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MATERIALS CHARACTERIZATION

Digital processing of SEM images for the assessment of evaluation indexes of cleaning interventions on Pentelic marble surfaces

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Abstract

In this work, digital processing of scanning-electron-microscopy images utilized to assess cleaning interventions applied on the Pentelic marble surfaces of the National Archaeological Museum and National Library in Athens, Greece. Beside mineralogical and chemical characterization that took place by scanning-electron-microscopy with Energy Dispersive X-ray Spectroscopy, the image-analysis program EDGE was applied for estimating three evaluation indexes of the marble micro-structure. The EDGE program was developed by the U.S. Geological Survey for the evaluation of cleaning interventions applied on Philadelphia City Hall. This computer program analyzes scanning-electron-microscopy images of stone specimens cut in cross-section for measuring the fractal dimension of the exposed surfaces, the stone near-surface fracture density, the shape factor (a surface roughness factor) and the friability index which represents the physico-chemical and physico-mechanical stability of the stone surface. The results indicated that the evaluation of the marble surface micro-structure before and after cleaning is achieved by the suggested indexes, while the performance of cleaning interventions on the marble surfaces can be assessed.

Keywords: Marble; Cleaning; Cleaning evaluation; SEM; Digital processing; EDGE

1. Introduction

As various forms of decay take place on stone surfaces (black-grey crusts, white carbonated crusts, biological crusts, black organic deposits, etc.), being the result of complex physico-chemical processes (e.g. sulphation of calcite) mainly due to urban environmental pollution, a cleaning treatment should contribute to the improvement of the properties of the material surface, revealing its artistic and aesthetic value [1].

The assessment of cleaning interventions on the stone surface of buildings is a complicated process, for which several parameters concerning the alterations to the surface should be taken under consideration. An understanding of the final aesthetic result and the chemical composition of the material after cleaning are essential but not sufficient; the morphological characteristics of the surface should also be included in the evaluation of a cleaning process. Therefore, in order to accomplish an objective characterization of the micro-structure, it is important to determine the specific evaluation criteria for the assessment of surface morphology. Scanning-electron-microscopy (SEM) is an invaluable and commonly used tool for the study of a stone surface

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before and after cleaning treatments, through which important topographical and compositional information can be extracted [2–5]. Furthermore, digital processing of the images obtained from SEM may determine properties of the micro-structure, such as porosity [6,7] or surface roughness [8,9].

In this work, SEM coupled with Energy Dispersive X-ray Spectroscopy (EDS), has been employed for the mineral, chemical and textural identification of samples cut in cross-sections, coming from weathered Pentelic marble surfaces that exhibit black-grey crusts. This type of decay on marbles is a result of the formation of gypsum due to the attack of sulfur-bearing atmospheric pollutants [10,11]. The study also included the investigation of the chemical composition alterations after the application of pilot cleaning interventions. Moreover and most importantly, the SEM images were analyzed by means of the computer program EDGE.EXE [8]. The EDGE program was developed by the US Geological Survey under the framework of the scientific study of the selection of cleaning interventions for the historic Philadelphia City Hall building [9]. EDGE is a computer program which analyzes scanning-electron-microscopy images for measuring the fractal dimension of the

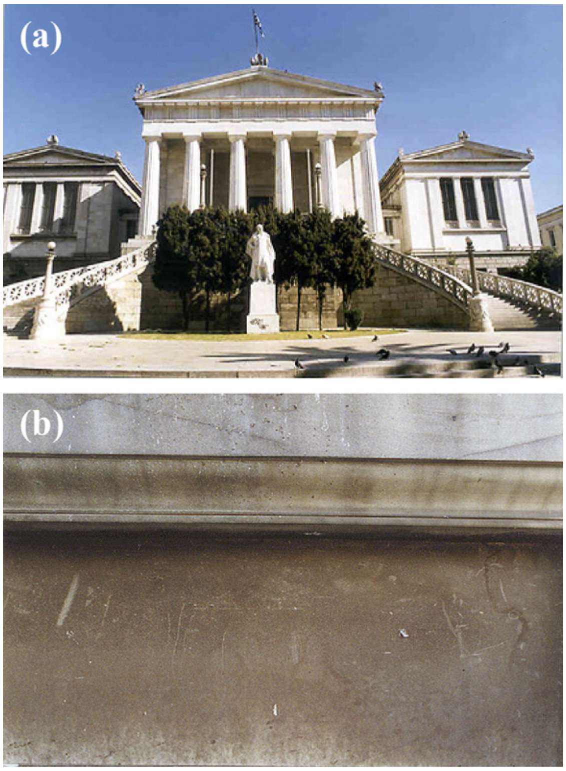

Fig. 1. Historic building of the National Library of Greece (a) and the investigation area (b).

