Conservation of the Surface of the Acropolis Monuments

Committee for the Preservation of the Acropolis Monuments

COMMITTEE FOR THE PRESERVATION
OF THE ACROPOLIS MONUMENTS
(CPAM)

CONSERVATION OF THE SURFACE OF THE ACROPOLIS MONUMENTS

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PROLOGUE

The Committee for the Preservation of the Acropolis Monumens (CPAM or ΕΣΜΑ in Greek) was established in 1975 by the Minister of Culture and Science, Professor and Academician K. Tripanis (†), in response to action taken by officials and citizens aiming to arouse the authorities' interest in confronting the threat to the Acropolis monuments posed by the increased atmospheric pollution in the Athens region.

The chairman of the Committee was the archaeologist, former Director of the Acropolis and Ephor of Antiquities, Dr. G. Miliadis (†); its members were S. Angelidis, Professor of Statics at the National Technical University of Athens (NTUA); Director of the Acropolis, archaeologist Dr G. Dontas; General Director of the Ministry of Culture and Science, archaeologist Dr D. Lazaridis (†); Professor of the History of Architecture, NTUA, Ch. Bouras; Professor of Physicochemistry and Applied Electrochemistry, NTUA, Th. Skoulikidis; and architect - archaeologist Dr. G. Travlos (†).

The office of Chairman was subsequently held by N. Platon (†), archaeologist, Professor Emeritus of Prehistoric Archaeology, University of Thessaloniki, and then by G. Mylonas (†) archaeologist, Professor, Academician and President of the Archaeological Society.

Since the Committee was formed, its members have also included: N. Gialouris, archaeologist, General Inspector of Antiquities; I. Theodorakopoulos (†), philosopher, Academician; A. Keramidas, mechanical engineer, Ministry of Culture and Science (MCS); I. Knithakis, architect, MCS; K. Konophagos (†), physical metallurgist, Professor, NTUA; I. Kontis (†), archaeologist, General Inspector of Ancient and Historical Monuments; A. Economopoulos, architect, MCS; G. Papathanassopoulos, Ephor of Antiquities; B. Petrakos, archaeologist, Ephor of Antiquities, *MCS; Th. Protopappas, mechanical engineer, MCS; P. Raftopoulos, mechanical engineer; K. Syrmakezis, civil engineer, Associate Professor NTUA; E. Touloupa, archaeologist, Ephor of Antiquities, MCS.*

The Committee currently comprises:

President: Ch. Bouras, architect, Professor NTUA.

Members: S. Angelidis, civil engineer, Professor Emeritus NTUA; A. Delivorias, archaeologist, Director of the Benaki Museum; G. Despinis, archaeologist, former Professor, University of Thessaloniki; I. Dimakopoulos, architect, head of the Department of Restoration of Ancient Monuments, MCS; G. Dontas, archaeologist, honorary General Ephor of Antiquities, MCS; P. Kalligas, archaeologist, Ephor of antiquities, Acropolis Director; G. Lavvas, architect, Professor, University of Athens (UA); B. Lambrinoudakis, archaeologist, Professor, UA; Th. Skoulikidis, chemical engineer, Professor Emeritus, NTUA; G. Tzedakis, archaeologist, Head of the Department of Prehistoric and Classical Antiquities, MCS.

According to its founding statutes, the task of the Committee is:

"Planning, directing and supervising the necessary systematic work entailed in the conservation of the Acropolis Monuments in Athens".

In addition to the rescue operations, such as removing the steel junctions from the monuments and replacing them with titanium, and the structural conservation and restoration works which have been widely published both in Greece and abroad, it was necessary to carry out a major surface conservation operation (consolidation, cleaning and protection).

- *The special properties (e.g. very low porosity) of the Pentelic marble of which the Acropolis Monuments are built,*
- *the widespread pollution in the Attica basin,*
- *the lack of international experience on how Pentelic marble reacts to pollutants,*
- *the gaps in international scientific knowledge relative to the mechanisms of the phenomena by which pollutants damage stone,*

- *the many drawbacks and side-effects of the methods and materials used internationally in conservation and*
- *the great responsibility to the most significant monuments of our cultural heritage,*

made it essential for studies and original research to be carried out in order to develop safe materials and implement effective methods for conservation.

Thus we present in this booklet the results of:

A. I. The research work conducted by Professor Th. Skoulikidis, member of the Committee for the Conservation of the Acropolis Monuments (CPAM), with his successive collaborators at the Physicochemical Laboratories and Applied Electrochemistry at the Department of Materials Science, Faculty of Chemical Engineering, NTUA. Research was conducted on the deterioration of the marble and metal and the conservation (consolidation, cleaning and protection) of the monument surfaces, in particular that of the Acropolis.

II. The studies and research conducted by Dr. K. Kouzeli, Dr. N. Beloyannis and Dr. P. Theoulakis at the Stone Centre, MCS, the subject of which was the colour traces on the surfaces, the aluminosilicate veins in the marble, the cleaning tests and the effects of the various methods on the Pentelic marble, and the properties of the various mortars that could be used in conservation.

III. a) The studies and research done to identify microorganisms and to find a suitable biocide, which were conducted by Professor S.R. Curri.

b) The studies and research on microflora by Professor K. Anagnostidis and his collaborators A. Economou-Amilli and M. Roussomoustakaki.

c) The studies and research conducted by Professor W.E. Krumbein of the University of Oldenburg, with his collaborators: researcher Dr. C.E. Urzi from the University of Messina and Dr. A. Pantazidou, Lecturer in the Biology Department of the University of Athens, *relative to the biological deterioration of the Acropolis monuments, the identification of the microorganisms that cause it, and the methods used to combat it (commissioned by CPAM).*

IV. *The studies by physicists L. Hatziandreou and G. Ladopoulos of the National Centre for Scientific Research "Democritus", on the gammagraphy of the Erechtheion and the detection of all metallic junctions and interior cracks in the marble (commissioned by CPAM).*

V. *Studies by K. Cholevas and I. Giannopolitis of the Benakeion Phytopathological Institute, to deal with plant growth on the Acropolis monuments (commissioned by CPAM).*

VI. *Studies by Dr I. Karakatsanis of the National Centre for Scientific Research "Democritus" on using ultrasound to keep pigeons away and installing appropriate electronic equipment to this end (commissioned by CPAM).*

B. *We also present the "Application Programme: The Conservation Work on the Monument Surfaces", which mainly describes the implementation of some of the results from the above-mentioned research. Conservation work is conducted by the conservators: A. Galanos, Y. Dogani, A. Babanika, A. Moraitou, A. Panou, M. Papadimitriou, G. Paganis and D. Maraziotis, and by the marble technicians K. Dimopoulos, I. Kladios, T. Kozokos, A. Lyritis, L. Michalakos, and I. Skalkotos, coordinated by the chemical engineer Mrs E. Papakonstantinou and under the supervision of Professor Th. Skoulikidis and the Acropolis Director.*

PART A

RESEARCH AND STUDIES

I. THE DETERIORATION AND CONSERVATION OF MONUMENTS

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National Technical University of Athens
Department of Materials Science and Engineering
Faculty of Chemical Engineering and Member of the
Committee for the Preservation of the Acropolis Monuments

Introduction

The deterioration of ancient monuments is caused by mechanical, biological, chemical and electrochemical factors. Some of these factors existed even before pollution became acute in the Attica basin, others were reinforced (or reduced) by it and yet others were generated by it.

The author and his collaborators have been conducting research on this issue since 1955, and more intensively since 1975, when the Committee for the Preservation of the Acropolis Monuments (CPAM) was established. The author has been a member of this Committee, responsible for dealing with physicochemical problems, since then.

