EVALUATION OF THE CLEANING METHODS

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ABSTRACT

To the several claims of the Venice Charter and its successive extensions for the rational cleaning of Monument Stones we added two more criteria for the selection of the appropriate method and materials:

- For the same area of marble or stone block, more than one method or material can be used successively;
- We must not eliminate the gypsum films, because the grain boundaries of marbles and stones are selectively sulfated and their elimination can lead to grain detachment. In addition to this we observed that the surface of gypsum films, details of the statues and ornaments are preserved, although they are sometimes eliminated from the marble surfaces; thus we must act against the definite loss of them, preserving the gypsum films.

According to all this, from the forty methods and materials used today we selected only four (ameliorated or new) for cleaning the West Frieze of Parthenon: micro-blasting, sorptive pastes, inversion of gypsum, LASER, all four are not destructive.

On the contrary, for the cleaning of the Parthenon Marbles in the British Museum they use today the following methods and materials: water solution of soap with ammonia, NITROMORSE (methyl

chloride) and afterwards they use a coating of polyethylene glycol. As it is described and proved with the present work, all three treatments are destructive for the marble surfaces. Thus, beside the great damages caused on the surface of these marbles between 1930-1938 by inappropriate methods of cleaning, their deterioration still continues today.

In the Venice Charter and its successive extensions, concerning the principles of conservation, and in the literature /1-4/ some specific criteria for the selection of the appropriate method and materials for cleaning soiled marbles in monuments are mentioned.

Thus the methods, the materials used and the conditions of their application:

- Must not deteriorate directly (mechanical or chemical attack) or indirectly the surface, they must not have dangerous byproducts for the surface or the workers, not to augment existing cracks or produce cracks, nor to lead to material loss.
- Not to eliminate the natural patina and the old polychromies.
- The rate of cleaning must be low in order that it can be immediately stopped before producing greater damages.
- The selection also depends on the chemical and crystallographic structure of the marble, its porosity, the type of deterioration and the type of the soiling particles.

I also think that two more criteria must be added:

- The cleaning must not eliminate the gypsum films, formed by SO_2 attack on marble.
- For the same marble block in the same or different area, it can be selected more than one method, material or conditions according to the local deterioration and it must also be taken into account all

the microstructure elements, that is besides porosity, grain size, shape, their orientation, structural and ionic defects, dislocations, active centers and active paths.

Thus, before using a cleaning method or material it must be tested if these criteria are accomplished. It must also taken into account the experience on their application to other monuments for a long time. As we have seeing and we may see none of these principles and criteria have being followed by the interventions on the sculptures in British Museum. The Venice Charter did not exist at that time but the principles were evident**;** nevertheless it existed after 1964.

The need of preserving gypsum films derives from two facts:

The grain boundaries are selectively sulfated due to dislocations produced in them during the formation of the grains and the collisions to each other. Thus the elimination of these gypsum films can lead to grain detachment /5/ (Fig. 1).

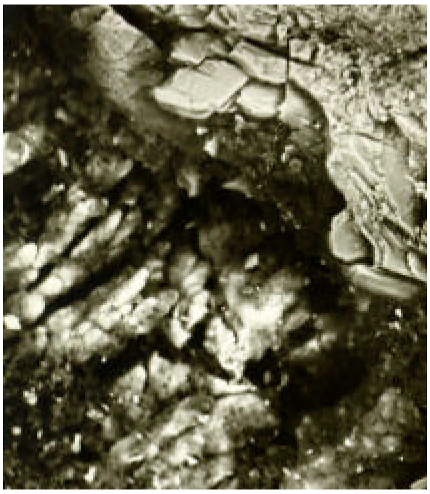

Fig.1, Sulfated grain boundaries, ready to be detached, after their washing with water.

- The second reason is based on our observation that on the gypsum films details of the statues and ornaments are preserved /5-8/ which are often eliminated from the marble surface (Figs.2,3) according to the mechanism of sulfation we revealed /9-14/.

