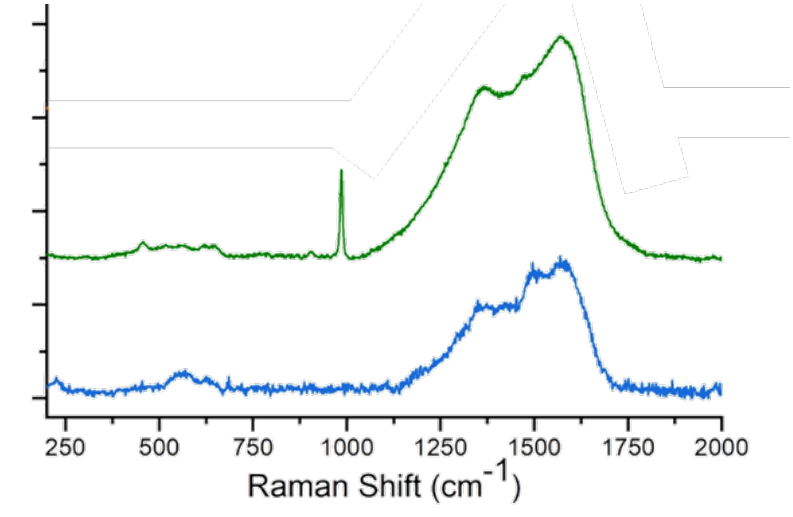

Figure 3.3.1. Representative Raman spectra of the inorganic composition the ink containing carbon (all traces); iron sulphate (green trace); gallotannate species (orange and blue traces); calcium oxalate (orange trace).

A common quite intense band can be related to calcium oxalates with bands at 1475 cm-1 and 909 cm^{-1} (Figure 3.3.2), as a major degradation product (Lee et al., 2008; Ferrer & Sistach, 2013). SEM-EDS analysis confirms that the inks is composed of various elements including S, Fe, K, Zn, Cu. The semi-quantitative EDS analysis provided the average mass composition in percentual terms of the three vitriols of Fe, Zn, Cu as 80/15/5, respectively. GC-MS identified several fatty acids, suggesting the use of vegetable oils, as linseed oil, used as binder in C-based inks.5 Although also gluconic acid and several monosaccharides as glucose, galactose and allose were identified. The presence of galactose, gluconic acid might be related to the hydrolysis and degradation of the arabic gum, used as binder in IGI.