The following text gives a brief presentation of all the problems involved in identifying monument deterioration and adopting conservation measures, and in particular those problems on which research has been conducted with a view to finding solutions applicable to the Acropolis and other monuments in Greece and abroad.

1. Mechanical deterioration

Freezing water

One of the mechanical causes of damage to monuments is the presence of water in pores and smaller fissures when the temperature drops below zero Celsius. When this water freezes, it expands, causing marble or limestone to crack and disintegrate. This phenomenon is inconsequential on the Acropolis, since a) the temperature of Athens rarely falls below zero, b) the Pentelic marble of which the monuments are constructed is of low porosity (0.35 - 0.7%) and c) there is a high pollution level. It is nevertheless the main cause of damage to other monuments, such as the Temple of Apollo Epicurius in Phigalia, where there is no pollution.

Pollution mitigates this phenomenon because the pollutants SO_X and NO_X, when dissolved in water, form strong acids which lower the freezing point and penetrability of water by increasing its surface tension.

A temporary solution is to cover the monument with some kind of roof to prevent it from coming in contact with rainwater, and to use infrared heating to prevent vapour condensation (dew point). The first solution was applied to the Temple of Apollo Epicurius on recommendation by the author.

Visitors

The millions of visitors to the Acropolis site have damaged the marble stairs, which have already been worn down by 3 cm. Owing partially to pollution, there has been a decrease in the number of tourists visiting Attica, as they frequently travel directly to their destination outside Athens, thus reducing this form of deterioration. Meanwhile, the steps have been covered with wood.

Salts

Some salt solutions rise up from the ground by capillary action through pores in the stone. The salts crystallize in the form of hydrates. Hydrates break down according to temperature and humidity conditions and then are reformed; this is a reversible phenomenon which entails fluctuations in volume. The pressure exerted during the formation of hydrates is also accompanied by the phenomenon of fatigue which intensifies the mechanical deterioration of marble. This of course occurs with materials of more than 2 - 3% porosity and with full - width pores. Such conditions do not prevail on Pentelic marble, and consequently this phenomenon is of minimal significance to the Acropolis monuments.

Expansion of steel junctions (1 - 18)

Metals expand during corrosion. This is caused both by the fact that the molecular volume of the corrosion products in the atmosphere, usually oxides, is greater than that of the metals and by the fact that these products are created on the surface of the metal toward the environment. If the metals are embedded in concrete or marble, strong forces develop during their expansion which cause these materials to crack (Fig. 1 - 3). The ancient

Fig. 1. *Cracking of marble due to expansion of the steel junctions.*

Fig. 2, 3. *Successive steps in the cracking of concrete and marble owing to corrosion of the steel reinforcement. Detail from Balanos' restoration of a column on the Parthenon.*

Greeks understood the phenomenon, which was why they embedded the steel elements used on the Acropolis and other monuments in lead. This method has proven to have been particularly effective, because only 20% of the ancient junctions have cracked the marble, and in these cases the cause was usually poor workmanship and/or the localised dissolution of the lead by the weak nitric acid solution in acid rain; whereas 90% of the junctions installed during the restorations by Pittakis (1837 - 1843) (bare steel with tips embedded in lead) and Balanos (1898 - 1940) (steel in concrete) have cracked the marble and continued doing so as the corrosion progressed.

The entire Erechtheion was dismantled and re-constructed after the steel junctions and frames had been removed and replaced by titanium ones (2-4), upon the author's suggestion. The use of titanium on restoration works constitutes an innovation on a world scale and presents the following advantages: the mechanical resistance of titanium is greater than that of stainless steel; its resistance to corrosion is also much greater, particularly in a marine environment such as Athens (where stainless steel becomes brittle due to stress corrosion), and it has the same thermal expansion coefficient as marble. The ancient technique (steel embedded in lead) was not used because it was observed that lead is depassivated, i.e. its corrosion resistance is lowered, by the pollutant sulphur dioxide in a humid environment and by acid rain. The use of titanium has also been extended to other monuments on the Acropolis

and elsewhere in Greece, and abroad (Italy, Japan, Spain, France, Portugal, Belgium, Poland).

Using data from past measurements and from measurements of the steel junctions taken after the Erechtheion was dismantled, we drew a corrosion curve for the past 150 years (8-10, 18), which shows a 30% acceleration of pollution-related corrosion. At the same time it was possible, using this curve, to pinpoint the onset of acute pollution in the Attica Basin at around 1955, a fact which coincides with the beginning of rapid industrialisation in the Athens region and the resulting population influx, as has been demonstrated in other ways as well. (See A.I.3).

Particle blasting

Particles with a diameter of more than 500 nm, mechanically suspended in the air, are whipped by the wind against monument surfaces and cause abrasion, mainly on the high reliefs of statues and sculpted ornamentation, like a kind of sand-blasting. This phenomenon is negligible with respect to the Acropolis monuments, but has had grave repercussions in e.g. Sounion, where it has caused serious damage to the Temple of Poseidon (in conjunction with the action of suspended NaCl). Efforts made abroad to set up aerodynamic shields to deflect the wind and mitigate its effects on the monuments have not as yet been effective. Pollution from suspended particles has increased as the industrialisation rate has accelerated.

2. Biological deterioration

Microorganisms in the class of fungal and fermentative microflora and microfauna, as well as sulphur-oxidating bacteria attack marble or, as in the latter case, accelerate the $SO_2 \rightarrow SO_3$ oxidation (A.I.4). Italian experts found from 2.10^6 to 7.10^6 microorganisms per gram existing on columns and from 5.10^4 to 8.10^4 on statues. These microorganisms can be combatted with the appropriate biocides while pollution eliminates certain species of them. (See also A.III).

3. Chemical deterioration

Pollutants damage marble (19, 20) through a combination of the following chemical reactions:

1) $CaCO_{3(s)} + CO_{2(g)} + aq_{(\ell)} \rightarrow Ca^{2+} (HCO_3)^{2-}_{2(sol.)}$

2) $CaCO_{3(s)} + SO_{2(g)} + 0{,}5\,O_{2(g)} + aq_{(\ell)} \rightarrow Ca^{2+} SO^{2-}_{4(sol.)} + CO_{2(g)}$

3) $CaCO_{3(s)} + 2\,NO_{2(g)} + 0{,}5\,O_{2(g)} + aq_{(\ell)} \rightarrow$

$Ca^{2+} (NO_3)^{2-}_{2(sol.)} + CO_{2(g)}$

The first is the familiar reaction that dissolves marble, which under other circumstances and over a long period of time, leads to the formation of stalactites and stalagmites after the water evaporates, when the $CaCO_3$ recrystallizes in the form of aragonite. This reaction was observed a long time ago and its mechanism is known: it is a very slow reaction which takes place only in the presence of rain, and the damage it causes, particularly on high reliefs, is minimal.

The second and third reactions – which essentially describe the attack on marble by sulphuric acid (SO_2 oxidises into SO_3 catalytically and, when mixed with rainwater, becomes H_2SO_4,) and by HNO_3 – are the most destructive. Obviously this reaction is due solely to atmospheric pollution by SO_x and NO_x, pollutants whose presence has increased significantly in all countries, including Greece, especially after its rapid industrialisation between 1955 and 1965. It is a very fast reaction which takes place only in the presence of rainwater. The mechanisms of these reactions are known. The combination of the three is called "acid attack" and, as has already been pointed out, is caused by "acid rain". This dissolution process is of course selective, as is usually the case with heterogeneous reactions; it primarily attacks macroscopic and microscopic active centres, i.e. high reliefs, active paths and the grain boundaries of the marble crystals. This type of attack causes high reliefs, such as details on statues and sculpted ornamentation, to dissolve: it causes marble to crack and spall and causes parts to break off because the cohesion of the grains is loosened. This type of attack is shown in the picture (Fig. 4a) of a Caryatid.

