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ORIGINAL ARTICLE

The Cathedral of S. Giorgio in Ragusa Ibla (Italy): characterization of construction materials and their chromatic alteration

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Abstract The Cathedral of St. Giorgio in Ragusa Ibla (Sicily) is one of the most important Baroque monuments of eastern Sicily. The restoration of the monument underway has put forward notable questions regarding the stone materials used and their state of degradation. The façade appears to be made mainly of a creamy white calcarenite, and of mortars and plasters. However, detailed analysis has highlighted a more complex use of the raw material. The mortar and plaster have a different composition in regards to their architectural use while the natural stone material is distinguished not only by a creamy-white calcarenite but also by a dark coloured bituminous calcarenite (pitch rock), which now appears whiter because of superficial chromatic alterations. This process was reproduced in the laboratory using an accelerated aging technique on samples of bituminous calcarenite, which allowed the cause of the alternation to be identified as photo-oxidation of the asphaltenes. Following this process of photo-oxidation, other forms of chromatic alterations affected the façade (brown–orange-coloured patinas). FTIR, Scanning Electron Microscope and thin section microscopic observation allowed the characterization of also the products of this process to be carried out, highlighting the complex mechanism which the processes underwent.

Keywords Construction materials · Ragusa Ibla · Italy · Chromatic alternation · FT-IR

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Introduction and historical notes

The diagnostic analysis of the degradation process of the monument stone has acquired ever more importance regarding their restoration and maintenance. Such studies require analysis of the materials used and an accurate characterization of the degradation products with the aim of evaluating the effects of the degradation (Bulakh et al. 2005). The Baroque monuments of eastern Sicily, which have only recently become part of the listed heritage of UNESCO, are often subject to the intensive processes of degradation, which may be cause of irreparable damage to these important historical and artistic buildings. However, research into the causes of this phenomenon is fragmented and for this reason, this paper proposes a new contribution to safeguard of one of the greatest expressions of Sicilian Baroque buildings, the Cathedral of S. Giorgio.

The Cathedral of S. Giorgio in Ragusa Ibla, which was designed by Rosario Gagliardi, has one of the most beautiful façades of eastern Sicily Baroque architecture. It has three super-imposed levels forming a pyramid shape, which is topped with a bell-tower and dome (Nifosi and Leoni 1998).

The façade is apparently constructed from the exclusive use of creamy-white calcarenite. According to historic information (Valente 2001), the buildings of the Ragusa area were built from locally quarried stone material. After studying historical documents and following a careful macroscopic examination, the use of bituminous calcarenite which is locally called "pitch stone" or "asphaltic stone", was used in some architectural elements as can be seen from the lithological mapping of the main prospect (Fig. 1a). The bituminous calcarenite was initially used only for the first order capitals. Subsequently the second