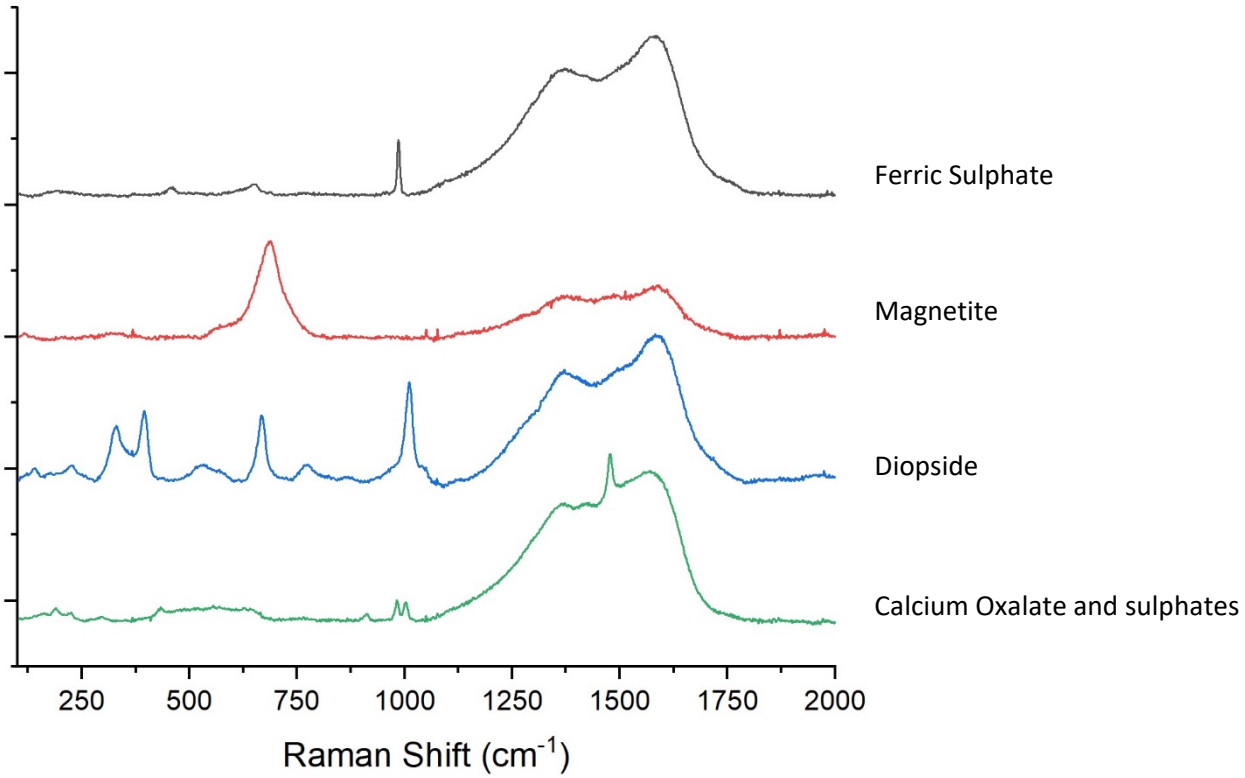

Figure 3.3.2. Representive Raman spectra of different chemical components found on Vanvitellian letters not directly related to iron gall or carbon inks.

3.3.2 Photograph by Robert Mapplethorpe

The microbial diversity of 'Skull and Crossbones', a 1983 photograph by Robert Mapplethorpe printed on silver gelatine, was assessed and the activity was published (Petraretti et al., 2024). We employed both culture-dependent and culture-independent methods to characterize microbial communities inhabiting this artwork. Vibrational Raman micro spectroscopy and FT-IR spectroscopy were utilized to assess the chemical degradation condition and characterize the chemical components of the silver gelatin print. The combination of molecular sequencing methods (Sanger and HTS approach) and non-invasive vibrational spectroscopy yielded valuable insights into the

microbial communities thriving on photographic material and the chemical degradation of the print. Isolated fungal strains were added to the Fungal Collection at the University of Naples Federico II, and their deteriorative potential was investigated by adding substrates, commonly used in canvas photographs to the culture media. These results establish a link between microbial communities colonizing ancient photographic materials, paper decomposition, and the enzymatic patterns of the retrieved microorganisms.

4. Concluding remarks

The results and outcomes of the activity reported in D2.2 are summarized in the following table:

	Diagnostic methods	*Degradation mechanisms*	*Publications*
PAINTINGS	XRF-based techniques; XRD-based techniques; Vibrational spectroscopies; UV-VIS-NIR spectroscopies; Electron microscopies; HPLC-MSMS; GC-MS; proteomic analysis	• Change of the oxidation state and/or the coordination environment of a specific element (e.g., lead, arsenic, sulfur, cobalt…) of selected pigments in different binding media • Pigment-binder Interactions giving rise to secondary organo-metal compounds (e.g., soaps, oxalates). • Deamidation of proteins used as binders	6 Articles - Botticelli et al *Heritage* 2024 -Ntasi et al *Heritage* 2024 -Alberico et al *Akta Imeko* 2024 - Preisler et al *Science Advances* 2024 - Monico L., Janssens K., Cotte M., Webb S. M. et al., *La Rivista del Nuovo Cimento* 2024. (Submitted). - Rosi F., Cartechini L., Monico L., Gabrieli F. et al., Fluorescence of Pigments in Late Nineteenth- to Twentieth-Century Paintings by Edvard Munch and Gerardo Dottori., Springer Series on Fluorescence. Springer, Cham., 2024. 24 Abstracts to Conferences -Cipolletta et al *MetroArcheo* 2023 - Ntasi et al *MetroArcheo* 2023 -Birolo et al *RAA* 2023 -Birolo et al *TECHNART* 2023 - Birolo et al *SCI ABC* 2023 - Cipolletta et al *SCI ABC* 2023 -Birolo et al *FEBS Congress* 2024 -Cipolletta *Workshop Omics & Heritage* 2024 - Caliri et al *EXRS* ***2024*** - Caliri et al *TECHNART* ***2023*** -Preisler et al *GRC* ***2024***