Fig. 4a. *View of a Caryatid showing the acid attack by acid rain on the front.*

The effects of this acid attack –i.e. cracking, the obliteration of high reliefs and the danger that pieces of the marble will be detached– have been recorded on photographs and drawings of all the monuments and statues on the Acropolis (12).

As pointed out above, the mechanism of this reaction was already known: the best thing to do was to protect the vulnerable parts of monuments such as statues from contact with rainwater. This was done *in situ* with wooden roofs over the Caryatids, the Parthenon statues of Cecrops - Pandrossos and Callirrhoe and the frieze sculptures (before they were all transferred to the Museum).

Comparing the original statue of Cecrops and its copy, a cast taken 50 years ago and now kept in the British Museum, one can see great differences. Specifically, many details have been obliterated from the original which are visible on the copy. From this fact we can conclude that the acute corrosion began after 1944.

A comparison was also made between photographs of the same statues taken at regular intervals of between one and three years from 1930 on. It was ascertained that the period of the progressive disappearance of details can be identified as being between 1955 and 1965. Consequently, the worst deterioration began after 1955, a fact which coincides with the rapid industrialization of the Athens region. (see p. 18).

4. Electrochemical deterioration

General remarks

When marble surfaces do not come into contact with rainwater, the following reaction takes place:

$$CaCO_{3(s)} + SO_{2(g)} + 0{,}5\,O_{2(g)} + 2\,H_2O_{(g)} \rightarrow CaSO_4 \cdot 2\,H_2O_{(s)} + CO_{2(g)}$$

This is the so - called "sulphation" of the marble, a process during which its surface turns into gypsum (Fig. 4b).

The mechanism of this reaction was not known until 1979, when we communicated (20) the first results of our research on the subject. Attempts had been made in the past to protect marble from sulphation damage, but ignorance of its mechanism

Fig. 4b. *Sulphation on the back of a Caryatid. Rear surface protected from rainwater.*

meant that these efforts were doomed to failure. We focused our attention on the mechanism of this reaction for three reasons:

(a) Because the sulphation of the marble caused by the reaction of SO_x pollutants with humidity is continuous, both in the open air and indoors, and can only be combatted by the use of a retarding or inhibiting intervention on the mechanism itself. On the contrary, as we have seen, acid attack takes place only when it rains, and can be prevented by the installation of a temporary shelter.

(b) Because successful intervention on the mechanism obviously presupposes sufficient understanding of it, and in particular of its rate-determining step which sets the conditions and rate of the entire reaction, and

(c) Because, as was confirmed, the methods which offer protection against sulphation also to a large degree provide protection against acid rain.

Thickness of gypsum film

The thickness of the gypsum film was measured at many points on statues and sculpted ornamentation (Caryatids, Cecrops, frieze) as well as on the walls of the Erechtheion and the Parthenon by a new, non-destuctive method we devised: the

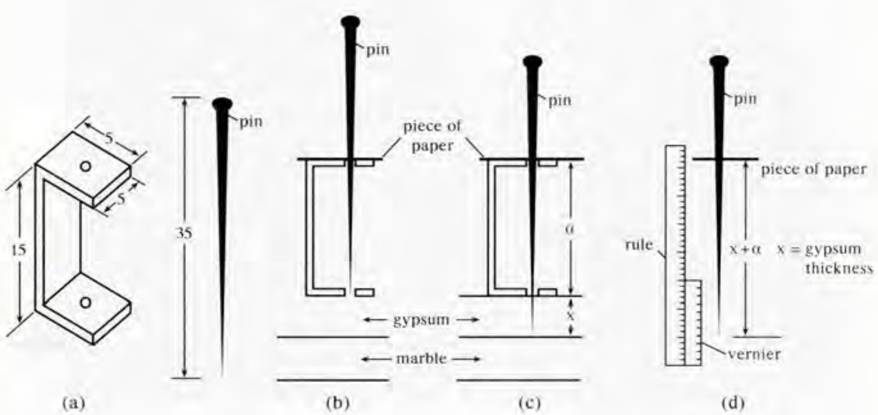

Fig. 5. *The "pin-probe method" for measuring the thickness of the gypsum film. (a) Configuration, (b), (c) and (d) stages in the measuring process.*

"pin-probe method" (20). Fig. 5 shows the principle of this method. It has now evolved, leading to the development of an instrument for measuring the gypsum thickness.

Statue details on the gypsum surface. Stabilisation

During the measurements, it was ascertained for the first time in the world (21), that details of the statues are preserved on the gypsum surface (Fig. 4b). If the gypsum was more than a few mm thick, those details would be lost from the surface of the marble (Fig. 6). Consequently, the gypsum films must be stabilised and not destroyed, in order to avoid the definitive loss of details on statues and sculpted ornamentation.

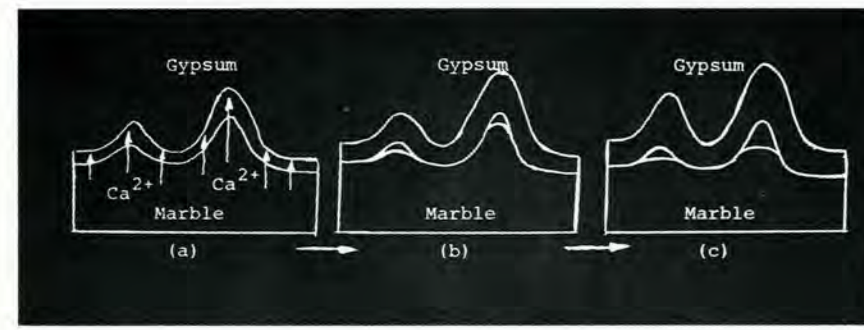

Fig. 6. (a) *Preservation (with the high relief slightly deformed) of the surface details on the gypsum film due to the sulphation mechanism (diffusion of calcium ions, p. 27), (b), (c) increase in the thickness of the gypsum and creation of cavities under high reliefs caused by the more rapid diffusion of calcium ions; disappearance of details from the marble and from the surface of the gypsum after a certain thickness.*

Since gypsum absorbs SO_2 more readily than marble, the view prevailed that the presence of gypsum accelerates sulphation. Thus in order to reduce the sulphation rate, the gypsum film used to be removed from surfaces by washing it off with water, after which the surface was covered with protective coatings. In this way the details of the sculptures were destroyed forever. It should likewise be noted that the gypsum film cracks and breaks off by itself when it exceeds several mm in thickness (Fig. 6). Experts from other countries also advised us to wash the statues with water, but our understanding of the phenomenon prevented us from adopting a practice which could have had disastrous effects: since the Caryatids' hair was converted almost exclusively to gypsum (Fig. 4b), having virtually disappeared from the marble surface, the Caryatids would today be bald if we had followed that particular piece of advice. Our observations were cited by many speakers at the UNESCO conference in 1978, with the result that from then on, statues were no longer washed with water.

It should be noted that the presence on the gypsum film of statue details that have disappeared from the surface of the marble is the result of the sulphation mechanism (p. 26).