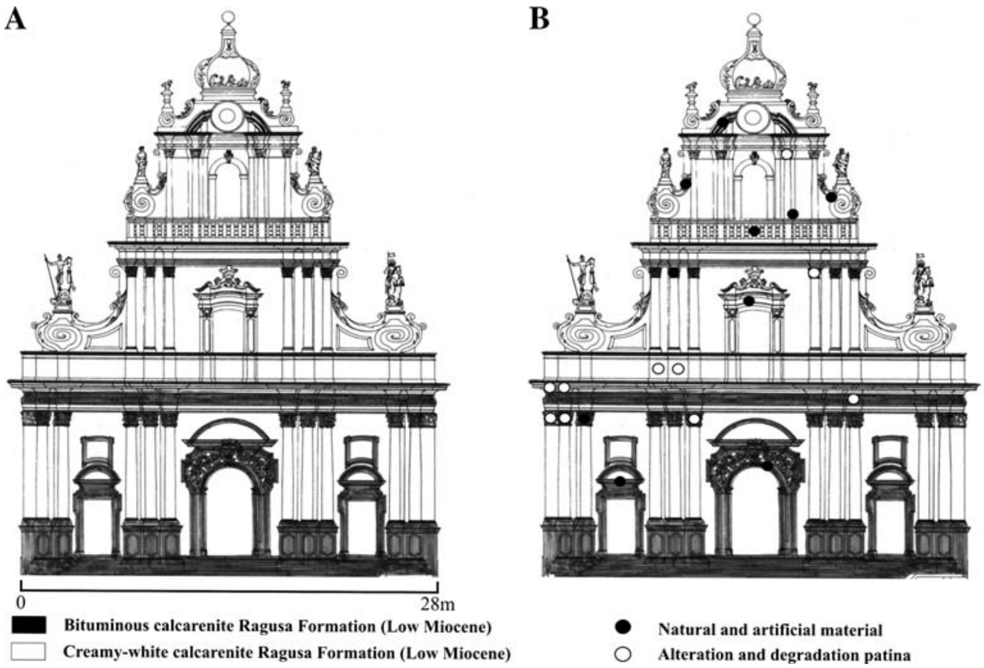


Fig. 1 **a** Lithologic map of the natural stone material used in the Cathedral; **b** positions of sampling points

order capitals, the cornices, and the decorative elements of the three doorways were substituted by those in bituminous calcarenite, still visible today. In addition, in the 1800s, the use of this material was extended also to the segments between the rib of the dome, to the horizontal framing of the dome-lantern complex, to the pine cone at the top of the dome and to the internal and external basements.

The decision in the past to use "pitch stone" supporting the calcarenite was connected to not only its excellent physical-mechanical properties (Fianchino 1988) but also to the desire to obtain an esthetic, bichromatic effect as is evident in other baroque period monuments of Ragusa such as the Badia, the church of the S. Francesco all'Immacolata, the entrance door and balconies of Sortino—Trono and the Cathedral of S. Giovanni.

Regardless of the importance of the monument and the diverse conservation measures carried out on it in the past, the Cathedral of S. Giorgio shows numerous forms of degradation: (a) chromatic alterations caused by the whitening of the "pitch stone"; (b) brown–orange-coloured chromatic alterations on almost all of the façade; (c) detachments which involves the base of some columns and some superficial plaster; (d) differential crumbling, present in some columns; (e) lichen colonies on the statues of the façade and on some columns; (f) black crusts localized on the capitals, on the base of some columns and under the balustrade.

Sampling and analytical methods

From the monument façade 25 samples of natural and artificial stone material were taken including their degrading products (Fig. 1b).

With the aim of finding a complete characterization of the material and the products of alteration and degradation, diverse analytical techniques were carried out on the samples: (a) thin sections petrographic analysis; (b) Fourier transformed infrared spectroscopy (FT-IR). The equipment used is a Nicolet 380 with a Smart Orbit accessory having the following measuring conditions: Number of sample scans 32, Resolution: 4.000, *X*-axis: Wave numbers (cm^{-1}), *Y*-axis: Absorbance; (c) Scanning Electron Microscope analysis (SEM) an Esem Quanta 200 by Fei/Philips; (d) X-Ray fluorescence (XRF) chemical analysis carried out with Philips PW2400 spectrometer.

Of the six samples taken from the monument, and five samples taken from the Streppenosa quarry (Ragusa) where the pitch stone is stilled quarried today, accelerated aging processes were carried out using a 300 W OSRAM Ultravitalux lamp with a UV-A component. The samples were placed at a 15 cm distance from the UV source while the temperature was kept at a constant using a ventilation system. The parameters of illumination and the UV-A component were controlled by a psycrometer, whereas a data-loger connected to a sensor was used for the temperature.