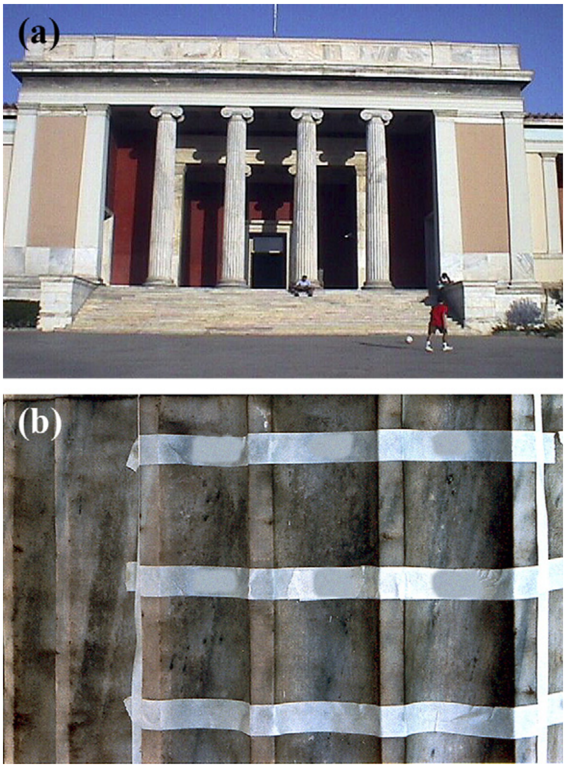

Fig. 2. The historic building of the National Archaeological Museum (a) and the investigation area (b).

exposed surfaces of stone specimens cut in cross-section [8,9]. The near-surface fracture density of the stone can also be computed, while the shape factor, a surface roughness factor, results from the traced fractal dimension [8,9]. In addition, the parameter of friability index is introduced, representing the physico-chemical and physico-mechanical stability of the stone surface, [8,9]. The application of the EDGE program on the presented SEM images resulted successfully in the assessment of Pentelic marble surface micro-structure before and after cleaning, permitting more information to be gathered on the performance of the applied cleaning interventions.

2. Experimental methods

2.1. Sampling

The areas of sampling were two architectural surfaces (Figs. 1b, 2b) of the historic buildings of the National Library of Greece and the National Archaeological Museum; both consisted of Pentelic marble [12,13]. The buildings were constructed at the beginning of the 20th century and are situated in the center of Athens (Figs. 1a, 2a). The samples obtained before the pilot cleaning intervention were used for the decay diagnosis of the investigated surfaces. After the cleaning interventions, samples were collected and examined in order to assess the different cleaning methods, in terms of their effectiveness, determining the most efficient among them. Table 1 lists the applied cleaning methods of the pilot interventions on the two historic buildings and the corresponding surface codes.

Analyses were carried out using a scanning-electron-microscopy (JEOL JSM-5600, OXFORD LINK™ ISIS™ 300 Energy Dispersive X-ray Microanalysis system (accelerating voltage 20 kV, beam current 0.5 nA, lifetime 50 s, beam diameter <2 μm).

