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# CRUST FORMATION PROCESSES ON ARCHAEOLOGICAL MARBLE, CONSERVATION METHODOLOGY AND TREATMENT EVALUATION

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## Abstract

This work presents the findings of a study that was conducted in order to reveal the geological processes that lead to the formation of different crust layers on the surface of buried archaeological marble. The case study is a group of about 3,000 marble fragments, belonging to the highly decorated altar constructed by Octavian Augustus in 31BC in Nikopolis at the western coast of Greece. The excavation lies at an area, which displays a hilly terrain with gentle slopes. The hydrographic network is composed of small streams with seasonal flow. The area of the monument consists of geological formations of the Neogene, of alternating conglomerates, sands, clays and marls which are covered by quaternary deposits and deposits of artificial materials.

The diverse burial environment led to the formation of different crust layers on the surface of the marble, which depended on the location and depth that the fragments were found. Representative samples were examined under the petrographic and scanning electron microscope, coupled with energy dispersive X-ray analyser (SEM/EDX). Mineralogical composition of the encrustations was determined by X-ray diffraction (XRD). The results of the study revealed different formation mechanisms that created three different types of encrustations, including loose depositions and impregnations with metal oxides and hydroxides, calcareous and siliceous encrustations.

At the second part of this work, the conservation methodology that was developed and the techniques tested in order to remove the encrustations from the marble surfaces are presented. Before the application of any cleaning treatment, the surface of the marble was thoroughly studied with microscopic techniques. To determine the depth of cleaning, a set of criteria was set, with a specific number of parameters, which were used during the treatments in order to control the quality of cleaning and to evaluate the result. The tested cleaning techniques included mechanical, chemical and laser cleaning. The results of each technique were evaluated in order to propose the most appropriate one for each case of encrustations.

**Keywords:** archaeological marble, crust formation, cleaning, treatment evaluation

## 1. Introduction

The archaeological site of Nicopolis is situated in the plain of the peninsula of Preveza, between the Ionian Sea and the Ambracian Gulf. A little to the south, opposite the tip of the peninsula of Preveza, lies the promontory of Actium, known for the famous sea battle between Gaius Julius Caesar Octavian, Cleopatra and Antonius in 31BC In the centre of this area, spread the ruins of the city that Octavian built in commemoration of his victory, a victory that constitutes a turning point in the history of the ancient world. North of Nicopolis lies the monument that Octavian erected after the sea battle of Actium. The building, a trophy as well as a sanctuary, was both a symbol of Octavian's victory and power and also a monument of political and religious propaganda.

The monument was built on two terraces, of which the lower is defined by two retaining walls. An inner court is formed measuring 38x38 m, in which stood a monumental altar (6x22 m) and three pedestals for over-life size statues. The entire complex formed a kind of open-air sanctuary (Figure 1). According to the votive inscription in the upper part of the façade of the monument, it was dedicated to Mars and Poseidon. Apollo's sacred hill and the Victory monument were already visible from the city's north gate.

From the first excavations at the aera, the Greek Archaeological Service marked the site as one of immediate interest. During the 1960s, interest was focused on salvage excavations and small-scale reconstructions. Since 1995, an initiative of the 12$^{th}$ Ephorate of Antiquities has launched the financing of the excavations in the archaeological site of Nicopolis. In the layers above and around the foundation, numerous smashed marble architectural fragments were found. In some cases the fragments were found in piles, which suggest deliberate dismantlement, rather than abandonment and natural collapse. More than 43,000 fragments have been found including a variety of moldings and fragments of relief sculptures from the altar's decoration. Of this total, most are undecorated, some of which are of small size (data acquired from the 12$^{th}$ Ephorate of Prehistoric and Classical Antiquities).

The burial environment caused the formation of different encrustations and impregnations on the stone surface. The aim of this project was to conclude to the most suitable method of cleaning the stone fragments. In order to reach to a conclusion, the stone was mineralogically characterised, the depositions on its surface were extensively studied and analysed in terms of their composition and physical characteristics, and a variety of different cleaning methods were tested and finally evaluated.