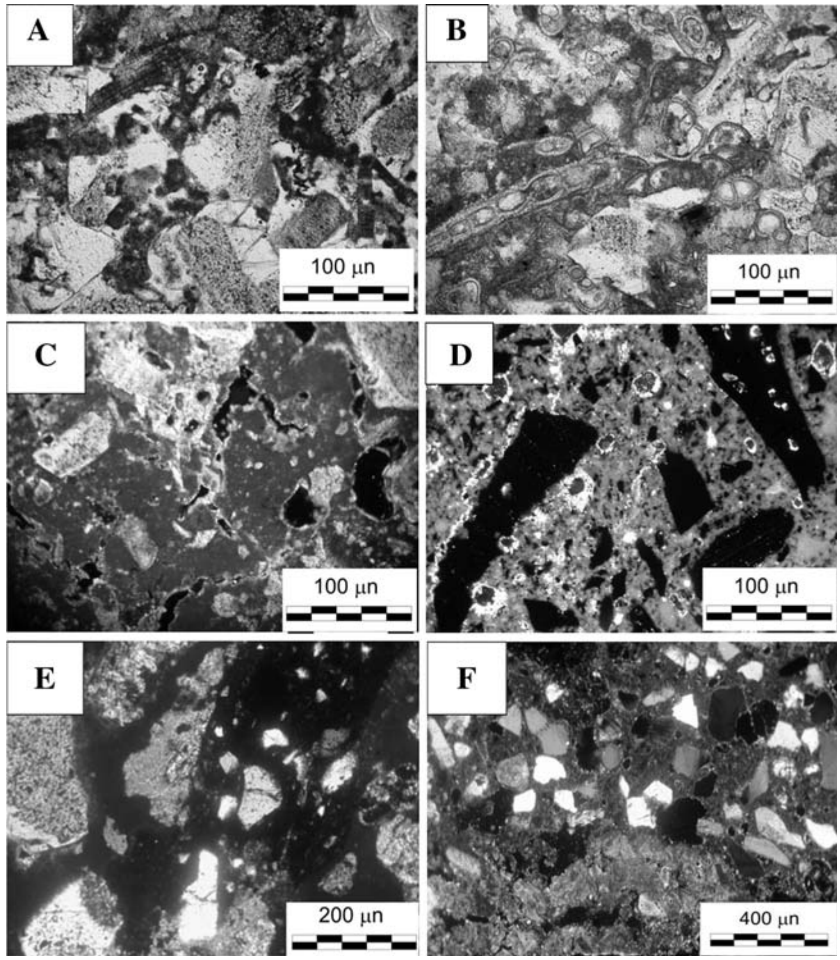


Fig. 2 Petrographic features in thin section of: **a** creamy-white calcarenite; **b** bitouminous calcarenite; **c** mortar with only carbonatic aggregates; **d** particular of the carbon clast; **e** particular of the cocciopesto used as inert; **f** particular of the iron-oxide present in the superficial layer of the covering plaster

The colorimetric characterization of construction materials was carried out by means of Konica-Minolta CM-2600d spectrophotometer.

Material characterization

Natural stone

The natural stone samples were taken while keeping in mind the macroscopic observations on the façade, which was in a cleaning phase. The autoptic analysis on the samples confirmed the presence of two lithotypes (Fig. 1a):

1. a calcarenite-calcirudite creamy-white (L*: 86,55, a*: 1,31, b*: 12.9 in the CIE lab system) coloured in fracture, which was quite homogenous, lightly compacted and crumbly;
2. a very compacted bituminous calcarenite-calcirudite dark brown (L*: 30,67, a* 4,13, b*:10 in the CIE lab system) coloured in fracture.

The creamy-white calcarenite, from a petrographic viewpoint can be classified as biomicrite (Folk 1959) or packstone (Dunham 1962) with occasionally small percentages of microsparitic cement. The allochemical components are bryozoa, fragments of echinoids and foramnifers. The porosity, estimated through microscope observations, is high (around 25%) and is prevalently primary (Fig. 2a).

The bituminous calcarenite show the same petrographic characteristics as the creamy-white calcarenite but differs from this as it has very low porosity because of the primary pores being almost completely impregnated by bituminous material (Fig. 2b).

From the petrographic characteristics, both the lithotypes are associated to calcarenitic locally outcropping and belonging to the Lower Miocene Irminio Member of the Ragusa Formation (Di Grande et al. 1977) which in some levels is impregnated by bitumen in percentages between 7% and 10%.

Artificial stone

Thin section analysis has allowed three different mortar and plaster to be identified:

Table 1 The result of chemical analyses performed on mortar and plaster by XRF

Samples	Tipology	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
SGR12	Plaster	9.56	0.09	1.60	0.35	0.01	1.90	42.85	0.61	0.12	0.23
SGR13	Plaster	10.53	0.08	1.43	0.29	0.01	1.98	41.37	0.75	0.47	0.20
SGR14	Plaster	9.27	0.09	1.53	0.35	0.01	1.64	44.12	0.63	0.00	0.25
SGR17	Plaster	3.90	0.04	0.74	0.00	0.00	1.78	49.07	0.46	0.00	0.35
SGR19	Plaster	2.03	0.01	0.36	0.00	0.00	1.33	52.92	0.20	0.00	0.25
SGR21	Mortar	1.73	0.01	0.28	0.00	0.00	1.60	52.95	0.14	0.00	0.24
SGR23	Mortar	2.99	0.02	0.39	0.00	0.00	1.99	52.52	1.06	0.00	0.39
SGR24	Mortar	3.96	0.03	0.47	0.02	0.00	1.29	50.23	0.03	0.00	1.89
SGR25	Mortar	6.18	0.04	0.82	0.10	0.00	1.16	48.89	0.66	0.00	0.53