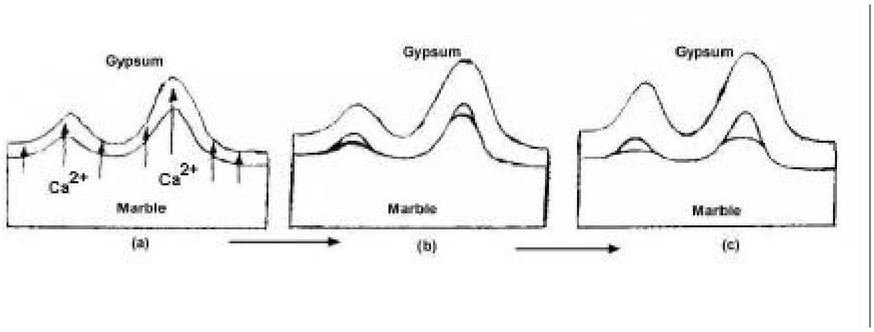

Fig.2, Schematic presentation of gypsum formation on stone and marble surfaces

Figs.3. Sulfation on the back of a Caryatid. Rear surface protected from rainwater.

When gypsum films become thicker than some mm they crack and are destroyed due to cavities formation beneath the high reliefs, because the rate of diffusion of calcium ions is higher according to the higher concentration of dynamic lines of the electrostatic field. Since the atmospheric pressure is higher than the vapor pressure in the cavities the film cracks. Thus in order not to obtain a definite loss of the details we must not destroy the gypsum films**;** on the contrary, we must consolidate them. In this way we thought to inverse gypsum back into calcite /15-19/. This was achieved by placing sulfated specimens of marble or gypsum statues in an autoclave in CO_2 atmosphere at 2-8 atm pressure and at a temperature of 30- 80^o C:

$$CaSO_4{\cdot}2H_2O_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} + [(H_3O)^+HSO_4^-]_{(sol)}$$

Since the equilibrium of the system as regards $CaSO_4{\cdot}2H_2O$ has one degree of freedom (C=3, phases F=4 and M =C+2-F =1), and two conditions change, the equilibrium is destroyed and the reaction moves toward the right (calcite).When the gypsum has been entirely converted to $CaCO_3$, we channel water into autoclave at the same pressure and temperature and wash off the $(H_3O)^+HSO_4^-$, so that when the calcite returns to normal conditions, will not reverse again by the reaction. Our laboratory managed to achieve the same inversion under normal conditions, by spraying a K_2CO_3 solution in situ. Recently, using the K_2CO_3 solution again, and with the presence of $CaCO_3$ in the solution, we achieved a reconversion, which led to oriented $CaCO_3$ crystals (Fig.4) with a hardness of 80 Kp/mm^2, i.e. about the same as marble. It should be noted that the sole purpose of this conversion is to preserve the details on the statues and consolidate the grain boundaries**;** that is obviously not a means of protection but of consolidation.

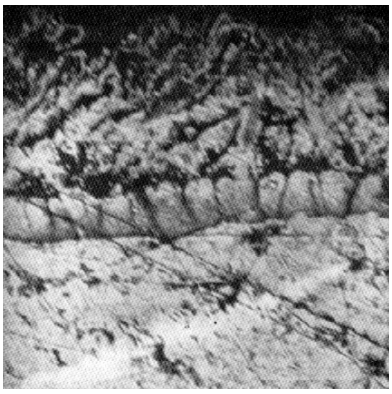

Fig.4 Calcite crystals originating from gypsun inversion.

Besides the consolidation of gypsum films the same method is a new cleaning method /20/, because the molecular volume of calcite is lower than that of gypsum and the calcite is porous the soiling particles are free to be removed by air blasting (Fig. 5).

Fig.5 Successive interventions with potassium carbonate solution on gypsum for cleaning.

This is among all the others the only chemical method we selected and we shall apply for cleaning parts of the Parthenon Frieze in Athens. Because according also to the new criteria for valuable sculptures in valuable monuments, we were obligate to exclude a great number of methods and materials.

It must be noted that the surfaces on which gypsum is formed and are preserved from rain water are the most soiled ones by loose deposition of suspended particles because of the roughness of the gypsum surface and the great number of active centers with high sorptive intensity.

