

Diagnostic study and efficiency evaluation of treatments against rising damp and salts crystallization in ornamental stones: the case of the green stone sacristy washbasin in the Church of San Domenico in Cosenza (Calabria, Italy)

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Abstract – The presence of water in masonry, especially in confined spaces, is one of the most important causes of deterioration of stone building materials. If water is present, particularly rising damp, degradation processes such as loss of surface material, encrustations, micro-cracks, salt efflorescences, etc., may arise and be intensified. Treatment against these phenomena is therefore strongly recommended for the protection and conservation of ornamental materials and buildings in general, before their restoration. In the present work, a multi-analytical approach was employed to study the stone materials and determine their state of conservation in the washbasin of the sacristy of the Church of San Domenico in Cosenza. The results allowed us to reveal details not visible to the naked eye that was important to conduct its conservation intervention. As for the state of conservation, the integrated use of various techniques enabled the detection of phenomena generally correlated with the occurrence of water infiltration and migration which appear to affect a large part of the area in which the asset is located, causing noticeable damage. Results concerning the cleaning, consolidating, and protective treatments on the artifact are also presented.

I. INTRODUCTION

Rising damp is undoubtedly the most widespread phenomenon that determines the presence of moisture in masonry, threatening the conservation of building materials with detachment, powdering, decohesion, salt crystallization, etc. Treatment against rising damp is generally recommended before carrying out a restoration

operation on ornamental or monumental works using the wide range of specific products on the market, appropriately selected based on the intrinsic properties of the material to be protected [1-2]. Only then, appropriate cleaning, consolidation, and protection operations could be carried out.

This contribution shows the results obtained on the characterization of the materials, the forms of alteration, and the cleaning treatments with both chemical and mechanical methods tested in the case study of the green stone sacristy washbasin in the Church of San Domenico in Cosenza (Figure 1). The artifact under study is a sacristy washbasin, used for preliminary ablutions before mass; the liturgical object is composed of a basin, surmounted by a wall element and flanked by three other elements with a decorative function.

Upon inspection, the stone artifact showed evident decay forms attributable to prolonged exposure to poor environmental factors and conservative conditions. In fact, the conservation state of an artwork is generally determined by multifactor, which may simultaneously occur: decay processes depend both on the environmental conditions to which the artifact/building is exposed (indoor or outdoor conditions) but also on the intrinsic features of the support, such as the different material compositions and the various manufacturing techniques. An accurate diagnostic investigation of both the constitutive material and the alteration and degradation phenomena allowed us to plan a suitable artifact's conservative work. Specifically, an in-depth study was first designed in order to analyze micro-fragments and powders taken from the ancient artifact. Seven samples were subjected to a complementary analytical approach

which included Polarizing Optical Microscopy (POM), Ion Chromatography (IC), Fourier transform infrared spectroscopy (FT-IR), and Scanning Electron Microscopy (SEM) coupled with microanalysis (EDS).

Then, having identified the conservation problems and the causes of decay, a detailed analytical approach was undertaken to conduct the restoration work.



Fig. 1. Green stone sacristy washbasin in the Church of San Domenico in Cosenza (Calabria, Italy).

II. SAMPLING AND ANALYTICAL METHODS

The sacristy washbasin was studied using laboratory investigations after obtaining some micro-samples of the material to be analyzed. Sampling (Figure 2) was performed with the assistance of the restorers and experts acting on behalf of the single-cycle degree course in Conservation and Restoration of Cultural Heritage of the University of Calabria, to collect representative micro-fragments useful for providing a correct interpretation of the data.

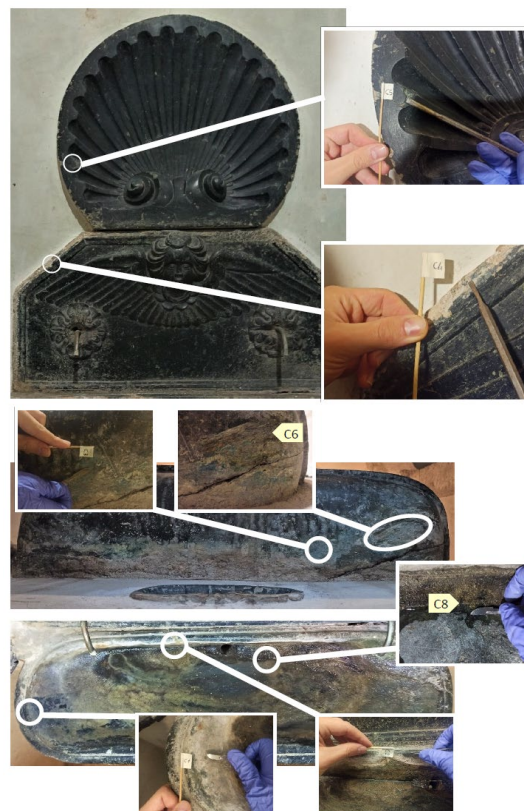


Fig. 2. Sampling points for the sacristy washbasin. Specifically, seven micro-samples were chipped-off from the object, using suitable stainless-steel tools (lancets and small chisels) to establish the composition of the raw materials and the possible presence of alteration products.