Major oxides are in weight %

1. from the principle façade, it is possible to take a single, very porous plaster sample with frequent fractures. This is composed of micritic binder (70% in volume) with dissolution lumps. The aggregate is composed exclusively of carbonatic clasts and fragmented fossils. Moreover, in this case the binder is at a superior percentage than that of the inert (Fig. 2c);
2. the samples taken from the principle doorway frame, the lateral doorway and the first order capital are very porous and composed of a dark-grey coloured micritic binder (60% in volume), with numerous dissolution lumps. The aggregate is composed of a few fragments of calcite re-crystallized and of prevalent carbon granules (Fig. 2d), used to colour the mortar and give a homogenous chromatism to the architectural parts in which this mortar was applied;
3. the plaster taken from the lateral façade, were frequently fractured and composed of micritic binder (60% in volume) with lumps, dissolution zone and high primary and secondary porosity. The aggregate is composed of magmatic rock and cocciopesto fragments (Fig. 2e) and by carbonatic rock, fossil fragments (bivalves, globigerinides and echinoids).

Analysis of the major elements of mortar and plaster (Table 1) identified the samples from the lateral façade which showed the highest content of SiO_2, Al_2O_3 and Fe_2O_3 connected to the presence of volcanic rock fragments and of cocciopesto even if SEM-EDS analysis of the binder does not highlighted the development of hydraulic phases. Moreover, the samples with carbon are easily distinguished based on the abundance of some trace elements (Table 2; Ni, V and Pb).

Chromatic alteration processes

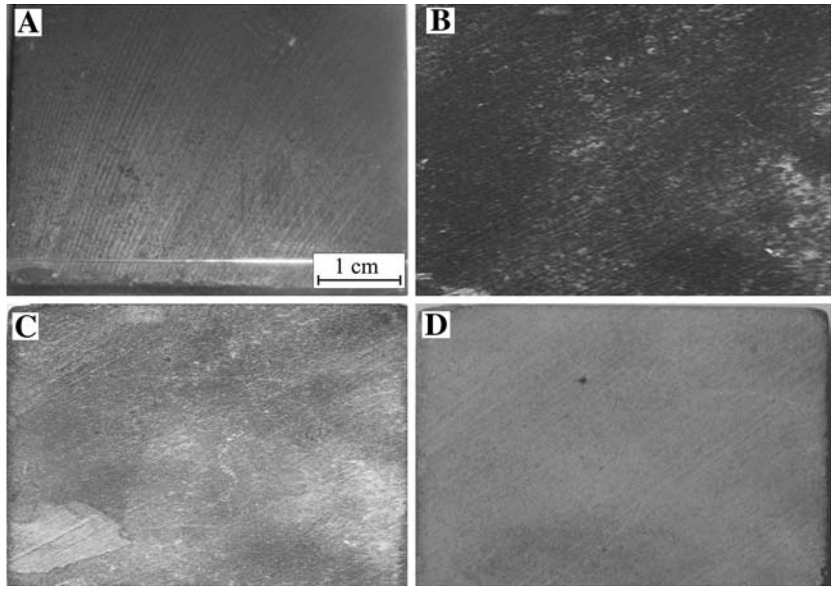
The characteristics of the materials used in the Cathedral of St. Giorgio has highlighted how the actual appearance is completely different from when it was built and how it was envisaged by the architect Gagliardi, particulary, the bi-chromaticc effect achieved through the use of calcarenite and light-coloured mortar supported by bituminous calcarenites and dark-grey coloured carbon bearing mortars. The degradation process is more obvious in the whitening of the surface of the bituminous calcarenite. In order to identify the causes, which produced this effect, five