A successful effort (21) was made in our laboratory to preserve these surface details and to stabilise the gypsum film by inverting the sulphation process and by converting the gypsum back into calcium carbonate. This was achieved by placing sulphated specimens of marble in an autoclave in a CO_2 atmosphere at 2 - 8 atm pressure and at a temperature of 30 - 80° C:

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

Since the equilibrium of the system as regards $CaSO_4 \cdot 2H_2O$ is univalent (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. When the gypsum has been entirely converted to $CaCO_3$, we channel water into the autoclave at the same pressure and temperature and wash off the $(H_3O^+)\,HSO_4^-$, so that when the gypsum returns to normal conditions, the reaction will not reverse again. Our laboratory even managed (22 - 24) to achieve the same inversion under normal conditions, by spraying a K_2CO_3 solution *in situ*.

Recently, (25) 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 with a hardness of 80 Kp/mm², i.e. about the same as marble. (Fig. 7).

It should be noted that the sole purpose of this conversion is to preserve the details on the statues and that it is obviously not a means of protection. The $CaCO_3$ thus formed is porous and more susceptible to attack by SO_2 than the $CaCO_3$ in aged marble. Consequently, this method should be applied only to statues which will remain in a museum under the proper conditions. In any event, this method has not yet been applied to any statue on the Acropolis, but only to flat surfaces.

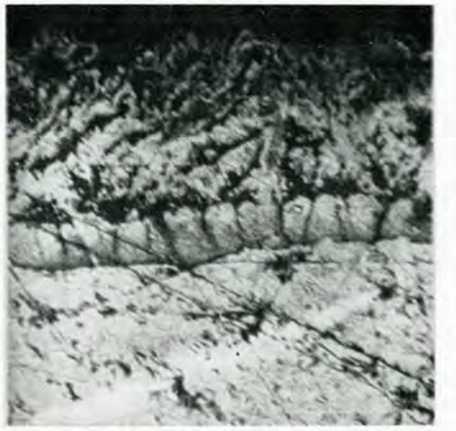

Fig. 7. *$CaCO_3$ crystals from the conversion of gypsum.*

Finally, by spraying cholesteric liquid crystals it was possible to make an *in situ* distinction between marble, gypsum and $CaCO_3$ from gypsum inversion (26). Marble takes on a deep azure colour, $CaCO_3$ turns sky blue and gypsum turns green (Fig. 8).

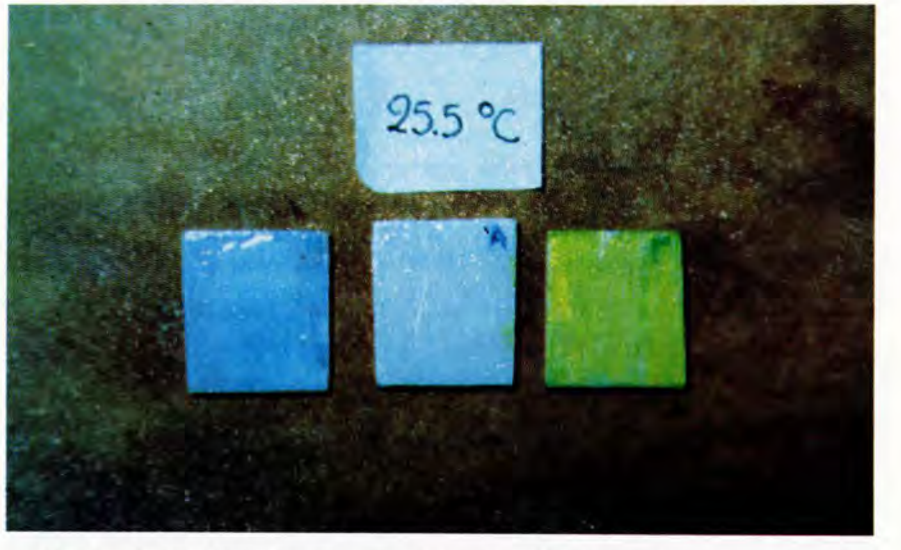

Fig. 8. *Distinction between marble, $CaCO_3$ (from conversion) and sulphated marble.*

The sulphation mechanism. Galvanic cell model

Through a series of measurements (7-10, 12, 19, 20, 27-38) using a quartz spiral balance and EPMA (Electron Probe Micro-analysis) on powdered $CaCO_3$, powdered marble and marble pieces at both high (450°C) and low (25°C) temperatures, at small (1%) and large (80%) concentrations of SO_2 and moisture, it was possible to reveal and demonstrate the sulphation mechanism. It was found that the evolution of sulphation is rectilinear up to a gypsum thickness of 300 Å, after which it becomes parabolic. In its parabolic progress, the rate-determining step is the solid state diffusion of Ca^{2+}, in accordance with a galvanic cell model. We thus concluded that the mechanism of marble sulphation is similar to that of uniform steel corrosion. (Fig. 9).

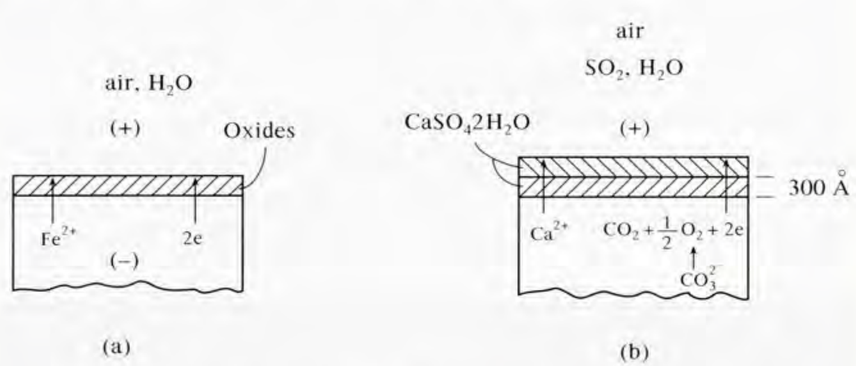

Fig. 9. *Galvanic cell model of the corrosion of steel and the sulphation of marble.*

On the basis of this galvanic cell model, which has been universally accepted today (p. 32), sulphation has been designated as the electrochemical decay of marble. This was proved in the following ways:

a) The system Pt, $CaCO_{3(s)}/CaSO_4 \cdot 2H_2O_{(s)}/SO_{2(g)}$ air, $H_2O_{(g)}$, Pt was formed: and it was proved that, indeed, it is a galvanic cell which conforms precisely to Nernst's law.

b) The diffusion of Ca^{2+} ions was demonstrated by EPMA using a cross-section after the marble had been coated with a polymer (Fig. 10).