Diagnostic investigations of the selected micro-fragments were carried out using different and complementary analytical methodologies also chosen based on the amount of samples available.

Polarizing optical microscopy (OM) was used to define the mineralogical and textural features of the constituent material of the artifact (samples C4 and C5). Thin section observation was carried out through a Primotech 40 (Primotech Zeiss) microscope coupled with a digital camera to capture images.

Scanning Electron Microscope, ultrahigh-resolution SEM (UHR-SEM) ZEISS CrossBeam 350 equipment, coupled with a spectrometer EDS/EDAX OCTANE Elite Plus-Silicon drift type, was used to obtain information about morphology and chemical composition (in terms of major elements) of samples C4 and C5, investigating both the stone substrate and the patina of alteration present on the surface. Instrumental conditions set for EDS analysis were HV: 15 keV and probe current: 100 pA.

As far as FT-IR investigation is concerned, the used spectrophotometer was a Perkin Elmer Spectrum 100,

equipped with an attenuated total reflectance (ATR) accessory. Infrared spectra were recorded in ATR mode in the 500–4000 cm^{-1} wavenumber range, with a resolution of 4 cm^{-1} . The survey allowed us to investigate alteration products. Due to the complexity of the FT-IR absorbance profiles, the samples' spectra were also compared with those of standard minerals and/or organic compounds from databases and literature for a reliable assignment of the bands [3-4].

Ion chromatography (IC) is to determine the nature of the salts dissolved in the substrate and to characterize the degradation forms that can be induced in the constituent material due to repeated crystallization cycles. For this reason, IC was performed to quantify cations (NH_4^+ , K^+ , Na^+ , Mg^{2+} , and Ca^{2+}) and anions (Cl^- , NO_3^- , and SO_4^{2-}) on the superficial layer.

A list of the examined micro-samples, brief descriptions, and the analytical techniques used are summarized in Table 1.

Table 1. Samples taken from the Washbasin, brief description, and analytical techniques employed. Notes: FT-IR: Fourier transform infrared spectrophotometer; IC: Ion Chromatography; OM: Optical microscope with polarized light; SEM-EDS: Scanning Electron Microscope connected to an energy dispersive microanalytical system.

Sample ID	Sampling Area	Brief description	Methods
C1	Washbasin bottom	Thin encrustation	FT-IR, IC
C2	Washbasin internal part	Thin reddish encrustation	FT-IR, IC
C3	Washbasin base	Thin greenish-blue patina	FT-IR, IC
C4	Left edge of the basin with bas-relief	Constituent stone material	OM, SEM-EDS
C5	Shell basin edge	Constituent stone material	OM, SEM-EDS
C6	Washbasin base	Altered constituent stone material	FT-IR, IC
C8	Basin bottom	Plastic fragment of probable restoration	FT-IR

The results of the diagnostic investigations made it possible to plan the conservative restoration intervention, starting from the cleaning procedure up to the consolidation of the liturgical object. The artifact was subjected to: a) desalination cycles using ion exchange resins (i.e., strong cation exchange resin), b) cleaning

procedures with tetrasodium EDTA and quaternary ammonium salts, c) the removal of the most tenacious encrustations using mechanical cleaning methods (i.e., scalpel and micromotor). All procedures were carried out after preliminary in situ tests in order to evaluate step by step the effectiveness of the products used and considering the nature of the incrustations/alterations to be removed, without ever damaging the constituent material.

III. RESULTS AND DISCUSSION

Samples C4 and C5 (Figure 2; Table 1) were subjected to minero-petrographic and geochemical studies to characterize the material and alteration forms.