Table 2 The result of chemical analyses performed on mortar and plaster by XRF

	Tipology	Sr	V	Cr	Co	Ni	Zn	Rb	Y	Zr	Nb	Ba	La	Ce	Pb
SGR12	Plaster	779.56	13.77	19.23	2.81	22.43	29.01	5.98	1.14	44.91	4.84	51.96	9.45	1.76	11.54
SGR13	Plaster	705.41	15.10	16.20	2.17	23.07	31.09	5.79	1.13	42.74	4.65	61.13	0.00	8.61	34.55
SGR14	Plaster	771.09	16.53	19.63	2.38	26.13	34.35	1.49	1.13	47.24	4.02	37.61	0.00	2.24	21.71
SGR17	Plaster	862.48	5.92	11.95	1.49	17.34	13.12	0.92	1.45	38.35	4.61	0.00	2.79	17.08	0.00
SGR19	Plaster	847.67	2.39	7.29	0.00	19.31	24.20	0.00	1.28	32.82	3.85	0.00	6.35	12.47	49.57
SGR21	Mortar	771.31	4.17	8.06	0.04	19.49	9.79	0.00	1.24	30.13	3.77	0.00	5.12	3.99	4.72
SGR23	Mortar	968.80	6.77	7.17	0.00	32.47	23.39	0.00	1.08	42.92	2.24	27.67	5.17	0.00	8.70
SGR24	Mortar	880.07	6.81	9.27	0.77	32.83	32.88	0.00	1.22	39.89	0.00	28.86	1.69	0.00	8.38
SGR25	Mortar	1,355.49	11.94	11.64	2.39	32.14	106.08	0.00	1.27	58.72	0.85	50.95	0.00	0.00	24.50

Minor element oxides are in ppm

Fig. 3 **a** Bituminous calcarenite. **b** Chromatic variations of the bitouminous calcarenite after 216 h of exposure a UV radiation. **c** Chromatic variations after 1,152 h. **d** Chromatic variations after 2,352 h



samples from the quarry and one from the monument were artificially aged using a UV-A lamp. After 216 h of exposure, the first irregular whitenings were observed; after 512 h there was visibly whitening; after 1,152 h a continuous layer was evident and finally, after 2,352 h a homogenous effect was noted (Fig. 3). The cause of this chromatic alteration can be assumed to be due to the presence of organic fractions as well as the maltenes or the asphaltenes. When these were exposures to UV solar radiation they underwent a photo-oxidation process (Boukir et al. 1998), which determined the de-colourization of the bituminous calcarenite as highlighted by the stratigraphic thin section of an aged bituminous calcarenite (Fig. 4) in which a light thin layer of on average 100 μm is distinguishable.

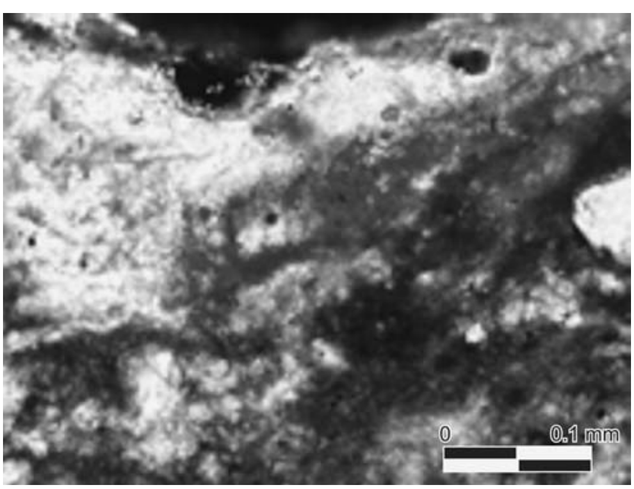


Fig. 4 Stratigraphic thin section microphotograph of a aged bituminous calcarenite showing the light superficial layer caused by organic fraction degradation

This process also showed a modification of the microstructure of the superficial layer (Fig. 5a) in which the porosity increase due to the disappearance of the bituminous fraction that envelope the grain and fill the pore (Fig. 5b).