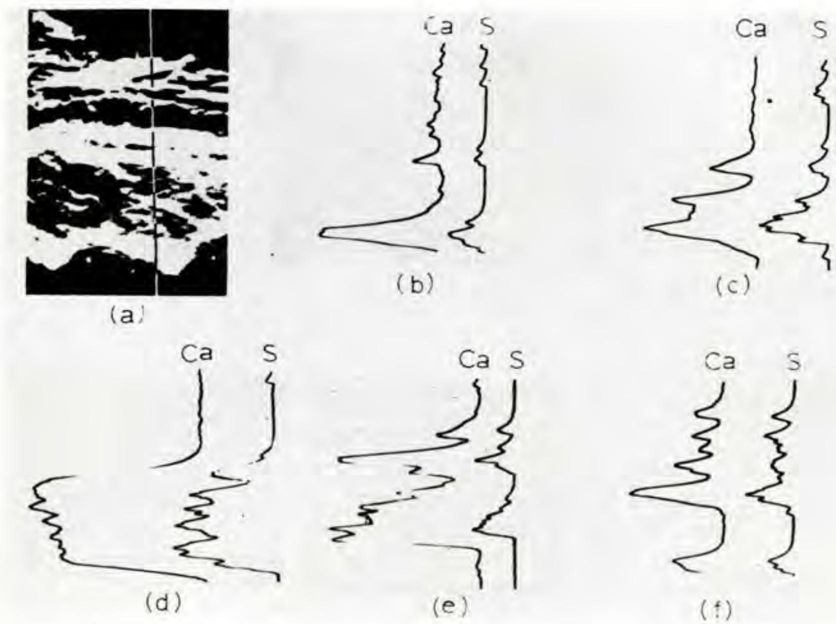

Fig. 10. *(a) Photograph taken by scanning electron microscope (magnified × 150) of the cross-section of a "protective" polymer on marble; this "protective" coating is 200 μm thick. (b) to (f) show the profile of the Ca and S concentration measured by EPMA on the cross-section of the "protective" coating after exposure to an atmosphere of 50% SO_2 + 50% air saturated with water vapour, (b) two days later, (c) six days later, (d) 7 days later, (e) 13 days later, (f) 20 days later.*

c) The evolution of the increased weight of the marble sample in a environment with SO_2, air and moisture, which is a measure of the sulphation rate, is identical with the Ca^{2+} diffusion rate as measured by EPMA.

d) Anti-corrosive steel paints such as Coal Tar Epoxy and Chlorinated Rubber also protect marble (Fig. 11).

The consequences of this mechanism are:

a) The preservation of details of statues and sculpted ornamentation on the surface of the gypsum, even though these details have disappeared from the marble-gypsum interface.

b) The cracking of all "protective coatings" which were not designed according to the mechanism in order to retard the Ca^{2+} diffusion (Fig. 12, 13).

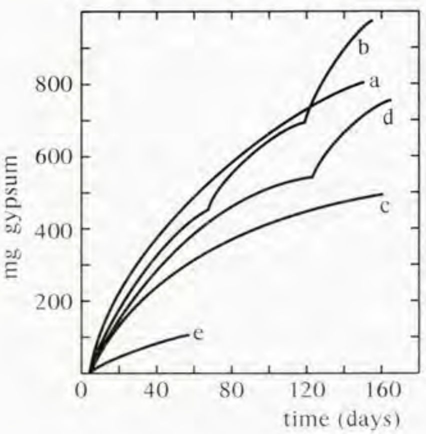

Fig. 11. *Amount of gypsum formed on the surface of marble samples as a function of time: a: bare marble. b: covered with acrylic. c: covered with Coal Tar Epoxy. d: covered with epoxy. e: covered with Chlorinated Rubber.*

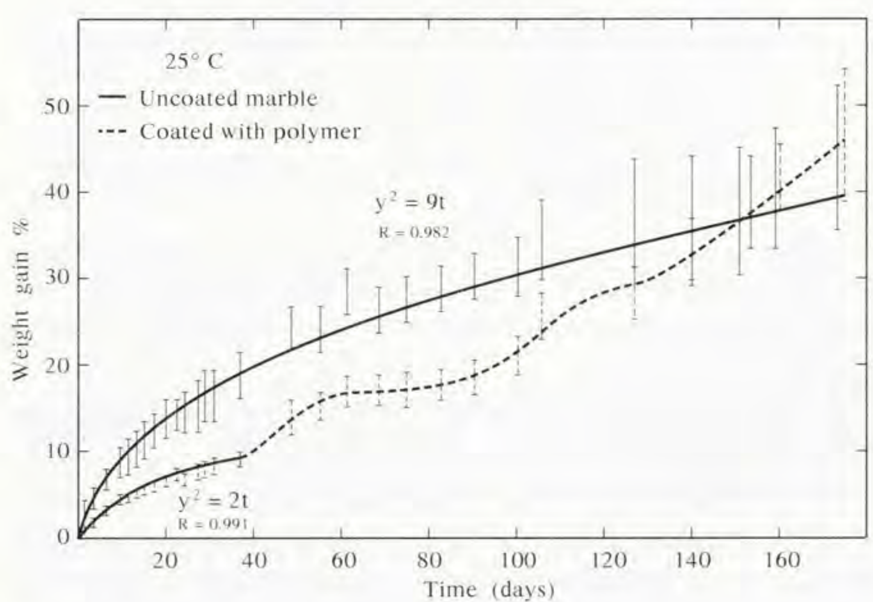

Fig. 12. *Effect of high concentration of sulphur dioxide, oxygen and water vapour on bare marble (unbroken line) and on marble covered with polymer (broken line). We can see the successive cracking of the coating and acceleration of sulphation.*

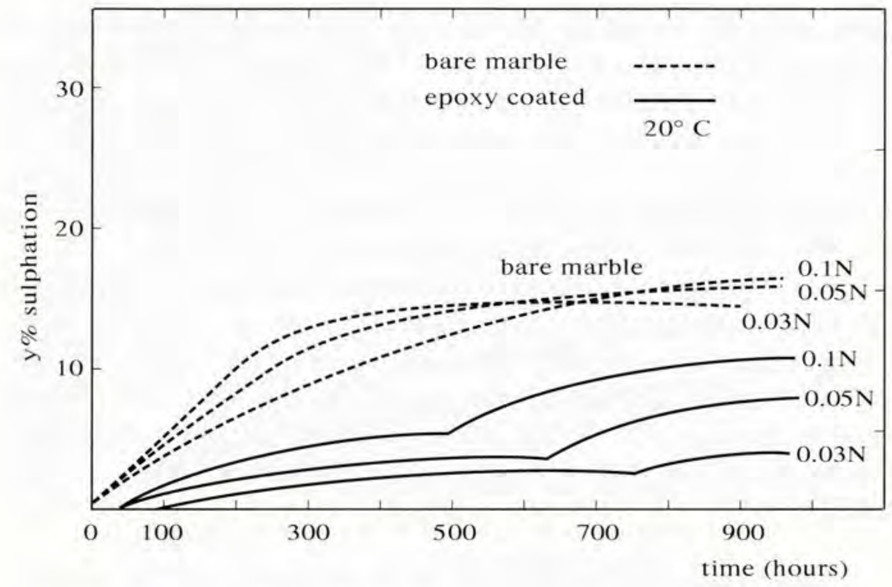

Fig. 13. *Percentage sulphation of bare marble and marble covered with epoxy at 20° C, for various concentrations of sulphuric acid.*

For these reasons, and after testing the effectiveness of various commercial coatings in an environment containing SO_2, the use of any "protective coatings" such as those used abroad, either organic or inorganic, was ruled out because it had become clear that they all accelerate sulphation. This was later confirmed by an extensive survey (39) of the monuments which had been "protected" by such coatings. For this reason, none of them were used in Greece. Cecrops and the Caryatids were moved to a conditioned nitrogen atmosphere in the museum, and the eastern metopes and the west frieze were also transferred to the museum.

Protection from sulphation

In accordance with the above, since the sulphation mechanism is similar to that of uniform metal corrosion, one might attempt to protect marble by applying the same methods used to protect steel. Of all these methods, the only suitable one is coating with anti-corrosive paint (9, 19, 30, 38). We have already seen that one of the proofs for the existence of this mechanism is the possibility of protecting marble with anti-corrosive paint such as Coal Tar Epoxy and Chlorinated Rubber (Fig. 11). Coal Tar Epoxy is black and suitable only for black marble. We have recently learned that, following our communication (36), Coal Tar Epoxy is now being used in China to protect black marble monuments. Chlorinated Rubber is vulnerable to ultraviolet solar radiation, and so anti-corrosive paints based on it should not be used.