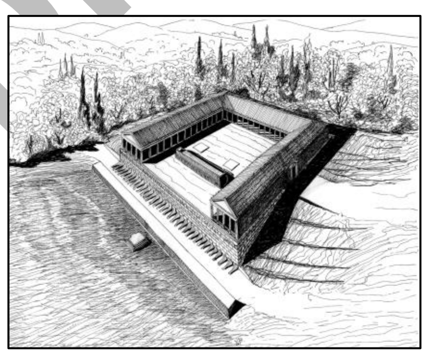

**Figure 1.** Reconstruction of the altar
(12$^{th}$ Ephorate of Prehistoric and Classical Antiquities)

## 2. The burial environment

The altar of Octavian Augustus occupies an area of approximately 6,300 m$^2$. The area displays hilly terrain with gentle, natural slopes. The hydrographic network, which the rainwater is drained through, is composed of small streams with seasonal flow. The area is not susceptible to intense erosion phenomena.

The area of the monument consists of geological formations of the Neogene which are covered by quaternary deposits and deposits of artificial materials. The Neogene formations consist of alternating conglomerates, sands, clays, mixtures and marls. These formations present a characteristic irregular form resulting to lateral transitions from one formation to another.

Specifically, the geological formations that structure the area, from the oldest to the youngest, are:

- Geological formations that are encountered at a depth of 30-35 m. They consist of marly clays and humus ash horizons. These formations contain organic materials. In between the marly formations, thin layers, of about 1-2 m, of sandy marls can be found.
- Marly formations that are covered by fine sand with thin conglomerate horizons. The fine sand is converted laterally into yellowish-brown sandy-clayey formations that are exposed at the archaeological site and at the area north of it.
- Fine sands that are covered with conglomerates with clayey binder.
- Conglomerates that are covered by a horizon of marls.
- Artificial deposits that are found in the superficial layer.

The monument has been fully excavated at various depths. Stratigraphic observations were made during the excavation, whilst the stratigraphy was documented at the deep sides of the trenches. The basic stratigraphic sequence is as follows:

- OM1 layer: surface (humus) with plants having a brownish colour.
- OM2 layer: yellowish sandy clay, either pure or strongly conglomerated.

The survey concluded that the foundation of the monument was constructed on clean soil of the OM2 layer. On these two main layers, several changes can be detected, depending on the use and the interventions to the monument, such as destruction layers and layers of deposits that consist of geological and archaeological material (data acquired from the 12$^{th}$ Ephorate of Prehistoric and Classical Antiquities).

The soil at that location is slightly alkaline with a pH of 7.4 to 8.0. Its chemical composition is mainly characterised by the presence of carbonates, while nitrates and magnesium ions are absent. In some samples, small quantities of sulphates and chlorides were identified.

The mineralogical analysis of the soil, carried out by XRD, showed the presence of the clay minerals montmorillonite ($Al_2O_3.4SiO_2.nH2O$), illite ($K_2O.3Al_2O_3.6SiO_2.2H_2O$) and kaolinite ($Al_2O_3.2SiO_2.2H_2O$), as well as a high content of calcite ($CaCO_3$) and quartz ($SiO_2$), and a few feldspars.

The analysis of the excavation data, show that 36 per cent of the fragments studied, were found at a depth of 2.5 to 2.9 m, 26 per cent of the fragments were found at a depth ranging between 1.0 and 1.5 m, and the rest were excavated from a depth between 0.0 and 0.5 m. Sampling was carried out in different fragments from different depths in order to obtain representative results.

## 3. The construction material

The stone used in the construction of the monument is marble. All the samples that were examined have the same general petrographic characteristics with slight variations concerning mainly the existence of impurities and veining in the parent rock. The impurities were detected mainly at fractured surfaces and not on sculptured surfaces, indicating the careful selection and placement the marble.

Mineralogical analysis of the stone was carried out by XRD, light microscopy (LM) and SEM/EDX. The analyses showed that calcite ($CaCO_3$) is the dominant mineral but dolomite ($CaCO_3.MgCO_3$) was also identified in relatively small quantities. The small quantity of dolomite is not able to characterise the marble as dolomitic. Many impurities and negligible mineralogical components were also identified. These are mainly phyllosilicate minerals of the mica group, such as muscovite $Al_2(Si_3Al)O_{10}(OH,F)_2$, quartz crystals ($SiO_2$) and in a few fragments ankerite $Ca(Fe,Mg,Mn)(CO_3)$ was identified in marble veining.

