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Ca-oxalate films on the stones of the medieval architecture: the case-study of Romanesque Churches

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***Abstract* – Traces of Ca-oxalate films were found on the stone surfaces of stones of some Sardinian medieval Churches of the 'Giudicati' period.**
The study aims to define their distribution and micro-stratigraphy on the different architectonic stone elements and to clarify their precise roles as result of probable ancient conservation.
Ca-oxalate films show a variable color from greyish, to rosy or yellowish and generally they are present on the decorative architectonic elements of monuments. Their thickness is variable (10-50 μm) owing to the roughness of the stone surfaces. XRD analyses performed directly on the collected microsamples and on powders gently scraped from their surfaces revealed calcite+weddellite (type 1) in some of them and calcite+weddellite+whewellite (type 2) in others. Preliminary observations at the polarizing microscope showed two different micro-stratigraphies.

I. INTRODUCTION

The decay of the stones used on the Cultural Heritage is due to weathering and bio-processes and it involves chemical-physical transformations / modifications of the stone, or the precipitation on the surface of inorganic compounds (*e.g.* atmospheric particles) or the deposition of organic substances. The chemical-physical alteration generally involves on the first decay stage a thickness of a few millimetres that can also reaches in following stages some centimetres. In addition to the aforementioned degradation processes and consequent chemical-mineralogical alteration products, among the various forms observable on the surface of the stone laid in the monuments, we also find the formation of calcium oxalate films. Numerous authors agree that these films are the result of man-made ancient treatments on the surfaces of the stone artefacts.

In this paper, two important Churches with high historical-cultural relevance belonging to Sardinian Romanesque medieval period (ranging from XI to XIV cent.) from North to South Sardinia have been taken as study cases: St. Antioco di Bisarcio (Ozieri), Fig. 1, St. Geminiano of Simassi (Samassi), Fig. 2.

Fig. 1. St. Antioco di Bisarcio Basilica in Ozieri territory, Central-Northern Sardinia (abside view).

The volcanic rocks are widely used as construction materials in historical times in Sardinia, from Punic-Roman to Romanesque [1-11]. The pyroclastic rocks, as well as the carbonate rocks, are those that have a major use in the historic architecture due, on one side, to their more easy availability in the territory and, on other hand, to their better workability with respect to other silicate magmatic or metamorphic rocks [12-14] which show greater difficulty in being worked.

A. Historic and architectural features of Romanesque monuments

The S. Antioco of Bisarcio Basilica, situated a few kilometres outside the village of Chilivani in NE Sardinia, was built between the late XI and early XIII century.

Fig. 2. St. Geminiano Church in Samassi village, Central-Southern Sardinia (abside view).

It was a diocese cathedral from the end of the XI to the beginning of the XVI century, when the episcopal see was suppressed. Longitudinal in plan, the St. Antioco di Bisarcio Basilica has a hall with an apse and three naves separated by pillars topped by Romanesque capitals. The original façade was overlain with a two-storey portico. The Romanesque fabric can be distinguished by the walls, built of medium to large ashlars, carefully hewn and lain using the technique adopted by builders of Tuscan tradition, employed in the 'Giudicato di Torres' since the XI century. The hewn stones were dry laid and carefully aligned, but did not achieve the refined features that distinguished Cistercian buildings.

The Codex Diplomaticus of Tola indicates that a Church dedicated to St. Geminianus, belonging to the Camaldonese monastery of St. Geminianus of the island of Montecristo, existed in thetown of Samassi (South Sardinia) starting from 1119 AD. However, the current form of the Church cannot be ascribed to that period and it is thought that it was rebuilt in the late XII or early XIII century on the ruins of an older Palaeochristian and Vandalic building. The Church of the San Geminiano (also called San Mamiliano) has a single nave, with the apse directed to the South-East. In the main façade and in those sides, the structural framework consists of a inclined skirting board, wide corner pillars, flat pilasters, and small arches with geometric and moulded decoration. The façade, with arches parallel to the pediment, supports the campanile and contains a portal with lintel on phytomorphic capitals and an arch set on anthropomorphic protomes.

B. Aims of research

The paper is addressed to mineralogical-petrographic characterization of films found on the stone surfaces of ashlars and on the decorative architectonic elements of two monuments taken as case study. The main focus of the investigations is define the microstructure of these films and their composition that can be related to the organic component present in the probable ancient treatments applied to the stone surface with protective and / or chromatic functions.

Thus, a survey of the distribution of the films on the different architectonic elements was made to clarify their precise roles.