In our earlier efforts to protect steel from corrosion (41-43)· it was shown that, if n-semiconductors such as Al_2O_3 or Fe_2O_3 were added to a polymer medium, very good protection was achieved, the coatings did not crack and the Al_2O_3 and Fe_2O_3 acted as anti-UV. These semiconductors in an epoxy resin medium, or even better in a cross-linked acrylic. (Fig. 14) were

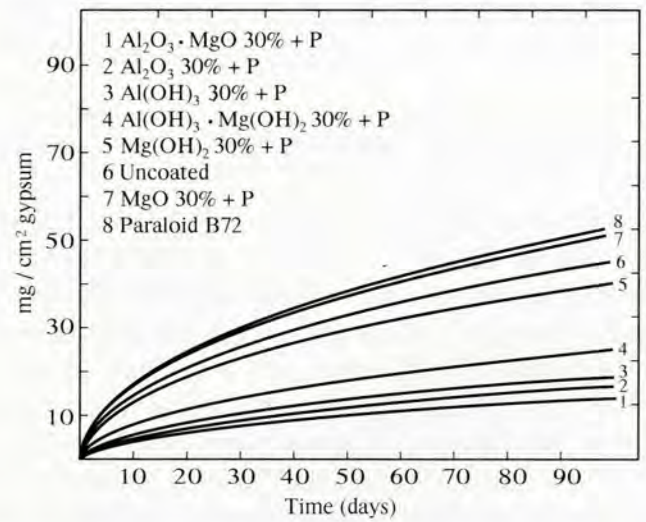

Fig. 14. *Evolution of sulphation in relation to the various protective coatings based on oxides and hydroxides of aluminium.*

likewise tested on the marble with extremely good results. We also used $Al(OH)_3$ or $Al_2O_3 \cdot MgO$ (doped), Fe_2O_3, $Fe_2O_3 \cdot MgO$ (doped) (Fig. 15) and TiO_2, $Ti(OH)_4$ system, also doped (Fig. 16). According to experience from industry, where these materials have been used as catalysts, they are not exhausted as materials and as electron donors. They also repulse suspended particles.

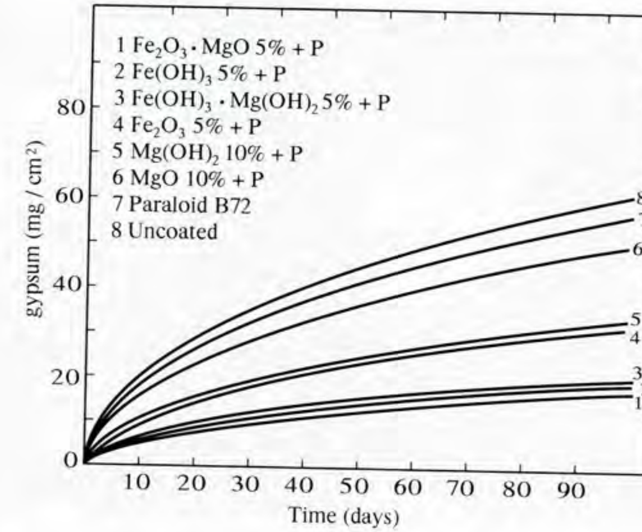

Fig. 15. *Weight increase as function of time. From top to botton: bare marble, covered with acrylic, with acrylic + 10% MgO, + 10% $Mg(OH)_2$, + 5% Fe_2O_3, + 5% $Fe(OH)_3 \cdot Mg(OH)_2$, + 5% $Fe(OH)_3$, + 5% $Fe_2O_3 \cdot MgO$.*

Admixtures with Fe_2O_3 can likewise be used to produce an artificial patina. (A.I.6).

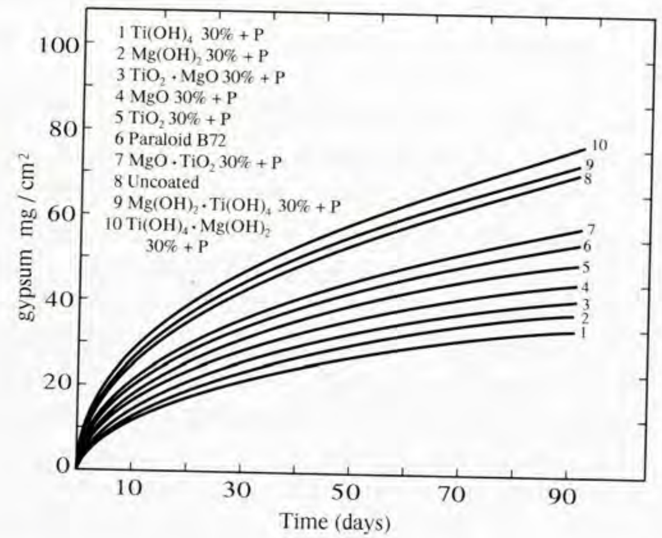

Fig. 16. *Evolution of sulphation in relation to the various protective coatings based on titanium oxides and hydroxides.*

For the research outlined in A.I.4, the author was awarded a Medal by the Permanent International Committee for the Organisation of Conferences on the Deterioration and Protection of Stone (1988), and received the Global 500 Honour Roll Award of the United Nations Environmental Programme (UNEP) (1989).

A European Community programme (Eureka: EU 595: Eurolith) is also under way for the manufacture of these systems (cooperation between the author, the French company SICOF-TOTAL, the Greek firm COPALIN and the University of Poitier in La Rochelle, France).

5. Precipitation of suspended particles. Cleaning

Particles of less than 500 nm, that are suspended in the air, i.e. colloids, precipitate onto the sulphated surfaces of monuments and statues staining them either red (Fe_2O_3), or black (C) (19). This colour can be removed by thermal LASER beams which are focused on these particles and sublimate them without damaging the marble, or by the new striking pulse LASER, as long as this process does not eliminate the gypsum films. They can also be removed with packs made of absorptive substances (such as attapulgite, sepiolite or bentonite) prepared with sulphate-saturated water or with a non-hydrous medium so as not to dissolve the gypsum, as has already been pointed out, preserving the details of the sculptures (see p. 23). The pack is not applied directly to the marble surface, but has Japanese paper in between. For the same reason, all other cleaning methods which entail the destruction of the gypsum film should be avoided.

It was also confirmed that the sulphation inversion process simultaneously cleans the surface (Fig. 17), since the molecular volume of the calcite is smaller than that of the gypsum, and the suspended particles which have settled are loosened and removed (51). (See also A.II.3, 4).

Monument surfaces onto which water runs and collects also become soiled by a combination of recrystallized calcium carbonate, sulphation and the precipitation of suspended particles. Thus a "black crust" is formed. In these instances, flat surfaces

Σχ. 17. *At points (a) treatment (spraying) was undertaken with a solution of K_2CO_3 saturated with $CaCO_3$.*

can be cleaned by tools, microparticle blasting, ultrasound, absorptive packs, LASER, sulphation inversion (51) and bacteria (52). On sculpted surfaces, the only methods advisable are those employing special tools, and possibly absorptive packs or the sulphation inversion method (51).

6. Creation of artificial patina

During restoration works, when new marble or white concrete reproductions are added, it may be desirable to give the new pieces a patina the same tone as that of the older members, to avoid any great contrast between the new and the ancient material (as is now the case on the Erechtheion); at the same time, the new pieces should be distinguishable from the old.