Details of the EDGE software program are given in Mossotti and Eldeeb [8] and Mossotti et al. [9]. The following discussion is a summary of the important features relevant to this study. The EDGE program was developed for the analysis of back-scattered electron-micrograph images stored in a binary file format that represents images with lateral resolution of 1.7 μm/pixel. However, in this work the images had a lateral resolution of 2 μm/pixel. EDGE measurements have to be made by computer analysis of 100× SEM images of core cross-sections, consisting of 512 rows with 512 pixels per row, where each pixel is encoded with 8 bits on a 256-shade gray-scale palette. The fractal dimensions of the exposed surfaces of stone specimens cut in cross-section are measured. An EDGE user during calibration defines the gray values of PORE state and MASS state, that is, pixels with gray values less than or equal to the lower threshold (T_L) are labeled as PORE, whereas pixels with gray values equal to or greater than the upper threshold (T_U) are labeled as MASS. The pixels of gray values between the threshold parameters belong to the state EDGE, from which the fractal dimension derives. It is obvious though, that the calibration procedure and the number of pixels identified as EDGE, depends on the user's experience with scanning-electron-microscopy images and the characteristics of the investigated material. The determination of the fractal dimension is based on a Richardson structured walk at a fixed contour level along the profile of the exposed surface of the specimen. The shape factor (Γ_R), a surface roughness factor, results from the traced fractal dimension. The near-surface fracture density (FD) of the stone can be also computed, and is a measure of the fraction of the stone volume filled by fractures, crevices, and pore space. The results are reported as the percentage of pixels identified as components of the fractures calculated to a 100 μm depth under the surface area. Moreover, the parameter of friability index (FI) is introduced, reflecting the relation between the fracture density (FD) and the surface roughness. It also refers to the friability of the stone on the micro-scale, representing the physico-chemical and physico-mechanical stability of the stone surface and is given by:

$$FI = \sqrt{(FD)^2 + (\Gamma_R)^2}\,. \quad (1)$$

Table 1
Applied cleaning methods and surface codes for both historic buildings

National Library of Greece		
Surface code	Applied cleaning methods	Application time
Pnc22	Poultice of $(NH_4)_2CO_3$, 10% w/v with deionized water	2 h
Pab12	Poultice AB57 (1 l deionized water, 30 g NH_4HCO_3,50 g $NaHCO_3$, 25 g of bi-sodium E.D.T.A., 10 ml Desogen, 800 g sepiolite)	1 h
Ps32	Poultice of sepiolite with deionized water	3.5 h
National Archaeological Museum		
Surface code	Applied cleaning methods	Application time
Ke3b	Poultice of ion-exchange resin with deionized water	30 min
Ke4	Biological poultice (1000 ml deionized water, 50 g $(NH_2)_2CO$, 20 ml $(CH_2OH)_2CHOH$ and approximately 800 g sepiolite)	18 days
Keg3	Wet micro-blasting method where spherical particles of calcium carbonate (diameter <80 μm), were springing with a maximum function pressure of 0.5 bar. The proportion of water and spherical particles of calcium carbonate in the device's commixture barrel was 3:1	–

3. Results and discussion

3.1. SEM/EDS observations

In this section, observations that derive from the SEM images and EDS analysis are mentioned briefly, in order to describe the decay on the two surfaces and also the alterations provoked by the cleaning interventions. For the decay diagnosis, samples that correspond to the two architectural surfaces have been examined (Fig. 3).

The National Library of Greece sample (code name Pm1) presented a crust that consisted mostly of gypsum grains mixed with dust-fall (mainly aluminosilicates and Fe), whereas the lower part of the crust was made of micro-crystalline gypsum (diameter < 10 μm). The layer seemed cohesive, retained an intense relief and a width of 20 to 80 μm. The calcite matrix was separated at

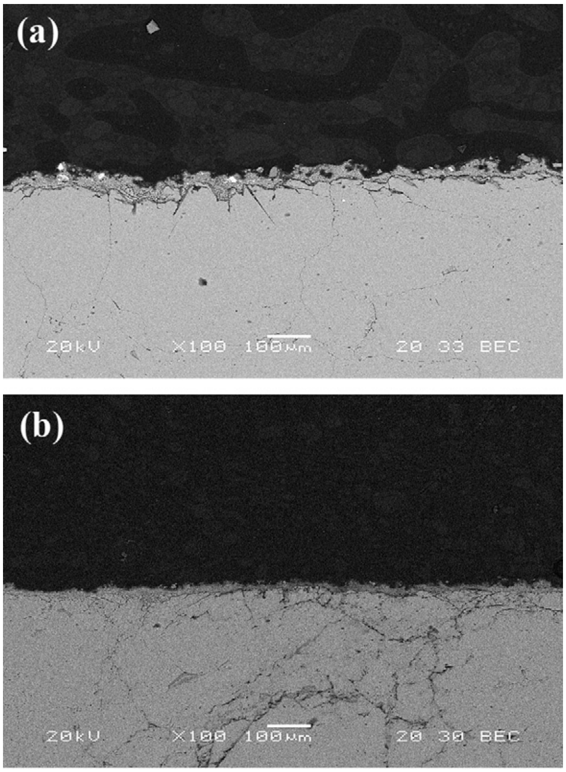

Fig. 3. SEM images for the decay diagnosis of (a) National Library of Greece surface and (b) National Archaeological Museum surface.

length from the crust with a fracture of approximately 3 μm width. From EDS analysis, *S* was not traced in the matrix, meaning that the sulphation of calcite did not extend to a greater depth— that is beyond the fracture. The National Archaeological Museum sample (code name Ke6), disclosed a distinct gypsum layer along with dust-fall of approximately 40 μm width. Although the calcite matrix appeared fractured, beneath the gypsum layer pure calcite without traces of *S* was found.