II. MATERIALS AND METHODS

A. Geochemical and petrographic characterization of volcanic stones

Petrographic determinations of mineralogical composition were carried out on polished thin sections by optical polarised microscope Leitz Wetzlar.

Chemical analyses on bulk rock were determined by XRF with spectrometer Philips PW1400 using a Rh-tube for the analysis of major elements and some trace elements (Rb, Sr, Pb, Zn, Y, Nb and Zr) and a W-tube for the analysis of the elements Ni, Cr, Ba, V, La and Ce. For calibration of major and trace elements were used over 30 international standards of reference. The measurement accuracy is ± 1% for SiO_2, TiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O and MnO and ± 4% for MgO, Na_2O and P_2O_5. The detection limits are about 3 ppm to 3σ for most of the elements; the accuracy of trace elements is ± 2 ÷ 3% to 1000 ppm; ± 5 ÷ 10% at 100 ppm and ± 10 ÷ 20% to 10 ppm. The loss for calcination (L.O.I.) was determined by calculating the loss in weight % at 1100°C, while the FeO was determined by volumetric titration with $KMnO_4$ 10N in acid solution. Classification of the volcanic rocks and relative nomenclature was carried out according to De La Roche et alii [15] classification.

B. Surface analyses

Sampling entails an accurate and detailed observation of the surfaces of the ashlars and of the architectonic elements present in the studied facades. Macroscopic recognition of surface film relics is not easy. The alteration that often affects them makes them look like whitish-greyish or yellowish-brown traces which can easily be mistaken for other surface deposits, so frequent on stones and bricks. Furthermore sometimes the films are covered by black crust, or dust, or soil deposits.

With this difficulty overcome, the sampling was carried out so as to acquire a significant number of microsamples from both the wall face and all the architectonic and ornamental elements of the façades. Micro samples were taken with a scalpel or small chisels.

About 40 and 25 microsamples were analysed from St. Antioco di Bisarcio and "San Mamiliano di Simassi" Churches, respectively.

The microsamples are studied, in a first phase, by stereomicroscope, and after by preparation of thin (thickness 30–40 μm) and ultra-thin (thickness 8–10 μm) sections, cut perpendicular to the surface, analysed by a polarising microscope in transmitted and reflected light (dark field). The observations of ultrathin sections are the only ones that allow sufficiently clear visualization of the structure and composition of microcrystalline layers. This makes easier a detailed reconstruction of the microstratigraphy, even when we are dealing with more than one overlapping film or with further complications induced by alteration processes.

As a standard procedure, XRD analyses are also performed on each sample, both directly on its surface and on powder gently scraped from it. Sometimes a scanning electron microscope with EDS EDAX microdetector was used to study some small areas of the films. Only combining all together these analytical data a sufficiently detailed characterization of the film can result.

III. GEOMATERIALS OF THE CHURCHES

A. Geological setting

The materials used in building the two Romanesque Churches consist of volcanic rocks belong to the significant Sardinian Late Eocene-Miocene orogenic magmatic phase occurred between 38 and 15 Ma [16]. Volcanic activity is generally related to a deep N-NW-trending subduction zone of the Ionian oceanic lithosphere. Volcanism started in Middle-Late Eocene, below the Paleo-European-Iberian continental margin, and during the Oligocene gave rise to the formation of the rift between Sardinia and Provence [16, 17, 18], Fig. 3. The intense igneous activity, widely widespread over the entire Island leds to emplacement of tholeiitic, calcalkaline, shoshonitic and ultrapotassic products, mainly along the Sardinian Oligo-Miocene rift, a large tectonic pit, which structure crossing Sardinia [17]. The Sardinian orogenic magmatism started in the North of the Island, in the Calabona area (~38 My; [18]), as revealed by a small microdiorite outcrop. Starting from 22 My [16, 17], a highly explosive fissural activity produced abundant pyroclastic dacitic-rhyolitic products, interlayered by basaltic and andesitic lava flows. The volcanic activity flows occurred in several areas of Sardinia, mainly along the Western graben, N-S trending (Fig. 3).