The OM allowed the identification of the C4 and C5 micro-fragments as Chloritoschisti (or Chloritic Schist), a green metamorphic rock essentially composed of minerals of the chlorite group (i.e., phyllosilicates such as chlorite and clinocllore). Epidote and zircon have been identified as accessory minerals. Calcite veins are also present (Figure 3). A patina with a thickness between ~ 50 and 500 μm was also identified on the edge of the section of both samples (Figure 4). It is fairly adhered to the stone substrate, with jagged morphology and the presence of micro-fractures. Given the dominant presence of microcrystalline calcite (micrite), it almost certainly has a carbonate composition; rare oxides can also be observed inside (Figure 4). The OM investigations of samples C4 and C5 were deepened by SEM-EDS. The dominant presence, in both sections investigated, of minute crystals distributed in fibrous-acicular aggregates is further confirmed; the chemical investigation (EDS), ascertains the presence of chlorite and clinocllore, followed by sporadic crystals of titanite and ilmenite. Moving the attention towards the edge of the section confirms the presence of a thin surface patina with a thickness close to 500 μm , already observed using OM. The chemical investigation performed by EDS microanalysis (in terms of major elements) ascertains its carbonate nature. The elemental composition also reveals a minimal presence of sodium, chlorine, and sulfur, with traces of copper.

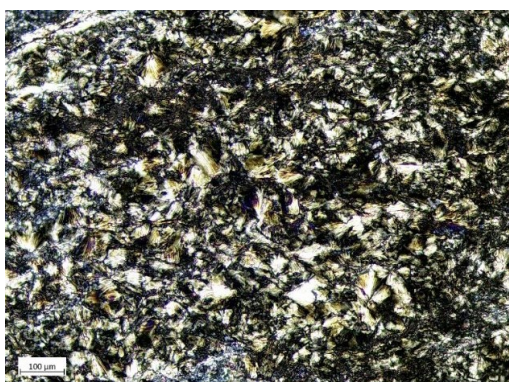


Fig. 3. Thin section photomicrograph of sample C4.

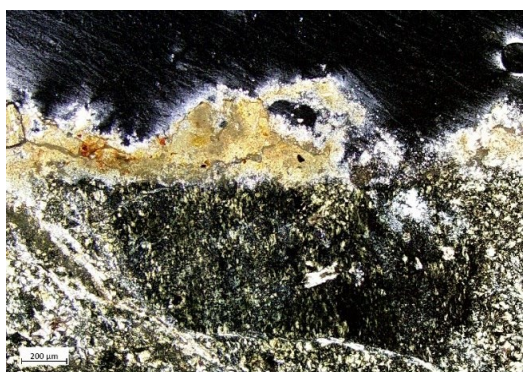


Fig. 4. Thin section photomicrograph of sample C4 with alteration patina.

Infrared spectroscopy was essentially addressed at eventually identifying inorganic (i.e., mineralogical phases resulting from alteration processes) and organic (products resulting from any restoration work) compounds within the samples. All the analyses referred to samples ground by an agate mortar and pestle. A representative spectrum is reported in Figure 5. Specifically, the acquisitions allowed us to identify: a) the stretching vibrations of calcite, with characteristic peaks at ~ 1492 , 429 , 879 , and 706 cm^{-1} , and the presence of silicate compounds with intense absorption bands at $\sim 1000 \text{ cm}^{-1}$ attributed to Si-O vibrations, in all samples; b) the presence of gypsum, with characteristic peaks at about 3500 , 3400 , 1700 , 1600 , 1150 , 1100 , 700 and 600 cm^{-1} only in samples C3 and C6; c) the presence of hydromagnesite, with absorption bands at ~ 800 , 850 and 880 cm^{-1} and around ~ 1420 and 1480 cm^{-1} , only in samples C1 and C2; d) the presence of bands compatible with a siloxane polymer in C8.

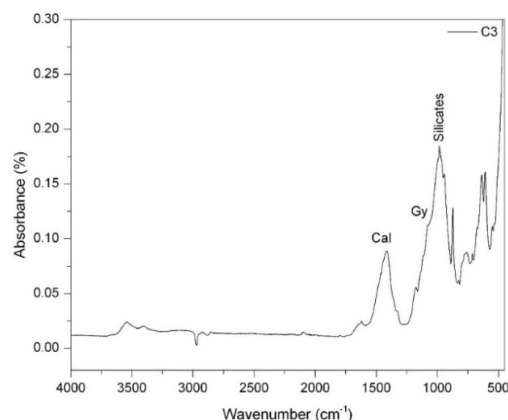


Fig. 5. FT-IR spectra of sample C3.