After cleaning, the surface of the National Library of Greece presented the following characteristics (Fig. 4); at the surface cleaned with a poultice of $(NH_4)_2CO_3$ (code Pnc22), gypsum was entirely removed. The marble surface presented an intense relief and it is assumed that loss of original material had occurred as the entire gypsum layer was removed, while many micro-cracks and fractures (with diameter up to 10 μm) appeared, probably as a result of the effect of the cleaning. After the treatment with AB57 poultice (code Pab12), the width of the gypsum surface layer had been reduced from 5 to 20 μm, preserving most of the micro-crystalline gypsum layer. The calcite matrix was deteriorated since micro-cracks and fractures were found to considerable depth. On the contrary, cleaning with the sepiolite poultice (code Ps32) did not reduce the gypsum layer, resulting in the retention of the black-grey crust.

After the National Archaeological Museum surface cleaning, samples corresponding to three different applications were collected (Fig. 5). After the cleaning intervention with the ion-exchange resin (code Ke3b), the layer of gypsum remained at a width of 10 μm. In contrast, on the marble surface treated with the biological poultice (code Ke4), no gypsum or traces of *S* were detected. At the surface treated with the wet micro-blasting method (code Keg3), only traces of *S* were found in distinct points of the surface up to a depth of 10 μm. Visual observation

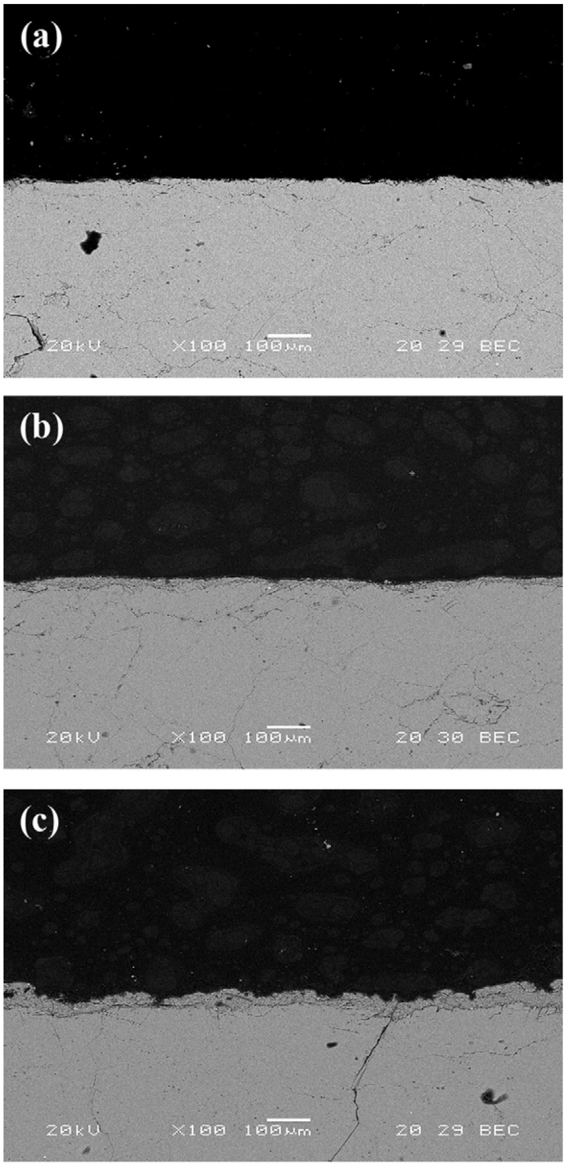

Fig. 4. SEM images of (a) Surface Pnc22, (b) Surface Pab12, (c) Surface Ps32, National Library of Greece.