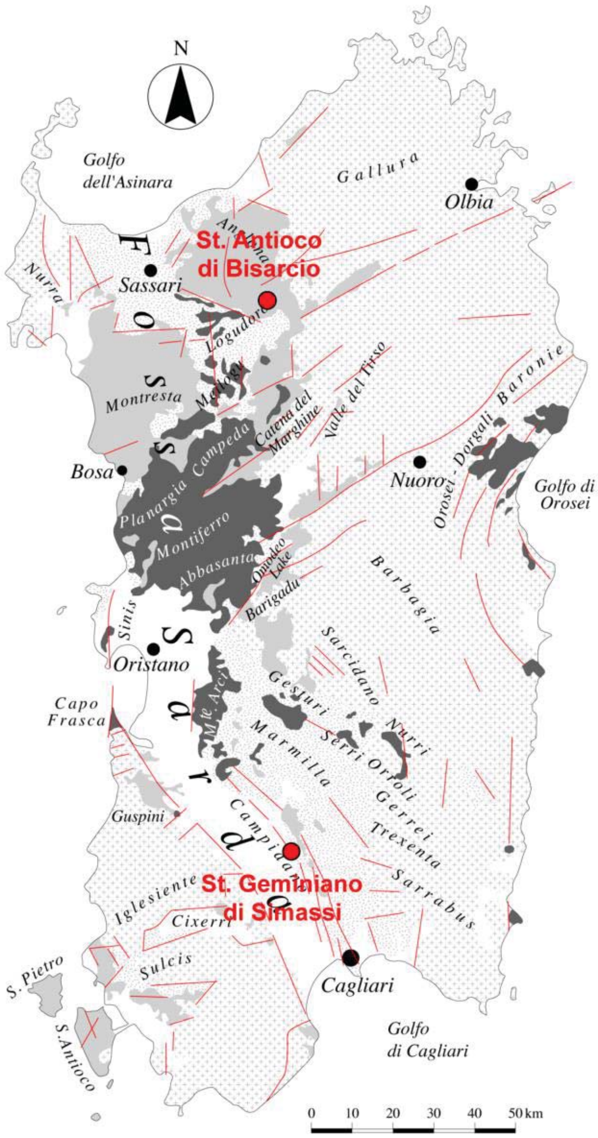

Fig. 3. Geological sketch-map of Sardinia, with the localisation of two Churches. Legend of lithologies: white = recent alluvial sediments; light grey = Oligocene-Miocene volcanics; dark grey = Pliocene-Pleistocene volcanics; grey dots = Miocene marine sediments; grey crosses = Paleozoic crystalline basement and Mesozoic formations; red continuous and dashed lines = faults.

The pyroclastic rock used for constructing the St. Antioco di Bisarcio Basilica can be attributed to the latter volcanic activity (21.2 ± 0.8 My, locality St. Antioco of Bisarcio). Epiclastic rocks, occasionally used in masonry for decorative purposes together with small amounts of green sandstone, occurs to a lesser extent in the area. The volcanic rocks used to construct the San Geminiano of Simassi Church belong to the Oligo-Miocenic volcanism outcrop in South-Western Sardinia (Fig. 3), placed along the Sardinian rift, where the volcanism mainly occurred.

B. Petrographic and geochemical features of rocks

Based on the petrographic and geochemical features, the pyroclastic rocks of St. Bisarcio Church and those outcropping in the Chilivani area were divided into two main groups: 1) welded pyroclastic rocks (including lava-like ignimbrites) (WPC); 2) unwelded pyroclastic rocks (UPC). According to De La Roche et alii [15], WPC rocks have been classified as quartz-latite, UPC (field samples) as rhyolite, rhyodacite and rare quartz-trachite, UPC (samples from the Church) as rhyodacite, rhyolite, alkali-rhyolite and subordinately of quartz-latite and quartz-trachite. WPC rocks have a porphyritic structure for phenocrysts of (in order of segregation) spinel, plagioclase, clinopyroxene, K-feldspar, quartz and very rare horneblende. UPC show a different paragenesis, characterised by phenocrysts (in order of segregation) of spinel, plagioclase, ± orthopyroxene, clinopyroxene, ± biotite, K-feldspar, quartz.

The volcanic rocks of the 'San Mamiliano di Simassi' Church have a dacitic to rhyo-dacitic composition. The walls of the Church are made of medium-sized vulcanite ashlars. These volcanic rocks present a porphyritic structure (porphyritic index 10÷20%) with phenocrysts of opaque minerals (magnetite and/or titanomagnetite), plagioclase, ± biotite and rare hornblende and quartz.

Fig. 4. Surface crust with Ca-oxalate in volcanic stone of ashlars from the abside of St. Antioco di Bisarcio

IV. OXALATE FILMS ON MONUMENTS

A. Sant'Antioco of Bisarcio Basilica

Traces of more or less continuous greyish, rosy or yellowish films (Figs. 4, 5) are present on the volcanic stone surface of abside ashlars (Fig. 1) and on the decorative architectonic elements of Church.

