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Multi-technique characterisation of medieval mastic encrustation sculptures

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ABSTRACT

Mastic incrustation sculptures were used to decorate different types of objects by filling the marble incisions with an impasto containing materials such as crushed pottery, glass or rock fragments, possibly in combination with organic substances, and was employed both in Byzantine and Occidental areas. From the 11th century onwards these sculptures are applied in important churches such as San Marco in Venice (Italy), but, despite their widespread use and conservation problems, the composition of these amalgams has never been thoroughly studied. Here we present the results of the examination of the mastic encrustations present on the medieval marble panels and precious cathedra in the San Nicola church of Bari (Italy). The matrix was analysed with Fourier transform infrared spectroscopy and pyrolysis gas chromatography-mass spectrometry. Organic binders were found and, in particular, the occurrence of heated *Pinaceae* resin, as well as of beeswax was assessed. The inclusions, including different types of rock, carbon black and opaque glass fragments, were characterised with optical microscopy, scanning electron microscopy, and powder X-ray diffraction. Micro-Raman spectroscopy was carried out on both inclusions and matrix.

1. Introduction

Mastic encrustation sculpture represents a specific artistic technique, documented since Roman times, which had a first moment of expansion in the proto-byzantine period and ample diffusion in the Mediterranean area between the 10th and 13th century CE. It was especially used for stringcourse cornices, capitals, and liturgical furniture. Shaped cavities were excavated in the stone substrate and then filled with impastos of various typologies with the aim of highlighting the figures or background and enhancing the artefacts through the employment of different materials. Additionally, this technique should have guaranteed major duration and better conservation as compared with the more common and simple application of pigments.

In the Italian territory three areas with high-quality mastic encrustation sculptures can be distinguished: Apulia with the sculptor *Acceptus* (first half of the 11th century CE) represents the first example in Italy; Venice, where in the San Marco church we can find the most extensive use of this technique in a unique context [1]; the Tuscan-Emilian area where the methodology was adapted at new requirements, as can be observed in the sculpture by Benedetto Antelami in the Cathedral of Parma [2].

In the Apulian territory, thanks to the intimate relationship with many countries of the Mediterranean Basin, departing from the first simple forms, highly articulated motives were developed. In the beginning red and black fine-grained mastic encrustations were used and their application was mainly limited to some parts of the furniture. In the first years of the 12th century CE coarse-grained decorations with coloured inclusions became distinctive for the area of Bari and diffused up to the Federician epoch.

The terminology referring to these sculptures is rather confused. They have been defined as *niello* or *champlevé*, otherwise as *opus sectile* or *opus interrasile*, respectively relating this technique to the typical manufacturing of precious metals or marble inlay, but thanks to Fabio Coden, author of the most exhaustive study on Italian mastic encrustation sculpture [2], any misunderstandings in the terminology have now been solved and supposed affinities with metallurgical or *intarsio* techniques have been discarded. Unfortunately, however, hardly any literature data are present on the nature of the materials and the techniques that were employed. In 1905 a study by Lucien Bégule reports on the composition of the so-called *ciment* of some French decorations, in the Cathedral of Lyon consisting of a mixture of iron oxides and gypsum, and in Vienne where the addition of 'resinous material' was mentioned [3]. Other studies generically refer to bituminous, waxy, and resinous amalgams containing pigments and different types of inclusions comprising crushed charcoal or lamp black for the black fine-

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grained mastic encrustation [4], but detailed scientific information is almost completely lacking. It is reported that the mixture was heated, pushed into the cavities of the stone, and when consolidated, levelled out by abrasion and then polished [5].

In this study the marble episcopal cathedra and the decorations in the presbytery of the San Nicola church of Bari (Apulia, Italy) dating back to the end of the 11th and first decades of the 12th century CE, respectively, are examined. They are decorated with the mastic incrustations technique in different shades ranging from reddish brown to dark green or grey (Fig. 1).

Here we present the results of the analysis of several samples taken from the rises of the steps of the High Altar, from the *synthronon* (structure in the apse at the back of the altar of an Orthodox Christian church that combines the bishop's cathedra and seats for the clergy) in the presbytery, as well as from the cathedra. A stereomicroscope was used for a first survey and separation of the matrix and clasts. The matrix was then analysed with Fourier Transform infrared (FTIR) spectroscopy, pyrolysis - gas chromatography - mass spectrometry (Py-GC-MS), and GC-MS. FTIR spectroscopy allows to obtain information on the different types of material used for these complex amalgams [6], whereas Py-GC-MS and GC-MS provide detailed data on the composition, state of degradation and manipulation of the organic fraction [7,8]. The inclusions, among which different types of rock fragments and opaque glass, were characterised with optical microscopy (OM), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), and powder X-ray diffraction (XRPD). SEM-EDS and XRPD were applied for the determination of the elemental composition and crystalline phases of the opaque glass fragments in order to gather info on the type of glass as well as on the fluxes, stabilisers, colourants, and opacifiers. For most samples the inclusions and matrix were also examined with micro-Raman spectroscopy.