Thus the need arose to create an artificial patina. Older empirical methods consisted of using an iodine solution, rust in vinegar, clay, $MnSO_4$ etc.; but the results were not satisfactory. After a number of tests, we came up with two new methods (53):

a) Use of an $Fe_2(SO_4)_3$ solution.

b) Various iron oxides in an acrylic medium.

The latter method, which has already been applied on a small scale on the Acropolis as a pilot project, not only achieves the appropriate shades ranging from light brown to yellow or pink, but also protects both new marble and the polymer medium.

7. Strengthening the mechanical resistance of $CaCO_3$

Lime CaO $\xrightarrow{H_2O}$ $Ca(OH)_2$, in the form of a saturated solution (lime water) or in suspension (lime-milk) or paste (lime-putty), is used according to each individual case to preserve and restore marble (attaching pieces, filling cracks) which has suffered surface deterioration from atmospheric attack and for which white concrete cannot be used because of its viscosity. $Ca(OH)_2$ reacts with the CO_2 of the atmosphere and becomes $CaCO_3$. This conversion is very slow, and the $Ca(OH)_2 \rightarrow CaCO_3$ mixture has a very low mechanical resistance over long periods of time. Even after the full conversion into $CaCO_3$, the resistance is limited, since large $CaCO_3$ crystals are formed, due to the slow rate of the reaction.

The increase in the mechanical resistance of $CaCO_3$, which is required in order to avoid the use of metallic clamps, can be achieved when the crystals are small: this occurs when the reaction rate is fast.

Tests were conducted at different temperatures (54) which should not exceed 32-35°C when lime is used. We also conducted tests with different CO_2 content in the environment (Fig. 18, 19) and found the maximum mechanical resistance at

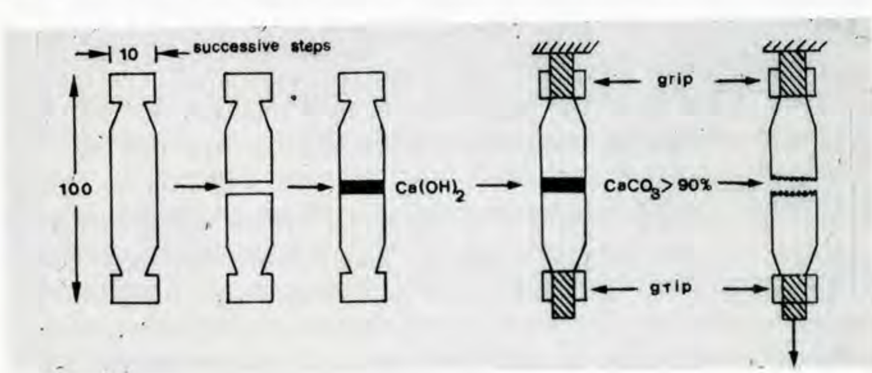

Fig. 18. *Form of samples.*

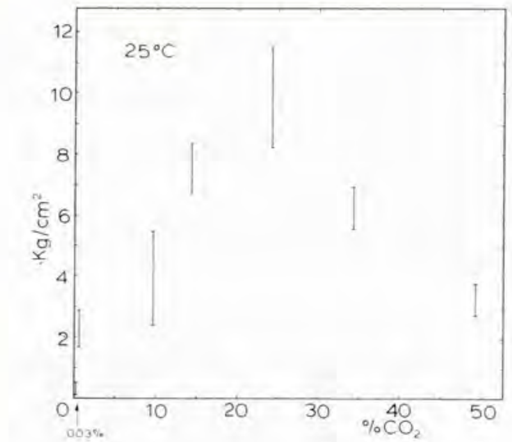

Fig. 19. *Kg/cm² for the detachment of marble pieces which were bonded with lime as a function of the % content of CO_2 in the environment (for a conversion* CaO $\xrightarrow{H_2O}$ $Ca(OH)_2$ $\xrightarrow{CO_2}$ $CaCO_3 > 90\%$*).*

25% CO_2, in an artificial environment, which can be achieved both in the conservation laboratory and *in situ*. Finally the $CaCO_3$ content in $Ca(OH)_2$ (auto-catalysis) offers maximum resistance when $CaCO_3$ is 6% of the solid lime (Fig. 20).

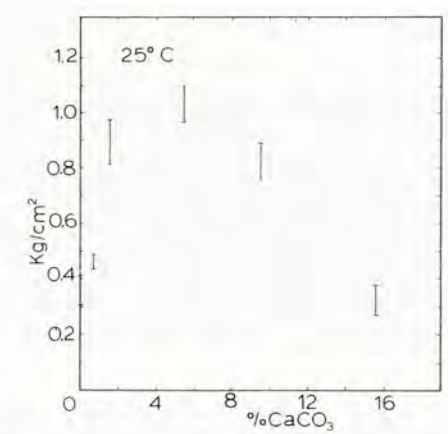

Fig. 20. *Kg/cm² for the detachment of marble pieces (which were bonded with lime) as a function of the initial content of $CaCO_3$ in the lime (for a conversion* CaO $\xrightarrow{H_2O}$ $Ca(OH)_2$ $\xrightarrow{CO_2}$ $CaCO_3 > 90\%$*).*

This method (addition of $CaCO_3$) is already in use on the Acropolis monuments (Fig. 20) and in the museum ($CaCO_3$ and CO_2). Sometimes white cement is added to the lime to improve its mechanical properties, especially because if the $CaCO_3$ is converted to $CaSO_4 \cdot 2H_2O$, over a long period, the parts which were attached will stay in place and will not fall off.

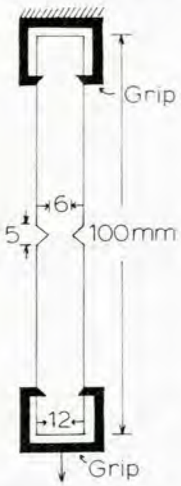

Fig. 21. *Form of samples*

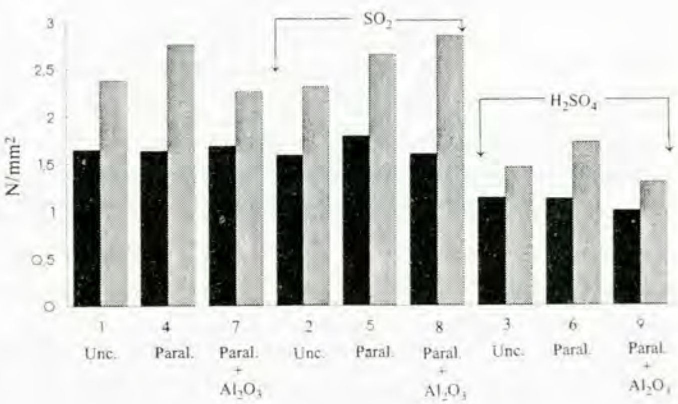

Fig. 22. *Histogram of the load to failure – pretreatment.*

8. Resistance of marble to tensile stress

Pentelic marble was tested (55) for resistance to tensile stress (Fig. 21) both before and after exposure to SO_2 for four days or to a weak sulphuric acid solution for 1 min. The results can be seen on the histogram (Fig. 22). It was found that acrylic + Al_2O_3 protects marble from this type of damage in the presence of SO_2.