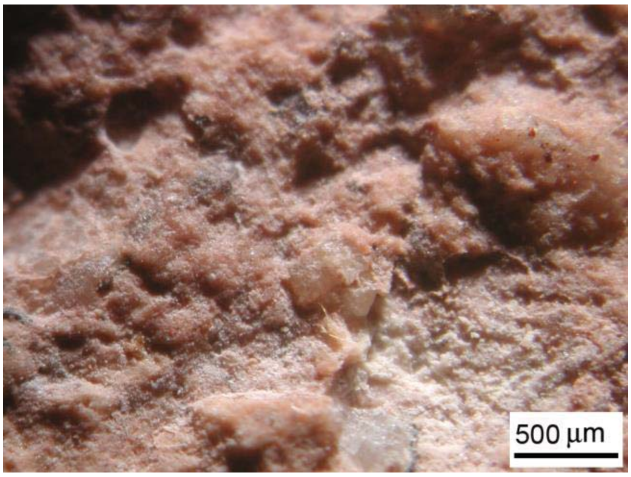

Fig. 5. Aspect of Ca-oxalate film (type 1) in St. Antioco di Bisarcio Basilica under stereomicroscopic observation

Their thickness is variable (10-50 µm) owing to the roughness of the stone surfaces. XRD analyses performed directly on the collected microsamples and on powders gently scraped from their surfaces revealed calcite + weddellite (type 1) in some of them and calcite + weddellite + whewellite (type 2) in others.

Observations at the polarizing microscope showed two different micro-stratigraphies. The first is a single film consisting of very fine grains of carbonate rock and even finer grains of yellow and red ochres in a micritic-weddellitic binder (type 1, Fig. 6a, 6b). In the second, a film similar to the preceding one is superimposed on another film made of pure whewellite (type 2). The Ca-oxalate films are due to the gradual transformation of preceding treatments containing organic matter applied to the stone surfaces. The purpose of these treatments was usually aesthetic-decorative, as shown by the frequent and non-random presence of pigment granules in the oxalate matrix.

B. San Mamiliano di Simassi Church

The Ca-oxalate films presented on the stone surfaces of San Mamiliano di Simassi are a pinkish to honey-yellow colour (Fig. 7). XRD data and polarizing microscope observations revealed at lEast two types of films:

- Type 1: weddellite + whewellite are present in the this type of oxalate film. In thin section, the films consist of a filler of fine yellow-orange ochres (Fig. 8a, 8b) and rare black carbon within an oxalate binder. They have a mean overall thickness of 70-100 µm. These films are often interrupted by fissures perpendicular to the surface and very similar to a craquelure.

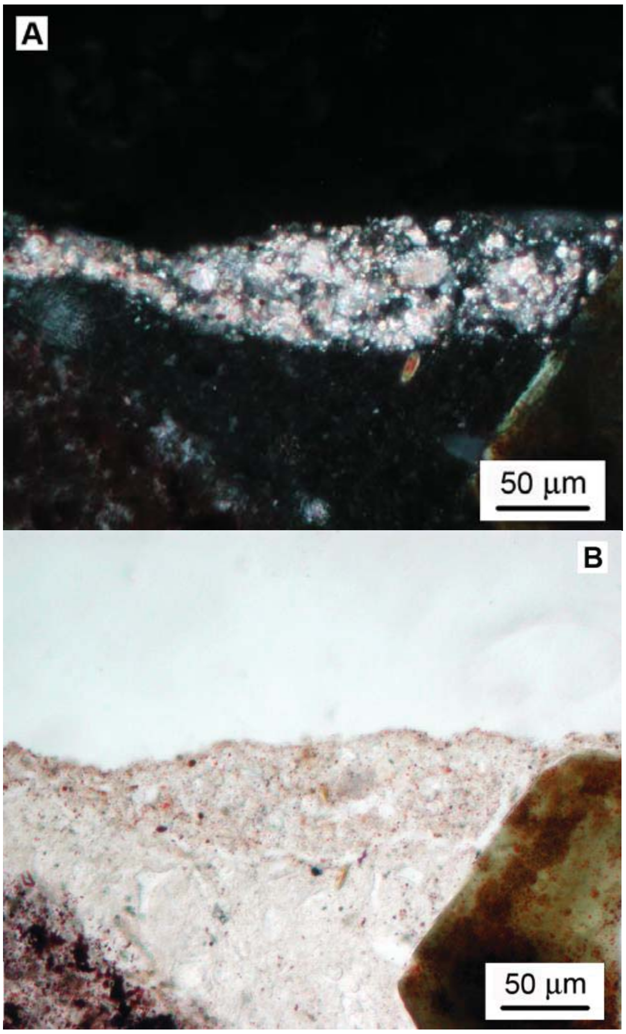

Fig. 6. Ca-oxalate film (type 1) in St. Antioco di Bisarcio under microscope: A crossed nicols, B one polariser.

