9th International Conference on NDT of Art, Jerusalem Israel, 25-30 May 2008
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MICRO-STRATIGRAPHY OF CA-OXALATE COATINGS: AN ATTEMPT TO INTERPRETATION

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ABSTRACT

This research is a part of a wider project aimed at cleaning and restoring "Fonte Gaia", a XV century large marble fountain, situated in Siena (Tuscany, Italy), sculptured by Jacopo Della Quercia.

This study has been focused on the mineralogical-petrographic investigations of superficial micro-stratigraphy with the goal to define the meaning and the intrinsic value of every superficial layer on the marble substrate.

In order to avoid as much as possible the damage to the monument, we have collected minute samples (less than 2 mm) and made thin and ultra-thin cross-sections (30 and 10 µm thickness) to analyze the composition and the micro-structure of the different layers lying on the surface.

A detailed observation allowed us to understand and define different regions as: i) areas where the surface shows alteration processes of the marble substrate; ii) areas characterized by the presence of different deposits accumulated and eventually transformed during time; iii) well-preserved areas presenting traces of ancient superficial treatments.

Analysing the well-preserved areas, we could identify Ca-oxalate coatings (patinas) (Weddellite and Whewelite) and study, by microscopic observations, their individual characteristics such as the uniformity and continuity of the layer's thickness and the presence of ochre particles. These characteristics led us to interpret those layers as the result of mineralization processes of ancient protective and/or decorative treatments applied on the marble surface. To understand the true age of those treatments it is a critical issue, since they could belong to the author himself. According to this approach patinas may acquire a very relevant historical and artistic value and the petrographic analysis of their characteristics represents, in any case, an important key when examining the surfaces. Thus, taking into account those aspects represent a crucial step leading to proper cleaning and preserving interventions.

Specific results, also supported by X-ray diffraction analysis, will be presented and discussed.

INTRODUCTION

At the beginning of the XV century Fonte Gaia was the considered the symbol of the prosperity and ability of the people living in the city of Siena, and their success in bringing fresh water to the top of the hill, were Siena is placed. Sculptured by Jacopo Della Quercia between 1414 and 1419, and located in the heart of the city, Piazza del Campo, Fonte Gaia was a wide marble fountain, characterized by a trapezoidal basin surrounded by a marble panel, finely decorated in relief (Fig.1).

Fig.1 Fonte Gaia before the restoring intervention, modified picture from Fratelli Alinari Fotografi a Siena nell'800, Alinari, Firenze, 2001, p.100

After four centuries, the fountain resulted very damaged and in a bad state of conservation; so during 1868 it was decided to dismount and replace it with a copy. A large number of the original marble elements were moved and recovered in the "Opera Della Metropolitana" Museum, and then assembled again in an open lodge. Nowadays the main and most beautiful elements are preserved and exhibited in the "Santa Maria Della Scala" Museum, after a long cleaning and protecting process lead by the Opificio Delle Pietre Dure, Florence.

This research has been a part of that wide project and was presented and discussed during the graduate dissertation at the University of Siena.

The study focused on the mineralogical and petrographic investigations of the superficial micro-stratigraphy with the goal to better understand and define the meaning and the intrinsic value of every superficial layer on the stone surface.

THE SAMPLING

In order to avoid as much as possible to damage the monument, 21 minute samples (less than 2 mm) belonging to the fine sculptured surfaces, were collected from areas not visible from a frontal view. Afterwards thin and ultra thin cross-sections (30 and 10 μm thickness) were made to analyze the composition and the micro-structure of the different layers lying on the surface.

Historical researches from the City Archive, regarding the material used to build the fountain, the construction phases, and accidental or vandal damages of the monument during the centuries, had been a useful support. The study benefited also from previous samplings (Bralia, 1989).

The marble used for the fountain belongs to the close Montagnola Senese area, and the oral tradition assignes its provenance to a specific quarry called "Jacopo's quarry". The marble is characterized by a pale yellow-whitish colour with frequent patterns of darker veins.

MICROSCOPIC OBSERVATIONS

Microscopic observations were carried out by an optical microscope with different arrangements of light. The possibility to obtain also ultra thin cross-sections made us able to have a better resolution for a larger number of details also in micro and crypto crystalline aggregates (Fig. 2, 3).

