

Mineralogical and petrographic analyses of a complex finishing plasters stratigraphy from a 17th century Sardinian Church

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Abstract – The work concerns the study of the original layers of mortar and finishing used in two historical phases of the Church of Madonna d'Itria in Orani (central Sardinia, Italy) which was built in the 17th century. The aim is to analyse the finishing pigmented layers that were superimposed between the 17th and 20th centuries. Furthermore, the study includes the analysis of the mortar substrate on which the pigmented layers were applied, to study their adhesion, mechanical resistance and composition. The general aim of the work is to highlight the techniques and raw materials used for made the finishing plasters and the presence of chemical-physical alteration processes aimed at restoration interventions.

I. ARCHITECTURAL FEATURES OF CHURCH

The main façade of Madonna d'Itria from Orani (Fig. 1), is surmounted by a curvilinear tympanum, has a small rose window above the entrance portal. On the northern façade of the monument is the tall square-plant bell tower of late Baroque style. The single-nave, barrel-vaulted building with narrow side chapels features a Gothic-style presbytery with a ribbed cross vault. This is decorated with *mezzo-fresco* [1] paintings from the late 17th century depicting angels and cherubs playing music, and in the apse the Triumph of Christ and the Last Judgement. The main altar houses the valuable wooden sculpture dedicated to the Madonna d'Itria, dating back to the 17th century, decorated with the *estofado de oro* technique. The façade features *graffito* created in 1958 by Costantino Nivola, representing the battle of Lepanto. The research aim is to study the compositional features of mortars and paints used in different times on the main façade of the Church according to the methodologies and analytical techniques well known in the literature [2, 3, 4].



Fig. 1. Façade of the Madonna d'Itria Church from Orani village (Central Sardinia).

II. ANALYTICAL METHODS

To study the mineralogical and petrographic characteristics of finishing plasters, optical microscopy in reflected light (OM-RL) was used, using an Olympus DSX100 digital microscope.

X-ray diffraction data on polycrystalline samples were first performed for a qualitative phase analysis, at the Department of Chemical and Geological Sciences (University of Cagliari, Italy). A PANalytical X'Pert Pro diffractometer (Malvern-PANalytical, Almelo, Netherland) was used, operating in θ - θ geometry and with Ni-filtered Cu-K α radiation, equipped with a Real Time multiple

strip (RTMS) X'Celerator detector. Data collection conditions were: 5–70°2 θ -range, step-size 0.008°2 θ , 0.19 s per step, 40 kV and 40 mA. Data were processed by the X'Pert HighScore Plus (TM) 2.1.2 software and using the PDF2 database (release 2010 by ICDD, Newtown Square, PA, USA). SEM analyses were performed on ten selected samples using a Quanta Fei 200 microscope equipped with a ThermoFischer Ultradry EDS detector. Raw samples were put into the sample chamber without conductive coating to preserve them for further analyses. Therefore, low-vacuum conditions (0.3 to 0.5 torr) were used to dissipate electrons from incident beam. Variable spot sizes of 4–5 (in arbitrary units given by the Quanta Fei equipment) and accelerating voltage 15–25 kV were adopted during the analytical sessions. Infrared micro Raman scattering measurements were carried out in back scattering geometry with the 1064 nm line of an Nd:YAG laser, by a compact spectrometer B&WTEK (Newark, NJ, USA) i-Raman Ex integrated system with a spectral resolution of 8 cm⁻¹. Spectra were collected with an acquisition time of about 30–60s and power excitation between 20 and 40 mW concentrated in a spot of 0.3 mm² on the surface through a Raman Video MicroSampling System (Nikon Eclipse for high-resolution and BAC151B in the other case) equipped with 20X/50X Olympus objectives. Other physical laboratory tests on the specimens performed according to Columbu *et alii* [5].



Fig. 2. Detail on a portion of top façade (near to the timpano) with different mortars and finishing paints.

III. RESULTS

A. Façade stratigraphy

The stratigraphy of the Church's façade is complex due to the presence of different construction / intervention phases to which the materials refer (Fig. 2). By macroscopic and microscopic observations, in chronological order, the finishing works (plaster, pigmented mural paintings, etc.) on the Church's façade are shown as follows.

Three different layers can be identified from the original

phase of the Church's initial construction (17th century), prior to Nivola's artistic phase:

- bedding mortar for the façade masonry;
- original plaster mortar likely dating between the Church's construction phase (17th century) and the early 20th century;
- ochre-coloured finishing paint overlying and adhering to the above-mentioned plaster mortar (not analysed in this preliminary research).

On the façade (Fig. 2), above the original ochre paint (17th century), a pink finishing paint can be observed, applied between the 17th and 20th centuries.