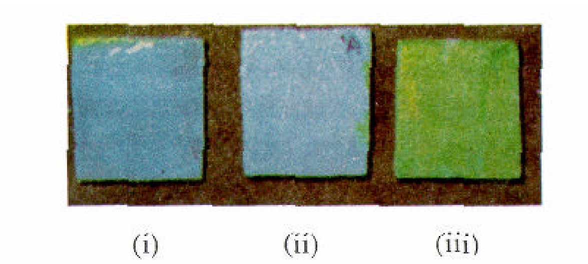

Fig.6, .i. Mixture of liquid crystals on marble. ii. The same mixture of liquid crystals on calcite from inversion of gypsum. iii. The same mixture on the surface of sulfated marble at 25^{o}C.

Before proceeding to the cleaning it is necessary to identify the gypsum areas under the soiling particles. This is possible to accomplish with a non-destructive method of ours using cholesteric liquid crystals, the color of which changes according to the soprtive properties of their support (Fig. 6) /21-23/. It is also necessary to find the thickness of the gypsum films by a non-destructive device we constructed (Fig. 7) /24/.

The second method we selected is the known one using sorptive paste of sepiolite, but prepared with water saturated in calcite in order not to dissolve gypsum. The conservators of the Acropolis Monuments have found the optimum conditions, using also Japanese paper between marble and paste. The third method is the miclo-blasting which was also studied in details to select the appropriate material, its grain size distribution, its shape, its hardness, the appropriate pressure, to use it for blasting and to offer the optimum results.

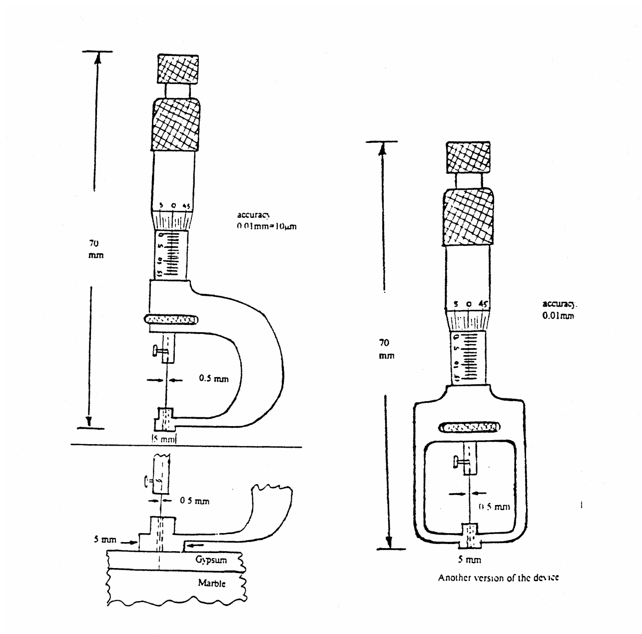

Fig. 7, The new device for measuring gypsum film thickness.

The fourth method under investigation is the LASER beam. We tested Nd-YAG LASER on sulfated and soiled ancient marble pieces as well as on graphitized gypsum specimens. The surface was cleaned but the gypsum surface turned yellow and some of the gypsum was removed (Figs. 8,9).

Fig.8, Graphitized gypsum and cleaned by Nd-Yag LASER. Increase from right to left in the energy density.

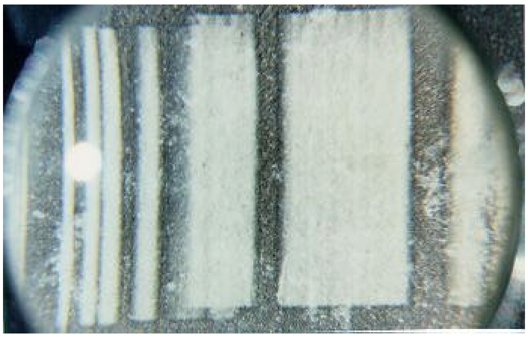

Fig.9. Graphitized gypsum cleaned by EXCIMER UV LASER. Increase from right to left in the energy density.

The same is valid for EXCIMER UV LASER but it did not color the surface of the gypsum /24/.

