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Full Length Article

An interdisciplinary approach to a knowledge-based restoration: The dark alteration on Matera Cathedral (Italy)

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ABSTRACT

An interdisciplinary analytical campaign was carried out on the exterior walls of the *Santa Maria della Bruna and Sant'Eustachio* Cathedral in Matera. Large areas of these walls have become darkened and the main objective was to evaluate the state of conservation of the stone material (a very porous, organogenic limestone called "Pietra di Matera"), and to suggest the best strategy for the current restoration. Several techniques were used *in situ* and *ex situ*-in laboratory analyses: X-ray diffraction, infrared spectroscopy, ion chromatography, pyrolysis/gas chromatography coupled with mass spectrometry, colour change measurements, laser-induced fluorescence together with biological techniques. *Ex-situ* and *in situ* cleaning tests were also carried out on the stone surface.

The results showed the presence of chlorophyll and bacteria on the surface, together with sulfation and calcium oxalate films as the main decay phenomena. In addition, the determination of saccharide and egg residues suggest both biological activity and past conservative treatments as the cause of oxalate films. Data obtained from the analyses proved to be very useful for the conservation work; a complex plan of restoration was adopted, including both traditional and innovative techniques (such as biocleaning, bacterial-gel and a laser system) together with a final evaluation of several protective methods.

1. Introduction

Matera Cathedral was built in a Romanesque-Apulian style in the 12th century in the old part of Matera (Italy), called "*I Sassi*", which is an agglomeration of dwellings made of the local rock (tufa) from the Gravina torrent valley. Matera lies at the western edge of a UNESCO World Heritage site.

The exterior walls of the cathedral are made from the local organogenic limestone. The lower part of the walls (up to 6–8 m) have become darkened since at least the beginning of the 20th century (Fig. 1). This is of major concern because of the serious aesthetic damage to one of the most important landmarks in Matera. No historical information could explain the alteration, for example whether it originated from past surface protection treatments or to unknown phenomena affecting the stone inside.

Conservation work undertaken from 2014 to 2016 was a unique opportunity to examine the state of conservation of the surfaces, to provide new insights into the dark alteration and to propose a cleaning strategy. The characterization of the stone surfaces of monuments was very important in order to identify the decay phenomena, which could be both biological and chemical, and indirectly provides information on the conservation history of the building [1].

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Fig. 1. Facade of Matera Cathedral (Matera, Italy) with the dark alteration in the lower part of the structure (up to 6–8 m) and details of the niche with St. Eustache statue (above). The provenance of the samples (bottom).

Table 1
Description of the analytical campaign.

Wall surface	Phases and site	Methodology	Instruments/Methods/Materials
Step 1			
Sampling			Manual scalpel and cuts
Analyses	*In situ* analyses	Physical	LIF
	Ex situ analyses	Chemical	FT-IR, IC, OM observation, Py-GC–MS, XRD
		Biological	Microbial viable counts, ATP assay
Step 2			
Cleaning	*Ex situ* test	Chemical cleaning	H_2O_2, Oxone®, TiO_2, UV
		Biocleaning	Impact biogel
		Ablation	Laser
	In situ test	Chemical	AB57 Impact – poultice, H_2O_2
		Biocleaning	Impact biogel
Monitoring		Physical	Water absorption
		Optical	Colorimetric analysis
Protection		Chemical	FT-IR, Py-GC–MS
Step 3			
Cleaning	At *in situ* full scale	Chemical cleaning	Impact - poultice
Restoration		Ablation	Laser
		Chemical	Choice of the most effective protective agents

Due to the importance of the monument and the age of the dark alteration, an interdisciplinary team of experts in conservation science with complementary and multiple expertise and skills, including biologists, chemists, geologists, and physicists, was created in 2015 in order to plan an extensive analytical campaign, consisting of both *in situ* and *ex situ* analyses and cleaning tests (Table 1). A multi-technique approach prior to a conservation work is fundamental in order to consider and study the decay phenomena from various points of view. This strategy is also a good practice to reveal the artistic techniques, the provenance of materials, and the testing of restoration materials as evident in the recent literature [2–8]. In addition, the cleaning procedure represents a particularly delicate phase in terms of the monitoring, selection, and preventive evaluation of the effects produced by the intervention. Safety, both for the restorer and the environment as well as for the work of art, is of primary importance for deciding the best strategy.

During the first step of the campaign (Table 1), a non-invasive monitoring of the surfaces, based on the use of laser induced fluorescence (LIF), was planned in order to map the presence of biodecay phenomena and to verify a selection of cleaning methods, including a biocleaning treatment. The sampling of small fragments from the most representative altered areas was also performed and the samples were characterized by traditional and innovative techniques, in order to highlight signs of ongoing decay, which include inorganic and organic components and microorganisms. X-ray diffraction (XRD) and optical microscopy (OM) were used to highlight the mineralogical phases and to evaluate the stratigraphy of the mortar, Fourier transform infrared spectroscopy (FT-IR) was used to identify inorganic compounds, ion chromatography (IC) was used to quantify water-soluble salts, pyrolysis-gas-chromatography coupled with mass spectrometry (Py-GC–MS) were used to characterize the organic fraction. The results guided the removal of the decay, depending on the presence of biocolonisation or insoluble compounds.

The cleaning strategy was studied in Step 2 (Table 1), evaluating bio- and chemical- methods both in *ex situ* tests on stone specimens and in *in situ* experiments, also considering ablation by laser. The *in situ* tests were monitored by evaluating the colour changes of the surface. In addition, various protective agents were tested and applied *in situ*, evaluating the results with non-invasive reflectance FT-IR and Py-GC–MS on micro-fragments.

The results from Steps 1 and 2 were used to define the best cleaning method and the best protective agent. This was carried out during Step 3, and was completed in 2017. The data concerning the choice and monitoring of the protective agents are discussed in detail elsewhere [9]. Only some aspects are mentioned in the conclusions of this paper, in order to emphasize the importance of a preliminary analytical campaign in protecting the stone surface.

2. The experimental

2.1. Step 1

2.1.1. Sampling

Eight samples (C1-C7, OG) of "Pietra di Matera" and mortar (C4 sample) were taken from the stone surfaces of the southern wall and from the façade, both as powder and fragments scraped off the surface using a scalpel (Table 2). Selective sampling of C4 and C6 sample was carried out by a micro-lancet under an optical microscope, in order to analyse the three and two layers of the stratigraphy, respectively. The samples of powders for the biological analyses (B1–B4) were scraped off the surface with a sterile chisel (Table 2). Fig. 1 shows the sampling points.

2.1.1.1. "Pietra di Matera" specimens. A block of 36 × 22 × 25 cm (about 40 kg) was sampled at 1–1.5 m from the ground on the left external facade wall of the Cathedral and removed. It was cut

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