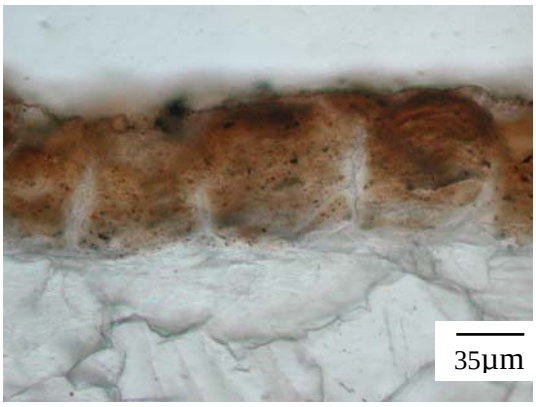

Fig. 2 Detail of the Ca-oxalate film, //N. The estimated thickness of the section is 40 µm .

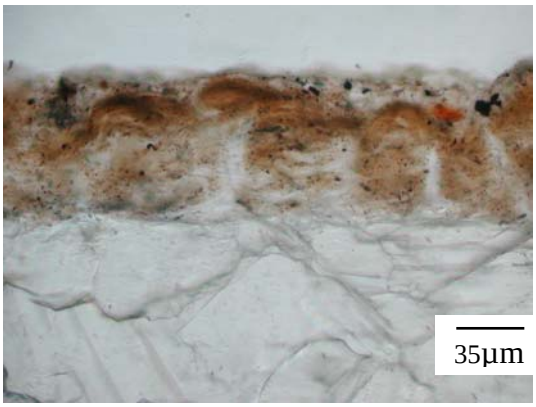

Fig.3 The same detail, //N. The estimated thickness of the section is 15 µm.

Three different regions were defined: i) areas where the surface shows alteration processes of the marble substrate; ii) areas characterised by the presence of different deposits accumulated and eventually transformed during time; iii) well-preserved areas presenting traces of ancient superficial treatments.

The first region includes the surfaces characterized by lack or detachment of the material, due to improper use /vandalism and weathering, especially leaching effects.

The second region is represented by surfaces with the presence of only gypsum deposits and black crusts, lying directly on the marble substrate, and by surfaces affected by the presence of carbonate incrustations. In both cases the marble substrate appears not cohesive and the calcite crystals look like brittle.

The surfaces belonging to the third region are entirely characterized by the presence of Ca-oxalate coatings (film). This yellowish layer lies directly on the marble substrate and it is possible to distinguish two different units. The lowest, in contact with the marble, is a Whewellite ($CaC_2O_4 \cdot H_2O$) layer and it is usually very thin (5-10 µm), *craquelure* effects are also visible. The upper one is a Weddellite ($CaC_2O_4 \cdot 2H_2O$) layer, it is thicker (50-80 µm) and shows a certain abundance of ochre particles. The main peculiar characteristics of the Ca-oxalate coatings were the uniformity and continuity of the layer's thickness and of the colour, and the presence of ochre particles (Fig.4, 5, 6). This led us to interpret those layers as the result of mineralization processes of ancient protective and decorative treatments applied on

the marble surface. Furthermore it seems that the Wewellite layer could represent the first coat as a preparatory work, while the Weddellite layer the main and secondly applied coat.

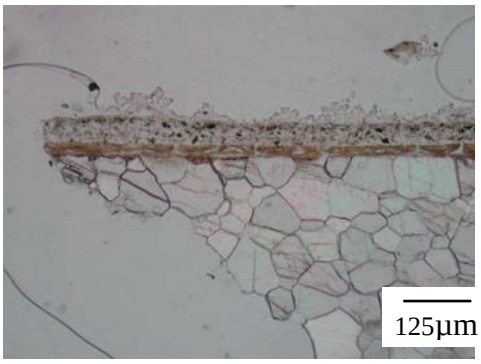

Fig.4 Example of the microstratigraphy of Fonte Gaia surfaces.
From the top to the bottom: black crust layer, Ca-oxalate layer, marble sustrate. //N.