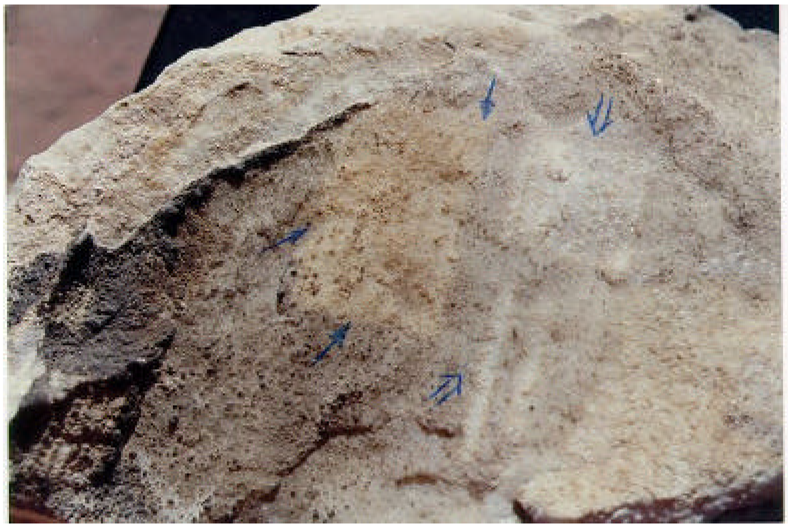

Fig.10, Sulphated and soiled ancient marble piece cleaned by Nd- YAG LASER (solid arrow) and by EXCIMER UV LASER (hollow arrow)

Professor Fotakis from the Crete Institute of Electronics and LASER with his team and personnel from the conservation of the Acropolis Monuments he constructed a LASER instrument with intermediate wavelength that does not damage the marble and the gypsum surface and does not turn yellow the gypsum films. We tested the instrument on many samples and on the surface of a Byzantine church with success, but it is still under examination.

These four methods were approved by an international group of experts in the frame of an international congress in Athens on "Conservation and Restoration of Parthenon"**;** concerning further consolidation of the surface we will use our method of reinforced lime (25-27) and for protection (if it will be decided) our method with n-semiconductors (28-35).

In 1976 the Frieze in Athens was sheltered, in 1993 it was taken into the Museum, the environment of which was conditioned in 1998.

Let us see now what has happened to the British Museum sculptures. The many interventions before and during 1938 as well as before 1968 will be presented by my colleagues Mr. Mantis, Archeologist, and Mrs. Papakonstantinou, Chemical Engineer, and they will give the estimations on the damage; in this report Mrs. Kouzelli, Chemist, has also collaborate. But there are other intervention too in 1968 and later on. It was used a water solution of soap with ammonia. According to the type of the soap, the pH of the solution can be higher than 8, where the calcite is converted into calcium hydroxide deteriorating parts of the high reliefs. The ammonium ions forme color complexes with metals, if they exists as precipitated suspended compounds, and attract the microorganisms. With the gypsum ammonium sulfate is formed and is hydrolised into sulfuric acid. NITROMORS (methyl chloride) was also used for 30 to 60 min and for many times and afterwards sepiolite. From our tests with NITROMORS on Pentelic marble for 20 min (according to the prescription), the thickness of the marble decrease by 50μm and its gloss was eliminated. They also coated the marble afterwards with polyethylene glycol, which changes the color of the surface and accelerates the sulfation.

CONCLUSIONS

For cleaning valuable parts of monuments such as the Frieze of the Parthenon only the following methods can be employed:

1. <u>Inversion of Gypsum</u> by spraying a solution with appropriate concentration of potassium carbonate, saturated with calcium carbonate.

2. Sorptive paste of sepiolith of appropriate grain size distribution with water of appropriate proportion saturated in calcium carbonate**;** the paste must not be in direct contact with the surface but through a Japanese paper.
3. Microblasting of appropriate materials, grain size and shape, pressure, rate, under a microscope and video.
4. LASER of an intermediate wavelength, higher than the one of EXCIMER UV and lower than the one of Nd-Yag LASER.

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