Regarding the size of the calcite crystals, the marble of the monument can be characterised as fine-grained with granoblastic tissue.

## 4. Study of the depositions on the marble surface

The macroscopic examination of representative fragments, in combination with mineralogical analysis with XRD, LM, and SEM/EDX, of the depositions on the marble surface, concluded to the categorisation of the depositions into three main groups:

- Dendritic depositions,
- Coherent depositions (encrustations) with either pure calcitic composition or with calcitic-aluminosilicious-ferric composition,
- Loose depositions and impregnations with either ferric and aluminosilicious composition of dark brown to black colour, or with aluminosilicious composition of light brown colour.

### 4.1 Dendritic depositions

The main characteristic of these depositions is the form in which they appear (Figures 2 and 3). They were found in several fragments after the removal of loose soil deposits. In some cases two layers were identified. The upper layer with thickness of 50-100 μm, which is more compact, and the lower layer with thickness of 150 μm containing confined grains of calcitic, silicious composition along with aluminosilicates (Figures 4 and 5).

**Figure 2.** Photomacrograph of the surface of the marble.

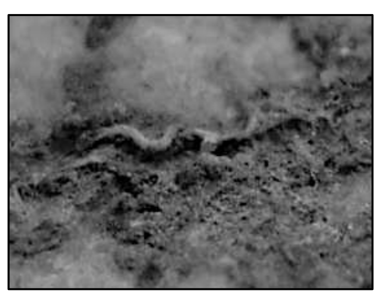

**Figure 3.** Photomacrograph of the deposition layer.

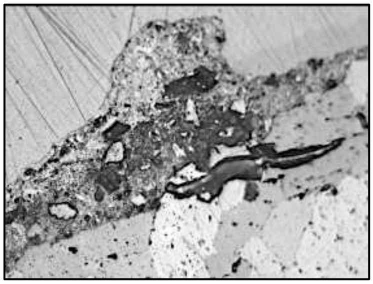

**Figure 4.** Light Microscopy //Nichols. The two layers of the depositions can be distinguished.

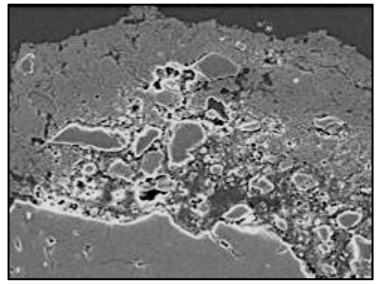

**Figure 5.** SEM photomicrograph of the deposition with the confined grains in the lower layer.

### 4.2 Coherent depositions (encrustations)

Case 1: These are hard, compact crusts of mainly calcitic composition with silicious material. Their main characteristic is their hardness and the relief in which they appear (Figure 6). Their thickness varies from 150 to 900 μm. In some cases two characteristic layers can be distinguished. The upper layer that is compact and has a thickness between 150 and 300 μm. In most cases a characteristic stratigraphy can be identified with alternating layers of calcite and quartz (Figures 7 and 8). The lower layer, where grains of calcite and quartz are confined (Figure 9). Its thickness ranges from 150 to 600 μm. In some cases, the trapped grains are large, measuring up to 500 μm. In general, the boundaries between the layers described and the stone substrate are quite clear.

Case 2: These are encrustations of ferric and aluminosilicious composition with a maximum thickness of 80 μm with an alternating calcitic layer, which is relatively compact. They present a maximum thickness of 200 μm and in most cases the limits with the stone substrate are very clear (Figures 10 and 11).