The aim of the present paper is to shed light on the composition and preparation of mastic encrustation sculptures, which have been widely used for the decoration of important medieval churches in Italy as well as in France. The results of this multi-technique approach will also be useful for the planning of proper conservation and restoration treatments of these precious artefacts.

2. Experimental

2.1. Materials

Tetramethylammonium hydroxide (TMAH) (25% in H_2O), methanol (99.8%), n-hexane (≥99.0%), hydrochloric acid (37%), diethyl ether (≥99.7%), isooctane (99.5%), N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA), potassium hydroxide, and potassium bromide were purchased from Sigma Aldrich (Milan, Italy).

2.2. Samples

Eight samples of mastic encrustation amalgam were taken from different parts in the presbytery of the San Nicola church in Bari (Italy): one from the cathedra and seven from the rises of the steps and the *synthronon*. Four opaque glass fragments were sampled as well in the same area (Table 1).

The episcopal cathedra, now located behind the High Altar, has probably been commissioned by the Benedictine Abbot Elia in 1098, in occasion of a Council promoted by Pope Urban II held in the church of Bari in that year with the participation of major exponents of the oriental, Greek and Italian churches as well as of Anselmo d'Aosta (archbishop of Canterbury). The cathedra, made of white pinkish monolithic marble with grey and bluish veins, was probably obtained from an ancient column. The mastic encrustations are composed of a compact fine-grained black amalgam. Significant parts have been lost, but residues are still present on the seatback and in the inscription.

The decorations in the presbytery date back to the governance of the Benedictine Abbot Eustazio (1105–1123) [9], successor of Elia. The High Altar presents three marble steps; the third contains a long inscription related to the interventions that were promoted by Abbot Eustazio; the first and second steps present phytomorph and zoomorph friezes. The mastic encrustation sculptures in this area are relatively well preserved and are based on middle-eastern schemes with Islamic matrices. Their colours range from red to brownish or dark grey and they contain relatively large clasts composed of rock and glass. The opaque glass fragments are present in the red, brown and greyish mastic encrustations and show bright yellow, orange, green, red and turquoise colours.

2.3. Optical microscopy

The optical microscopic investigations on the mastic encrustations were carried out using a Nikon SMZ 800 and a Zeiss Axioskop 40 POL optical microscope, both equipped with a Nikon DS-5MC digital camera.

In particular, the rock fragments present in the eight samples (SN1-SN8) of mastic encrustation were embedded in epoxy resin and then prepared as polished 30 μm thin sections for the microscopic observations.

2.4. SEM-EDS

SEM-EDS investigations were carried out on four glass fragments using a Zeiss-Leo EVO50XVP scanning electron microscope. The electron microscope is equipped with an X-max (80 mm^2) Silicon drift Oxford detector. Operative conditions of SEM were: 15 kV accelerating potential, 500 pA of probe current (corresponding to about 25,000 output cps on Co standard), counting time 50 s and 8.5 mm working distance. X-ray intensities were converted into oxides using the XPP model for matrix corrections, developed by Pouchou and Pichoir [10,11], granted as software support by Oxford-Link Analytical (U.K.). Microanalytical data were checked using reference standards from Micro-Analysis Consultants Ltd. (U.K.).

2.5. Powder X-ray diffraction

Structural information of the glass samples was obtained using an X-ray diffractometer Philips X'Pert Pro equipped with an X'Celerator

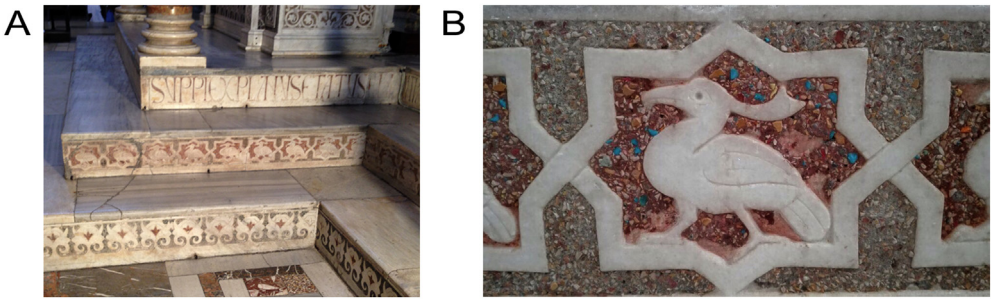

Fig. 1. A) Mastic encrustation sculptures on the rises of the steps at the right side of the High Altar in the San Nicola church (Bari, Italy); B) detail with a zoomorph decoration.