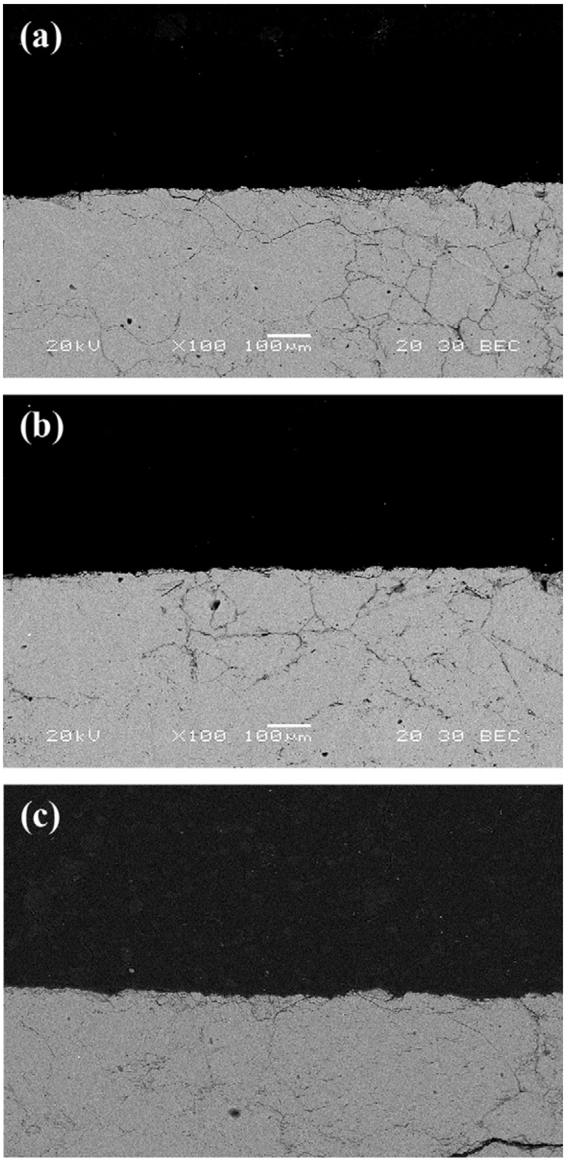

Fig. 5. SEM images of (a) Surface Ke3b, (b) Surface Ke4, (c) Surface Keg3, National Ar chaeological Museum.

of the surface grains denoted the removal of gypsum layers and over all an increase of irregularities of the sample outline. In general though, all three samples displayed fissures at grain boundaries at increased depths, a remark noted also for the decay sample.

3.2. SEM image processing

The results from the measurements of digital image processing using EDGE [8,9], are reported in Table 2. Higher values of fractal dimension entail increased roughness or irregularities of the sample's profile [14], meaning that shape factor values (the EDGE roughness indicator) would be higher. This does not play a direct role in the values of fracture density, but values of the friability index are definitely and directly affected, since it is given by Eq. (1).

The surface indexes of both of the black-grey crust baseline samples (codes Pm1, Ke6, Table 2) retained higher values of fractal dimension (1.114, 1.085, respectively), and shape factor (3.48, 3.02, respectively) compared to the corresponding values after the cleaning interventions, except for the cleaning by the wet micro-blasting for the National Archaeological Museum. Both micro-structure indexes described a rough relief of the gypsum crust. In parallel, the relatively high values of fracture density (23.2, 14.1, respectively) can be attributed to the porosity of the gypsum layer mixed with dust-fall. However, the high values of the friability index (41.82, 33.3, respectively) indicate the physico-mechanical and physico-chemical instability of the examined surf aces, revealing that the surface friability refers to possible loss of gypsum grains and dust-fall. Comparing values of indices between these baseline decay samples it was concluded that the National Library of Greece sample was more deteriorated than that from the National Archaeological Museum. This is probably due to the fact that the historic building of the National Library of Greece had never been cleaned since its construction in 1905 [12]; whereas at the surfaces of historic building of the National Archaeological Museum, some cleaning interventions occurred 10 years ago [13].