**Figure 6.** Photomacrograph of the encrustation (case 1) on the surface of the marble.

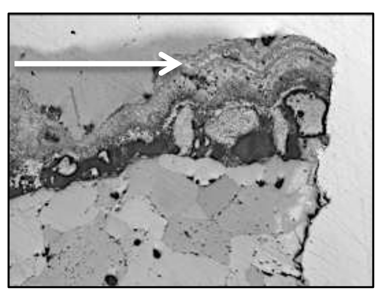

**Figure 7.** Light Microscopy //Nichols. Alternating deposition layers of calcite and quartz.

**Figure 8.** SEM/EDX mapping of Ca and Si of the same area shown at figure 7. Alternating layers of siliceous and calcareous deposits.

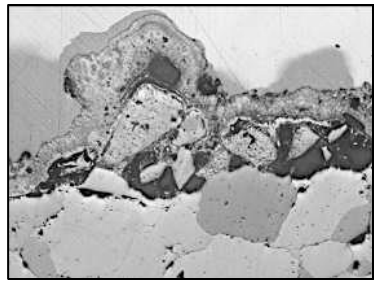

**Figure 9.** Light Microscopy //Nichols. Two deposition layers can be identified as well as the grains of calcite and quartz.

**Figure 10.** Photomacrograph of the encrustation (case 2) on the surface of the marble

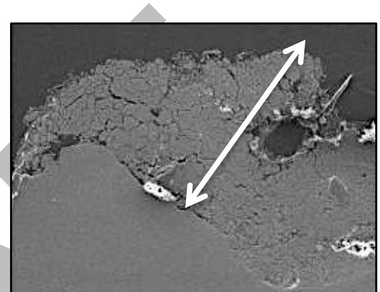

**Figure 11.** SEM photomicrograph of the encrustation. Small Al-Si grains can be identified. Clear limits with the substrate.



### 4.3 Loose depositions and impregnations

Case 1: They mainly consist of silicon, aluminium and iron. In some cases, they appear as a layer of loose deposits of moderate consistency (Figure 12). The thickness of this layer does not exceed 100 μm.

Case 2: Loose depositions and impregnations of aluminosilicious composition. They penetrate between the crystals of the stone, to a depth of 500 μm (Figure 13).

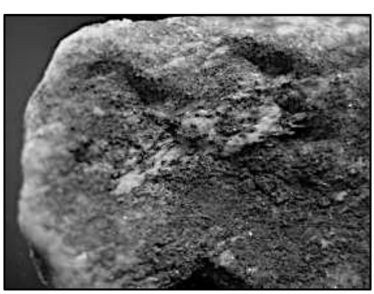

**Figure 12.** Photomacrograph of the deposition (case 1) on the surface of the marble

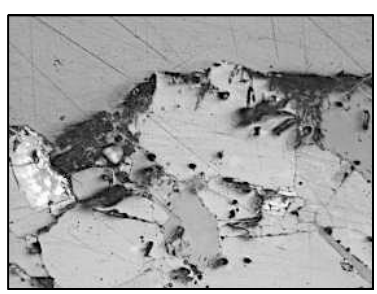

**Figure 13.** Light Microscopy //Nichols. Impregnations (black stains) of ferric and aluminosilicious

composition.

## 5. Cleaning

Cleaning is one of the key stages of conservation interventions, aiming at removing the substances that promote stone weathering as well as to restore the aesthetic value of the work by revealing the original surface and its details. The most important step is to determine the cleaning depth (Papakonstantinou *et al.*, 2007), which is defined by the preservation state of the original surface of the substrate, protecting at the same time the relief of the sculptured surface (Webster, 1992). In order to evaluate the cleaning treatments, clear criteria were set with a number of parameters that were used during and after cleaning treatments, to control the quality of each treatment (Moropoulou *et al.*, 2002).

Acceptable cleaning limits were determined by the study of the morphology of the depositions and the substrate. For each deposition category the desired cleaning depth was determined. After the application of the cleaning methods the treated surface was examined in order to evaluate the result.

### 5.1 Cleaning depth

Dendritic depositions: The aim of cleaning was to remove the top layer of the deposition having thickness of 200-250 μm. The interface of this layer to the substrate was the cleaning limit. Since the outer layer of the stone displayed an intense relief, of 40 μm, particular care was taken in order not to affect it during cleaning (Figure 13).