The ionic species present in the solution inside of the stone constituting the washbasin have been investigated. The main salts detected are sulfates and carbonates. Specifically, the data suggest the presence of calcium sulfate, magnesium, and more rarely sodium. The differences between the soluble species detected in the samples taken inside the basin (C1 and C2) and those on the bottom (C3 and C6) should be highlighted. In particular, the samples from the bottom of the basin (C3 and C6) contain low concentrations of alkaline ions (i.e., Na^+ , K^+), perhaps due to the greater rising damp deriving from the underlying wall with which the lithotype (washbasin) is in close contact; these conditions can inhibit the precipitation of sodium/potassium salts since the latter are generally more soluble than calcium/magnesium salts [5-6]. Considering the scarcity of sodium ions and the low magnesium ion content for C3 and C6, gypsum may have crystallized as one of the main salts in these samples, but not the only one. Among the recognized salts, gypsum has the highest deliquescence RH, which stands at around 99.6% at 20°C , which implies that this phase is stable even in conditions of extreme humidity. The presence of gypsum as the dominant phase is confirmed by the FT-IR investigation which detects this crystalline phase only in C3 and C6. With regards to carbonates, Ca^+ is the cation present in all samples, particularly in those coming from inside the basin (C1 and C2), the presence of carbonates could be partly attributed to the intrinsic composition of the investigated materials and/or their long-term coexistence with calcium-rich materials (e.g. plasters, lime mortars, etc.), even under humid conditions. Both ways can be pursued, in fact: a) sample C2 comes from inside the basin near the water drainage and stagnation area. This condition would have favored the formation of carbonates; b) for samples C2, C3, and C6 the formation of carbonates could be related to the presence of plaster/mortar near the sampling areas. The data obtained are in line and represent a further confirmation of what has already been observed by FT-IR.

IV. CONCLUSIONS

In this study, a multidisciplinary investigation was carried out to determine the material features and state of preservation of an ancient sacristy washbasin. The study deals with the decay affecting the artifact and provides an in-depth scientific survey performed to understand and demonstrate the causes of deterioration, before restoration.

Specifically, investigations performed on the constituent materials (i.e., C4 and C5) by using both OM and SEM-EDS revealed that samples have mineralogical and geochemical parameters compatible with a Chloritoschist.

As regards the state of conservation, inherently to the surface patina present in both samples (i.e., C4 and C5) it can be assumed that: a) the presence of calcium carbonate in the patina is due to traces of mortar present on the surface of the lithotype near the sampling area; b) the presence of sodium, chlorine, copper, and sulfur may derive from an alteration of the material due to the presence of soluble salts deriving from an alteration of the artifact and/or from the exposure environment (presence of humidity, rising damp, etc.).

As far as the FT-IR investigations are concerned, samples C1 and C2, both taken from inside the basin, respectively from the bottom and a side portion, are mainly carbonate encrustations (calcium carbonate and hydrated magnesium carbonate). These encrustations almost certainly derived from the flow and consequent stagnation of the mains water inside the basin. As regards the presence of silicate compounds, they would derive from the rocky substrate which, from the OM and SEM-EDS investigations, appears to be a chloritoschist: a metamorphic rock essentially composed of minerals of the chlorite group (i.e., phyllosilicates). Samples C3 and C6, from the external bottom of the basin near highly detached areas, and with micro-fractures, are encrustations of a compositionally similar nature with respect to samples C1 and C2. In addition, the presence of a chalky component is noted. The latter could have different origins; for example, it could derive from the materials constituting the monument or closely adjacent to it, or have a completely different source, i.e. external and/or relating to the confined environment. Both options are feasible in this study. The plaster may have originated a) from the plaster/mortar that covers the wall surfaces of the room in which the stoup is located and with which it is in close contact; b) from the basement of the building; in the latter case, the sulfate species may have been dissolved in the ground water and by capillary action may have reached the stoup where they gave rise to precipitation phenomena on the surfaces of the walls. In this regard, it should be remembered that the washbasin is

located near a sacristy, in a very humid environment with evident capillary rising damp phenomena. Finally, sample C8, consisting of a plastic material interposed in a micro-fracture, between a layer of grouting and the rock constituting the stoup (probably a previous and undocumented restoration intervention), is compatible with a siloxane polymer, although the presence also of calcite and silicates as for other samples. Finally, the IC data are in line with the FT-IR one, and suggest that the main salts detected causing decay processes inside the artifact are sulfates and carbonates.

Through studying alteration and degradation phenomena affecting the constitutive material, it was possible to define a conservation plane to remove the patinas, and the encrustation layers, and consolidate and preserve the materials against the possible arising of new decay phenomena mainly due to environmental conditions.

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