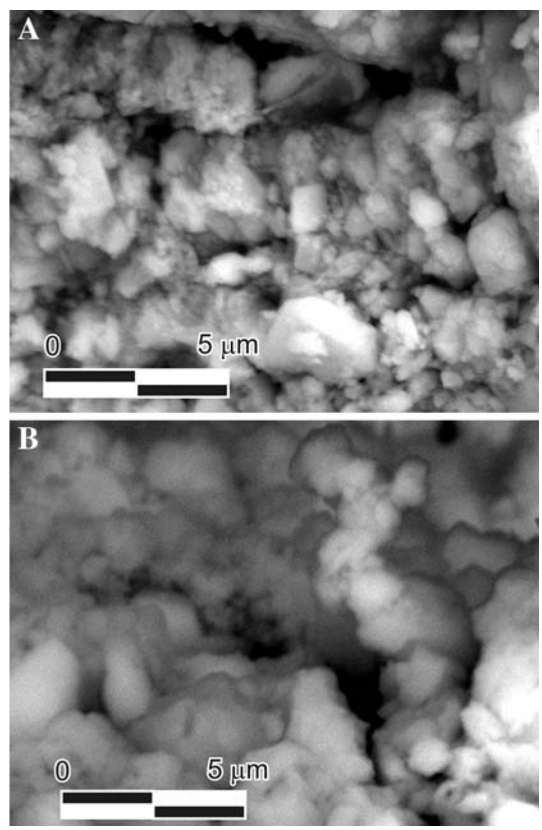


Fig. 5 SEM image of: **a** superficial altered layer of bituminous calcarenite after 2,352 h of exposure to UV radiation; **b** bituminous calcarenite below the alteration layer

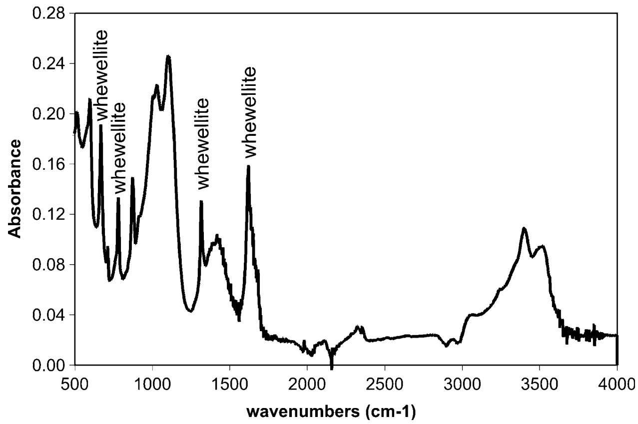


Fig. 6 FT-IR spectra of the orange–brown patina

The appearance of the façade was also modified by other processes following the whitening of the bituminous calcarenite. In particular, the presence of brown–orange coloured patina is caused by thin layer of red iron oxide bearing plaster as shown in a stratigraphic section (Fig. 2f). However, in many cases this plaster in not present while the SEM analysis highlighted the presence of fungus (*Zygomiceti*) and bacteria (*Attinomiceti*) which in literature are frequently associated to orange–brown chromatic alterations (Urzi and Reailini 1998; Krumbein 2002). Furthermore, the patinas analysed by means of IR spectroscope on samples treated with HCl 0,1, were characterized by the presence of calcite residue, gypsum and in some cases by whewellite (Fig. 6). The latter could be formed by; (a) microflora metabolic processes (lichens or bacteria) spread on the stone surface as shown in other archeological sites (Del Monte 2000-2001); (b) protective conservation measures carried out in the past, as indicated by historic documents (cfr. introduction) by means of organic substances and mixed with natural pigments which, in time, transformed into oxalates (Camaiti et al. 1996; Rampazzi et al. 2005).

Conclusion

The façade of St. Giorgio's Cathedral was designed, and contrary to what is present today, with particular attention to the bi-chromatic effect, which is also found in other Baroque monuments in Ragusa. This architectural effect was achieved by the use of white calcarenites and dark-coloured bituminous calcarenites, and also of the knowledgeable use of light and dark mortars because of the abundance of carbonaceous particles.

Successively, the bi-chromatic character of the façade was lost due to the alteration process connected to the photo-oxidation of the asphalt of the bituminous calcarenite. Lastly, the actual appearance of the monument was furthermore modified because of extended brownish-orange patina due to both the presence of oxalates and fungal and bacteria activity; (*Zygomiceti*) and (*Attinomiceti*) and of the application of a thin layer of plaster which gets its colour from the presence of iron-oxide.

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