Coherent encrustations: The scope was to remove the coherent calcitic depositions of 200-1,000 μm thickness. The interface of this layer to the substrate was the cleaning limit. The outer layers of the stone presented a relief of 20-50 μm, and particular attention was paid in order not to affect it during cleaning. The original surface of the stone was protected by preserving a very thin layer (20-30 μm) of the deposition. This layer is translucent and it does not affect the aesthetic values of the stone surface (Figure 14).

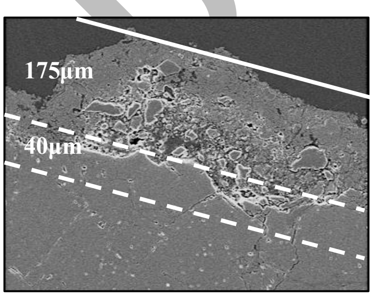


**Figure 13.** Cleaning limits for dendritic depositions

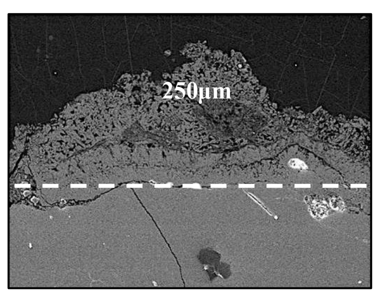


**Figure 14.** Cleaning limits for coherent depositions

### 5.2 Cleaning methods tested

Based on the chemical-mineralogical composition and the morphology of the deposition layers, the tested cleaning methods were:

- Poultices, based on aqueous solutions of ethylenediaminetetraacetic acid (EDTA) with sodium bicarbonate ($NaHCO_3$) and ammonium bicarbonate ($(NH_4)HCO_3$), mixed with sepiolite.
- Mechanical methods: hand tools, micro-sandblast, and ultrasonic scaler. In the case of micro-sandblast, aluminium oxide ($Al_2O_3$) with grain size ranging from 25-250 μm was used as the abrasive material, at an operating pressure ranging from 100 to 600 kPa.
- Two types of laser systems, developed at the Institute of Electronic Structure and Laser – FORTH, Greece (Pouli *et al.*, 2003): The Q-switched Nd:YAG @1,064 nm (ElEn) and the SL805 Nd:YAG @1,064 nm (Spectron). Both laser systems were tested with different fluence ($J/m^2$) and pulse duration.
- Water-based methods: Wetting, vapour blasting.

All cleaning methods were tested on each of the three categories of the deposition layers. After the treatment and the removal of the depositions, the stone surface was studied by the use of SEM/EDX and LM, in order to evaluate the result.

## 6. Results

The results from the cleaning tests performed are presented by category of deposits. The evaluation of each method was based on the results of laboratory examination and analyses as well as on the macroscopic characteristics of the stone surface after the application of each cleaning method. The results were then classified based on the following scale:

- "Effective method": The cleaning was successful. Depositions are removed without disturbing the substrate and the patina layer.
- "Method partially effective" due to one of the following reasons:
  - The thickness of the depositions is reduced but the cleaning is not fully achieved.
  - A complementary method is required to achieve the result
  - Can be applied to specific sub-cases.
- "Method ineffective" due to one of the following reasons:
  - Cleaning is not achieved and the depositions are not removed.
  - The method is aggressive and causing damage to the substrate.



### 6.1 Dendritic depositions

The method of micro-sandblast with small grain size of $Al_2O_3$ was excluded without further testing, because it was not possible to apply it to the limited areas of this type of depositions. The method was evaluated as "ineffective".

The method of poultices showed no satisfactory results. The depositions were not removed, but their thickness was reduced. The results were good in cases where, after the application of the poultice, ultrasound scraper was applied. In these tests, the dendritic deposits were removed to a greater extent. The method was evaluated as "partially effective".

The method of the ultrasonic scaler at low ultrasound intensity on a wetted stone surface produced satisfactory results but the depositions were not completely removed. The method was evaluated as "partially effective".

The method of vapour blasting had no effect in removing the deposits. The method was evaluated as "ineffective".

The method of laser (Q-switched Nd: YAG laser@1,064 nm) had a very good result with optimal operating conditions of fluence at 0.62 J/cm$^2$, pulse rate at 10 Hz and a variable number of pulses. The substrate is not disturbed while the time required to remove the deposits is small. The method was evaluated as “effective”.