			- Preisler et al *MAXRF&RIS* ***2024*** - Preisler et al *TECHNART* ***2023*** - Ravan et al *Convegno Partenariato Esteso CHANGES* ***2025*** - Ravan et al *GRC* ***2024*** - Ravan et al *EXRS* ***2024*** - Ravan et al *TECHNART* ***2023*** - Romano et al *Convegno Partenariato Esteso CHANGES* ***2025*** - Romano et al GRC **2024** - Romano et al TECHNART **2023** -Monico L. et al., Convegno Partenariato Esteso CHANGES **2025** -Monico L. Science@CERIC 2024 Symposium **2024**. -Monico L. et al. INdAM International Workshop – MACH2023 **2023** -Monico L., XX Congresso Nazionale della Divisione di Chimica dell'Ambiente e dei Beni Culturali, Società Chimica Italiana, **2023**.
STONES	XRF-based techniques; XRD-based techniques; Vibrational spectroscopies; UV-VIS-NIR spectroscopies; Polarized optical microscopy Electron microscopy Mercury intrusion porosimetry Hydric tests	Alterations due to chemical, physical and biological causes (wetting-drying cycles, freeze-thaw cycles, sulfate attack, salt crystallization within the pore network, biological growths): • Loss of material, deposition and/or formation of secondary products; • reduction of mechanical resistance, chromatic alteration, etc. • Identification of microplastics outdoor, and their	4 Articles -Bretti & Belfiore *rXiv:2411.11129 [math.NA]* **2024** -Capozzi et al *Biology* **2023** -Capozzi et al *Chemosphere* **2024** -Rossi et al *J Haz Mat* **2025** 15 Abstracts to Conferences -Belfiore et al *Convegno Partenariato Esteso CHANGES* **2025** -Bretti & Belfiore *Convegno Partenariato Esteso CHANGES* **2025** -Braun et al *Convegno Partenariato Esteso CHANGES* **2025**

		potential action on stone Cultural Heritage	-Cappelletti et al *MetroArcheo* 2023 -Di Fazio et al *SGI-SIMP* 2024 -Fiorani et al *Convegno Partenariato Esteso CHANGES* 2025 -Masi et al *MetroArchaeo* 2024 -Medeghini et al *MetroArchaeo* 2024 -Medeghini et al *TMMCH* 2025 -Menta et al *SGI-SIMP* 2024 -Occhipinti et al *SGI-SIMP* 2024 -Rea et al (a) *SGI-SIMP* 2024 -Rea et al (b) *SGI-SIMP* 2024 -Rea et al (c) *SGI-SIMP* 2024 -Vergara et al *ICCE* 2025
METALS	XRF-based techniques; XRD-based techniques; Electron microscopies;	• Tarnishing of silver caused by sulphurisation due to atmospheric hydrogen sulphide (H_2S) and organic sulphur compounds	1 Abstracts to Conference Brancolini Metal 2025 -
WRITTEN DOCUMENTS	Vibrational spectroscopies; UV-VIS-NIR spectroscopies; Optical and electron microscopies; Immunochemical essays; DNA-analysis	Alterations due to chemical, physical and biological causes: • Degradation mechanism of C-based-iron gall mixed inks • Fungi-induced degradation on black & white photographs front and rear pages; • Decolouring effect due to fungi	1 Article -Petraretti et al *Her. Sci.* 2024 5 Abstracts to Conferences -Sannino et al *XXIV Convegno Nazionale di Micologia* 2024. -Alberico et al *INART* 2024a° -Alberico et al *INART* 2024b -Alberico et al *EUCHEM* 2024 - Ma et al. *CHEMCH* 2024

The above D2.2 results and some of the ongoing activities will be the ground for the forthcoming delivarable D2.3 ("Report on monitoring strategies and preventive conservation guidelines of heritage objects at degradation risk).

The research activity from UNIBO has been disseminated through 2 contributions to 2

conferences.

The research activity from UNICT has been disseminated through 4 contributions to conferences and in 1 submitted paper.

The research activity from UNINA has been disseminated through 17 contributions to 10 conferences and in 3 published papers.

The research activity from UNIROMA1 has been disseminated through 8 contributions to conferences.

The research activity from CNR has been disseminated through 16 contributions to conference and in 2 published papers.

The research activity from OPD has been disseminated through 1 contribution to 1 conference.

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