Furthermore, the mortars of the decorative cornice at the top of the façade, the ochra-yellow finishing overlying and adhering to the cornice mortar, and the red finishing paint overlying the plaster or sometimes directly adhering to the cornice mortar, belong to the original phase.

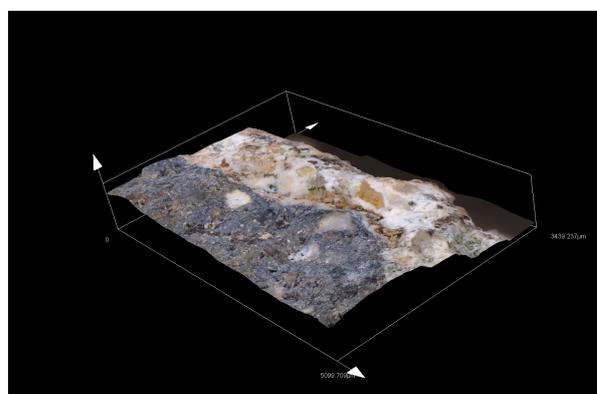


Fig. 3. 3D view image by digital optical microscopy of a sample with two mortars layers (greyish and whitish) made by Nivola on the façade.

Recognizable from Nivola's intervention phase are:

- squaring and gap-filling mortar (not analysed) applied as a base over the original plaster mortar of the façade, used to prepare and level the substrate;
- layer of originally white (lime-based) paint (*scialbo*) applied only on the upper part of the façade to provide a light background on which to apply the subsequent blue paint;
- dark plaster mortar (greyish 1st innermost layer, Fig. 3, 4) adhering directly to the original plaster mortar from the original phase (?) and to the base plaster mortar prepared by Nivola;
- plaster mortar (whitish 2nd outermost layer, Fig. 3, 4);
- blue paint present on the upper part of the façade and adhering partly to the original plaster mortar and partly over the white lime paint (*scialbo*), sometimes slightly light blue in colour due to the overlying layer of blue paint (Fig. 2);
- blue paint present on the base of the façade and adhering to the original plaster mortar (Fig. 2).



Fig. 4. Detail of greyish and blackish mortar works by Nivola on the façade of the Church.

B. Compositional analyses

The results of petrographic, XRD and SEM analyses indicate that the samples from the recent phase (20th century) show a different composition with respect to the proportions of binder and aggregate of the original mortar layer of the 17th Church.

The two mortar layers, belonging to the recent finishing interventions made by Nivola artist (in 1958), in turn have different features. The external whitish mortar layer (Fig. 3, 4) has a lime-based binder (now carbonated in calcite) and an aggregate composed of quartz, plagioclase, K-feldspar and phyllosilicates (biotite and chlorite). The internal greyish innermost layer has a similar composition in the aggregate while the binder appears different in macroscopic characteristics with a dark colour.

Two significant differences are also observed, the second mortar layer has a much higher content of feldspars and especially chlorite which in the first mortar layer is almost absent.

Furthermore, in the first layer in the XRPD analysis pattern peaks between 30° and 45° are observed compatible with the presence of tobermorite-type phases typical of cements and/or hydraulic limes. Such peaks are absent in the first mortar layer.

Finally, the first dark layer of mortar presents a higher background which suggests the presence of a certain quantity of amorphous or slightly crystalline phases, a characteristic compatible with the presence of a certain quantity of hydraulic binder (C-S-H or C-A-H phases), or deriving from the residual amorphous phases of ashes from burning wood (or coal) probably used in the mixture by Nivola to darken the mortar [6].

Results of Raman analyses performed on the surface pigments of finishing paint layers of façade show a

different composition between the pinkish pigmented fine lime-based paint realized before 20th century (Fig. 6, Tab. 1) and the recent 20th century blue finishing plaster on upper façade by Nivola artist (Fig. 7, Tab. 2).

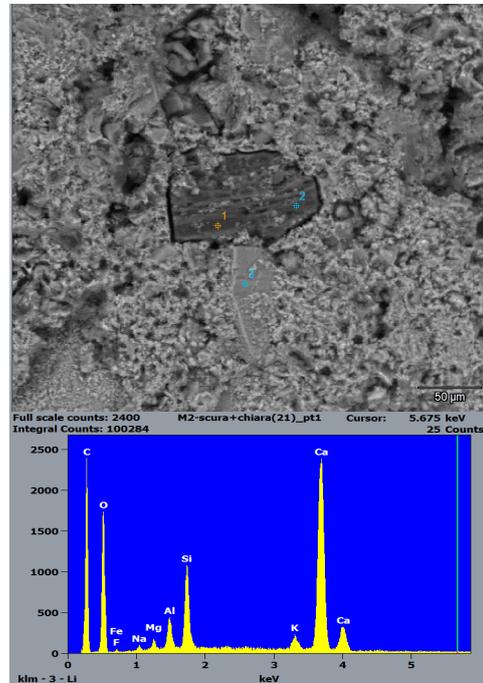


Fig. 5. Detail of the first greyish mortar layer in a hydraulic binder-rich area with a organic fragment (from the structure it could be wood or coal; note the intensity of the carbon signal in the spectrum of points 1 and 2); analysis point 3 refers to a K-feldspar of aggregate.