The method of laser (Spectron laser system SL805 Nd: YAG laser@1,064 nm) had better results with optimal operating conditions of fluence at 1.7 J/cm$^2$, pulse duration 10 ns and a variable number of pulses. The substrate is not disturbed while the time required to remove the deposits is small. The method was evaluated as “effective”.

### 6.2 Coherent depositions (encrustations)

The method of micro-sandblast with small grain size of $Al_2O_3$ did not give satisfactory results. The substrate surface appeared rough and it the method was likely to cause damage to the substrate in areas where the encrustation is less thick. The method was evaluated as “ineffective”.

The method of poultices did not produce good results. Although application times were quite large, the depositions were not removed nor was their thickness reduced. The method was evaluated as “ineffective”.

The method of the ultrasonic scaler at low ultrasound intensity on a wetted stone surface removed the crusts of aluminosilicious composition and reduced the thickness of the calcitic ones. The method was evaluated as “partially effective”.

The method of vapour blasting had no effect in removing the deposits. The method was evaluated as “ineffective”.

The method of laser (Q-switched Nd: YAG laser@1,064 nm) had satisfactory results with optimal operating conditions of fluence at 1.43 J/cm$^2$, pulse rate at 10 Hz and a variable number of pulses. After the application though, remains of the crust on the stone surface were observed which were removed by the use of ultrasonic scaler. The method was evaluated as “partially effective”.

The method of laser (Spectron laser system SL805 Nd: YAG laser@1,064 nm) was the most effective of all methods tested. The optimal operating conditions were 3.8 J/cm$^2$ of fluence, with pulse duration of 10 ns and a variable number of pulses. The substrate was not disturbed and the crust was completely removed. In the case where the operator persisted in a specific area, the high operating power could possibly disturb the substrate. The method was evaluated as “effective”.

### 6.3 Loose depositions and impregnations

The method of micro-sandblast with small grain size of $Al_2O_3$ was excluded without further testing, since the impregnation does not create a surface layer. Its use may have caused damage to the substrate. The method was evaluated as “ineffective”.

The method of poultices did not achieve adequate cleaning. Further tests with poultices of hydrogen peroxide ($H_2O_2$) and ammonia ($NH_3$) gave very good results. The method was evaluated as “effective”.

The method of the ultrasonic scaler at low ultrasound intensity on a wetted stone surface was excluded without further testing, since the impregnation does not create a surface layer. Its use may have caused damage to the substrate. The method was evaluated as “ineffective.

The method of vapour blasting had good results on flat surfaces with no or little relief. The impregnations were removed without disturbing the substrate. Particular care was needed in relief surfaces where the highest points received greater amount of vapour resulting in uneven cleaning. The method was evaluated as "partially effective".

The method of laser (Q-switched Nd: YAG laser@1,064 nm) had satisfactory results with operating conditions of fluence 1.43 J/cm$^2$, pulse rate at 10 Hz and a variable number of pulses. The impregnation was completely removed without disturbing the patina layer and the surface of the substrate. The method was evaluated as "effective".

The method of laser (Spectron laser system SL805 Nd: YAG laser@1,064 nm) is the most effective with optimal operating conditions of fluence at 2.8 J/cm$^2$, pulse duration 10 ns and a variable number of pulses. The substrate was not disturbed and the deposition was completely removed. The method was evaluated as "effective".

## 7. Conclusions

By comparing the results of the cleaning tests, some general remarks can be made. The marble surface after cleaning with micro-sandblast appeared rougher. According to the degree of control of each method they were classified as follows: laser, ultrasonic scaler, micro-sandblast, vapour blast, poultices. Poultices and ultrasonic scaler produced the slowest cleaning times of the all the methods tested.

The SL805 Nd:YAG laser@1,064 nm laser system proved to be the most suitable for the removal of all three types of depositions since the quality of the final result was high and the possibility of damaging the original surface was minimum. The settings of the laser system though, are different for each case of depositions. Other cleaning methods gave satisfactory results and the factor of cost-effective treatment has to be carefully considered.



## Acknowledgements

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