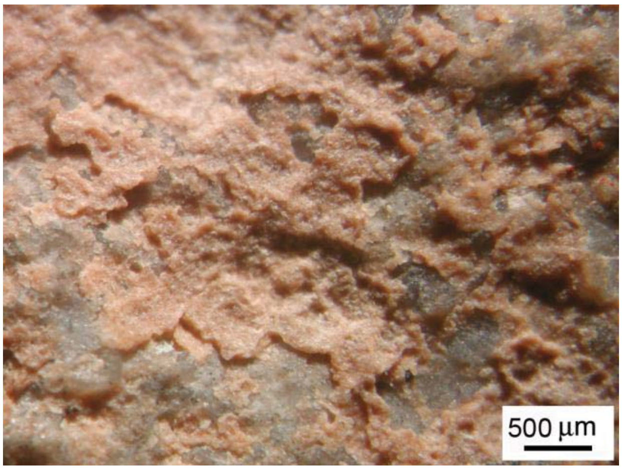

Fig. 7. Aspect of Ca-oxalate film (type 1) in St. Geminiano Church under stereomicroscopic observation

- Type 2 (sample VS47): this type of oxalate film is made of whewellite. Microscopically the films show a peculiar globular microstructure, are much thicker than the type 1 films (200-300 µm) and have low content of pigment grains.

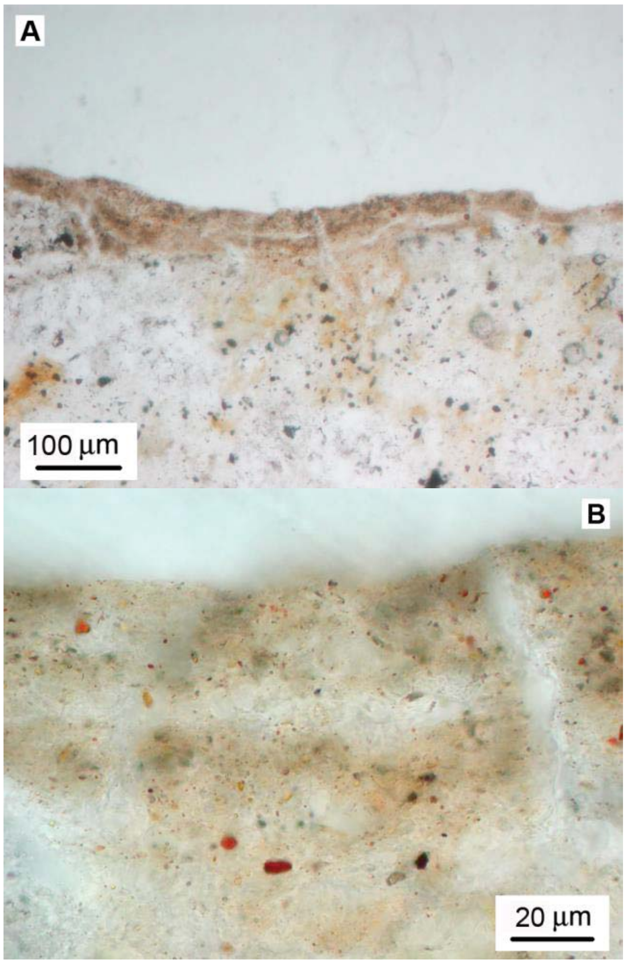

Fig. 8. Ca-oxalate film (type 1) in St. Geminiano under microscope (one polariser): A general view, B detail

V. CONCLUSIONS

In the studied surfaces of Sardinian Romanesque Churches the Ca-oxalate films are due to the gradual transformation of preceding treatments containing organic substances applied on the stone and brick surfaces. The purpose of these treatments was usually aesthetic-decorative, as shown by the frequent and non-random presence in the oxalate matrix of pigment granules. In each case the aim of the treatment was to improve the typical colour of the material by rendering it homogeneous, highlighting it and preserving it in time, as well as creating a better chromatic harmonization of the entire façade. In the case of brickwork, sometimes using variable shades of the typical red colour, these treatments emphasized the architectonic and ornamental elements, thus increasing the aesthetic appearance of the façade.

In the case of Sardinian monuments Ca-oxalates have never been found before. These case studies are a reference point for further studies to conduct on other Tuscan and Sardinian monuments, including fortresses. Ca-oxalate films have historical memory value linked to the evolution of the artefacts and the finishing techniques that, together with the protective features outlined against the substrate, paves the way for the theme of the preservation of the films themselves.

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