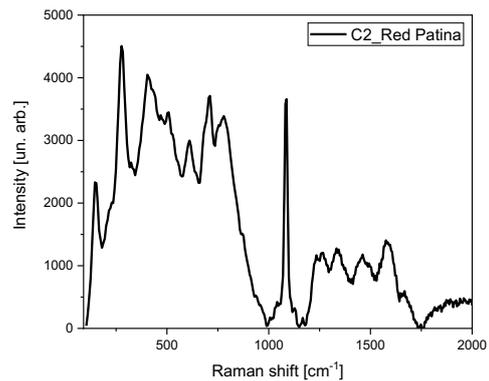


Fig. 6. Raman pattern of pinkish pigmented paint present in the façade (realized in 17th-20th) of the Church.

The pinkish pigment shows a based hematite composition, while the blue pigment used by Nivola a mix of azurite and subordinated Scheele green and lazurite.

Picks (cm ⁻¹)	Intensity	Phase/Crystal
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155	Medium	Calcite
225	Medium	Hematite
279	Strong	Calcite
410	Medium	Hematite
493	Medium	Hematite
615	Medium	Hematite
710	Medium	Calcite
780	Medium	Luminescence
1087	Strong	Calcite
1260	Weak	Binder
1347	Weak	Binder
1453	Weak	Binder
1583	Weak	Binder

Tab. 1. Results of Raman analysis of pinkish pigmented patina from the original façade (17th) of the Church.

IV. CONCLUSIONS

Laboratory results indicate that the original plaster mortar on the Church façade was made with a binder based on non-pure hydrated lime (which subsequently carbonated poorly) and with an unselected silicate aggregate, which was washed before use. By contrast, the mortar of the cornice appears to be significantly better made, using a pure, well-carbonated and compact binder (very light in colour) and a selected, clean silicate aggregate. Above the cornice and façade mortars, original ochre-yellow and red coloured paints can be observed and, in some areas, a pink-coloured hematite-based paint, attributable to prior to the Nivola period, which occurred between the 17th and 20th centuries. Regarding Nivola's artistic interventions, the dark mortar and the overlying whitish mortar applied to the façade to create the 1958 drawing of the Battle of Lepanto, two different mixes are evident.

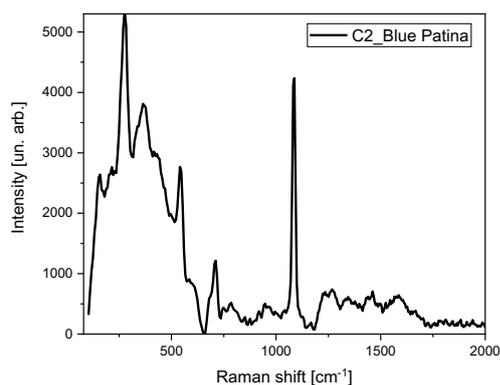


Fig. 7. Raman pattern of blue pigmented paint present in the upper façade of the Church.

The dark base internal layer shows a hydraulic binder consisting of silicates and hydrated aluminates of calcium (attributable at least in part to the cementitious C-S-H and C-A-H phases) associated with calcite (from carbonation of the hydrated lime), and a silicate aggregate consisting

of quartz, K-feldspar, plagioclase, and crystalline phyllosilicate phases likely originating from granitoid rocks. For the external whitish layer, a binder based on hydrated lime (now carbonated to calcite) and a silicate aggregate very similar to that of the previous layer were used. On top of the pre-existing mortars, partly original, partly belonging to the lime-based plaster base applied by Nivola himself to level the external surface, in the upper part (tympanum) and at the base of the church's façade the artist used as a blue lime-based paint using a pigment mix of azurite and subordinated Scheele green, lazurite.

Picks (cm ⁻¹)	Intensity	Phase/Crystal
159	Medium	Calcite
281	Strong	Calcite
377	Strong	Scheele green?
427	Medium	Azurite?
542	Medium	Lazurite?
711	Medium	Calcite
1084	Strong	Calcite
1256	Weak	Binder
1363	Weak	Binder
1455	Weak	Binder
1582	Weak	Binder

Tab. 2. Results of Raman analysis of blue pigmented patina from the upper façade of the Church.

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