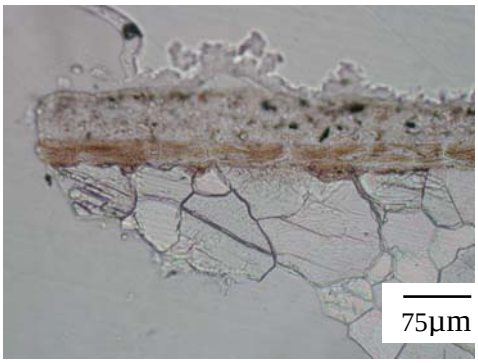

Fig.5 Detail of the microstratigraphy, //N.

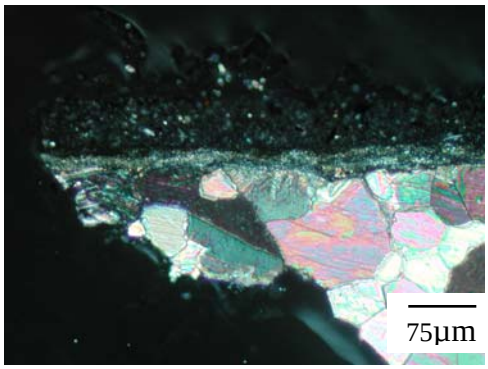

Fig.6. Detail of the microstratigraphy, XN

To understand the true age of those treatments it is a critical issue, since they could belong to the author himself. According to this approach, the films may acquire a very relevant historical and artistic value and the mineralogical-petrographic analysis of their characteristics represents, in any case, an important key when examining the surfaces.

X Ray Diffraction analysis (Philips, X'Pert) confirmed the results achieved by miscroscopic studies testifying the presence of the two oxalates.

It was also possible to test the utility of thin and ultra thin sections to monitor the effects of cleaning treatments by laser techniques on three samples partially cleaned by laser. On a first macroscopic observation, the not cleaned parts of the three specimens show the presence of a

thick layer of black crust, whose colour varies from dark brown to black, while the cleaned parts clearly showed strong differences in colour according to more or less intense laser treatments, obtained setting the instrument under different conditions.

Fig. 7 Fragment partially cleaned by laser technique. Stereomicroscope view

The microscopic observations of the thin and ultra thin sections show the different effects of the cleaning treatments: the more intense is the treatment, the less thick is the black crust layer and less frequent are the included black particles, responsible of the dark colour.

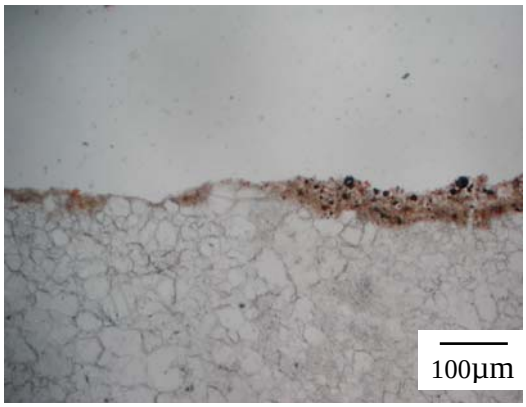

Fig.8 Detail of a thin section crossing the direction of the laser cleaning. From the right to the left the thickness of the black crust layer is gradually reduced by the laser action. //N

CONCLUSIONS

Through the study of the thin and ultra thin sections it can be concluded that in Fonte Gaia:

- The Ca oxalate coatings are finally interpreted as the result of mineralizing process of ancient treatments;
- Weddellite results to be the main component of the Ca-oxalate layer, while Whewellite could represent only a first preparatory coat;
- The sections are an important tool in monitoring and verifying the effects of cleaning treatments on surfaces;
- Accordingly to the generally acknowledged criteria of "minimum intervention" for the Conservation of Cultural Heritage, the laser cleaning could be limited to the removal of the black crust, which is the main cause of the darkening in colour, leaving the Ca-oxalate coatings on the surfaces, due to their historical value.
- Results from thin and ultra thin sections and the relative interpretation could be considered a crucial aspect when dealing with the study of the Cultural Heritage, specially when it is suggested an irreversible intervention.

ACKNOWLEDGEMENT
The author is the recipient of a Marie Curie PhD fellowship (EPISCON Project).
A special thank to the Dept. of Environmental Geochemistry and Conservation of Cultural Heritage, University of Siena, Italy, and to the Opificio Delle Pietre Dure, Florence, Italy, for advice and support.

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