The application of $(NH_4)_2CO_3$ poultice (code Pnc22) at the National Library of Greece resulted in a relatively smooth surface of a medium value of shape factor (2.47), while the superficial gypsum layer was not preserved. Nevertheless, the values of friability index (29.76) and fracture density (16.3) were the higher among the

Table 2
Results of digital image processing with EDGE program

Sample code	Fractal dimension	Fracture density FD (%)	Shape factor (Γ_R)	Friability Index FI (%)
Surface of National Library of Greece				
Pm1 [a]	1.114	23.2	3.48	41.82
Pnc22	1.040	16.3	2.47	29.76
Pab12	1.043	10.4	2.63	28.25
Ps32	1.036	10.0	2.42	26.18
Surface of National Archaeological Museum				
Ke6 [a]	1.085	14.1	3.02	33.3
Ke3b	1.053	13.2	2.57	28.8
Ke4	1.037	4.3	2.44	24.8
Keg3	1.144	18.1	3.94	43.3

[a] Samples removed before cleaning interventions.

examined surfaces at the National Library of Greece. Loss of original material is further assumed by these microstructure indexes, as well as susceptibility to decay, since the superficial stone friability refers only to calcite grains. On the contrary, when the AB57 poultice was applied, the resulting surface (code Pab12) retained the micro-crystalline gypsum layer, which is acceptable and desirable [15]. Micro-crystalline gypsum is the first and compact part of marble sulphation process [10,16], and the desirable remaining part of the black-grey crust during cleaning, since it preserves the details of carved and plane surfaces [15]. The morphological characteristics, described from the medium values of shape factor (2.63), and fracture density (10.4), indicated a relatively low surface roughness and low superficial fracturing. Furthermore, the value of the friability index (28.25) corresponded to a surface which was relatively unstable. However, the friability index reflects the physico-mechanical and physico-chemical instability of the remaining gypsum layer. Finally, the surface cleaned with the sepiolite paste (code Ps32) maintained a smooth relief, as the value of the shape factor (2.42) is the lowest of the investigated surfaces of the National Library of Greece. Still, macroscopic observations [12] and EDS analyses indicated that the crust was not removed after cleaning, meaning that the low value of the shape factor describes the removal of dust-fall and possibly part of the superficial crust, while the remaining zone of the sample consists of pure cohesive gypsum (low value of fracture density −10.0), to which the lowest friability index (26.18) corresponds.

The cleaning intervention of the ion-exchange resin (code Ke3b) at the National Archaeological Museum was the only one of the applied methods that did not entirely remove the gypsum layer. The remaining gypsum layer of approximately 10 μm width is acceptable and desirable on cleaning black-grey crusts, as mentioned above [15]. Furthermore, the shape factor (2.57), and fracture density (13.2), had intermediate to low values compared to the other cleaning methods. The friability index (28.8), also presented a median value, suggesting the relative instability of the preserved gypsum layer and not of the calcite matrix. The biological poultice-cleaned surface (code Ke4) exhibited the lowest values of shape factor (2.44), fracture density (4.3) and friability index (24.8), demonstrating low surface roughness and fracturing, as well as physico-chemical and physico-mechanical stability. On the other hand, for this case, the values of the micro-structure indexes refer to the pure calcite matrix, because cleaning had removed the gypsum layer. Additionally, when compared to the other values, especially those of ion-exchange resin surface, small differences are disclosed. In parallel, taking into consideration the extremely low fracture density value and that the observed micro-cracks of the decay sample were not present in the Ke4 sample, the suspicions that original material loss had occurred were increased. The surface cleaned by wet micro-blasting (code Keg3) displayed the highest values of all the examined micro-structural indexes (even higher than the values of the decay diagnosis sample). The surface held the highest value of shape factor (3.94), ascribing the extremely high surface roughness. Furthermore, the value of the fracture density (18.1) was extremely high quantifying and demonstrating the incompatibility of the applied cleaning method, especially if we consider the removal of the gypsum layer. Additionally, the extremely high value of the friability index (43.3), pointed out the great physico-mechanical and physico-chemical instability of the surface, revealing that the surface friability refers to possible loss of calcite grains that is susceptibility to further decay.

4. Conclusions

The application of the EDGE program of the US Geological Survey to the SEM images presented in this study provided encouraging results. It was determined that the evaluation and classification of the Pentelic marble micro-structure before and after cleaning can be accomplished, whereas the performance of cleaning interventions can be assessed by the suggested micro-structure evaluation indexes. The contribution of stone morphological evaluation that includes quantified parameters which describe roughness, fracturing and friability is invaluable in providing an integrated decay diagnosis, as well as better decision making on the planning for cleaning of decayed marble.

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