II. CHARACTERIZATIONS, MORTARS, CLEANING

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N. Beloyannis, PhD Chem. Eng.
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Ministry of Culture

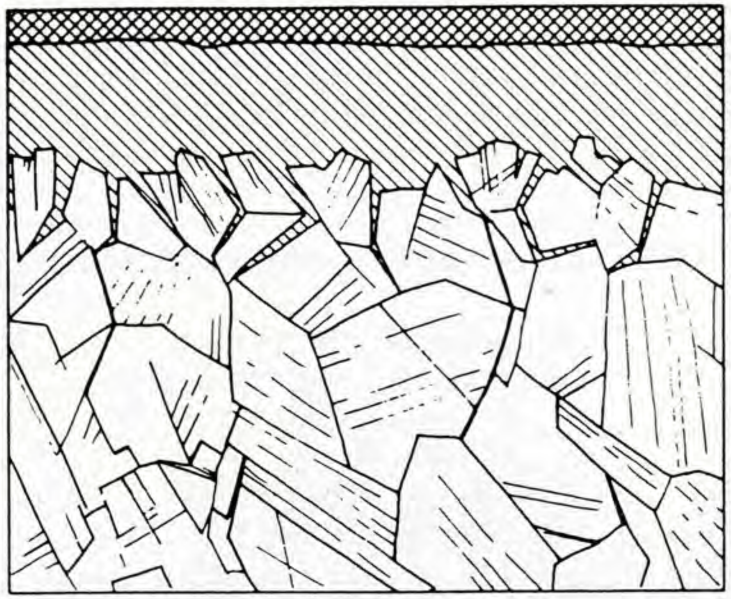
1. Study of the remaining monochromatic surface layers and polychromy on the Parthenon surfaces

In this study (56, 57), an analysis was conducted on two types of colour traces on the Acropolis monument surfaces, raising questions about their nature and origin:

a. An orange-brown layer adhering to the marble surface which has also penetrated in intergranular regions of the marble and is described as an "epidermis" (skin). This layer has a total thickness of about 150 μm. Its characteristic feature is the presence of phosphorus uniformly distributed in the form of apatite throughout the entire thickness. Calcium oxalates were also detected (but in very small concentrations) as was gypsum. On the outer part of the skin, to a depth of about 30 μm, traces of the elements Fe, Al, Si and K, were found, a fact which led us to the conclusion that the colour of the skin was attributable to deposits. (Fig. 23).

b. An off-white (beige) layer covering the skin is superficial and is described as a "coating". Analysis proved it to be a thin artificial layer (lime wash) about 70 μm in thickness, which has become sulphated to a large degree.

Finally, analysis of the blue colour found on the mutule, the heads of the metopes and the triglyphs showed that it was



Ca, Si, Al, Fe, Mg, K, P, S, Cl, Na are detected

Ca, P, S, Cl, Na are detected.

Marble crystals

Fig. 23. *Cross-section of sulphated, stained marble.*

Egyptian blue ($CaCuSi_4O_{10}$), while the analysis of the red colour found on the intermediate paths of the cornice, proved it to be an iron oxide (hematite).

2. Aluminosilicate veins in the Acropolis marble

This study (58) reports on the examination of foreign (non-calcitic) inclusions in the Acropolis marble. The minerals in all the veins were identified: micas (muscovite, biotite, glauconite, sodium-muscovite, fengite), feldspars (sodium and potassium), quartz, chlorite, titanite, iron oxides and mineral sulphates (mainly of iron), and their contribution to the deterioration of the marble was explained.

3. Trial applications of surface cleaning methods to remove the black crust

This project (59) consisted of establishing all the criteria for selecting a cleaning method and conducting trial applications of some of the internationally proposed methods that met these criteria. The best results aesthetically were achieved by applying a "biological pack" (59a). This method is inexpensive to use and not excessively time-consuming.

4. Effects on the Pentelic marble of the various methods for removing black crust

This study (60) investigated the effects on Pentelic marble of the various methods used internationally to remove the black crust (which contains gypsum, soot etc.). Particular emphasis was given to the biological pack, given that this method offered highly satisfactory results during its test applications.

It demonstrated that the biological pack has no effect on Pentelic marble. It was, however, stressed that the biological pack acts selectively to remove gypsum and consequently, where sculpted ornamentation is involved, it obliterates any details which may have been preserved on the surface of the gypsum layers (21-26).

Tests were likewise conducted to determine the effects on surfaces cleaned by the biological pack method and on those covered by a black crust, under conditions of accelerated aging (SO_2 atmoshere, moisture). The black crust appeared somehow to have slowed down the SO_2 attack on the marble, giving up its own calcite to be sulphated.

5. Preparation and study of the properties of mortars suitable for use on Pentelic marble in an urban environment

Mortars (61, 62) of various compositions were formulated and prepared for the following uses:

a. Sealing
b. Injection grouting
c. Attaching small flakes

The properties of each mortar studied were a function of the use for which it was intended. Also, the effect of the mortars on marble was examined under conditions of accelerated aging (SO_2 atmosphere, moisture) and acid rain.

Finally the mortars with the best properties were selected.

III. CONTRIBUTION OF THE BIOLOGICAL FACTOR TO THE DETERIORATION OF THE ACROPOLIS MONUMENTS

The problem of the biological factor in the deterioration of the marble on the Acropolis was recognised by CPAM soon after its establishment (1975). Studies and research have been conducted by Greek and foreign experts aiming to identify and combat the effects of microorganisms. The research is still in progress.

S.B. Curri
Professor, Molecular Biology Centre, Milan

In 1979 a series of papers were published on the microbiological deterioration of Cecrops-Pandrossos, the Caryatids and the Parthenon column surfaces. Bacterial colonies were identified and quantified (63-66). Isothiazolinone chloride was selected as the most suitable biocide for the bacteria identified. The Caryatids and the statue group Cecrops-Pandrossos were sprayed with a 5% solution of isothiazolinone chloride in acetone before they were enclosed in glass cases with circulating nitrogen (p. 29).

K. Anagnostidis
Professor, Biology Department, University of Athens and
A. Economou-Amilli and **M. Roussomoustakaki**

A study of the epilithic and chasmolithic (cyanophyta, bacillariophyta) microflora on the Parthenon marble was published in 1983 (67).

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Professor of Geomicrobiology I.C.B.M.
University of Karl von Ossietzky, Oldenburg

C.E. Urzi
Researcher at the Microbiology Institute
Faculty of Science, University of Messina
A. Pantazidou
Lecturer, Biology Department, University of Athens

As part of CPAM's efforts, we were assigned to study and record microflora, to research methods of combatting them and to examine the possible interrelations between the biological factor and the various types of deterioration which have been ascertained by conservators on and in the Acropolis marble.

To this end samples were taken (68, 69) in April and June 1991 from areas where the marbles showed typical deterioration and colour alterations. In almost all cases the mass development of microorganisms was ascertained macroscopically within the fissures and cracks, under the spalling, between the grains of the marble and elsewhere.

Fig. 24. *Biological attack. Fungi penetrating under a marble grain and detaching it. Parthenon. (Scanning electron micrograph, Krumbein).*

Analysis of natural and cultured material using an optical microscope and a scanning electron microscope revealed the presence of a variety of microbial colonies. These colonies consisted of bacteria, actinomyces, cyanobacteria, algae (mainly green algae), fungi and lichens (68, 69).

It was found that the contribution of the biological factor to the physico-chemical decay of the marble was significant. The epilithic and chasmolithic microflora on the Acropolis marble play a large part in tinting the Pentelic marble, which was initially white. This colour alteration is mainly due to the pigments of the micro-organisms and less so to the inorganic particles (soot) deposited on the marble. Secretions of organic acids and other corrosive substances by some microorganisms cause the calcium carbonate to dissolve and exacerbate the existing situation. In addition, most of the microflora provoke damage through various mechanisms by exerting minute pressures on the marble, extending the network of tiny cracks and creating microscopic cavities (Fig. 24, 25).

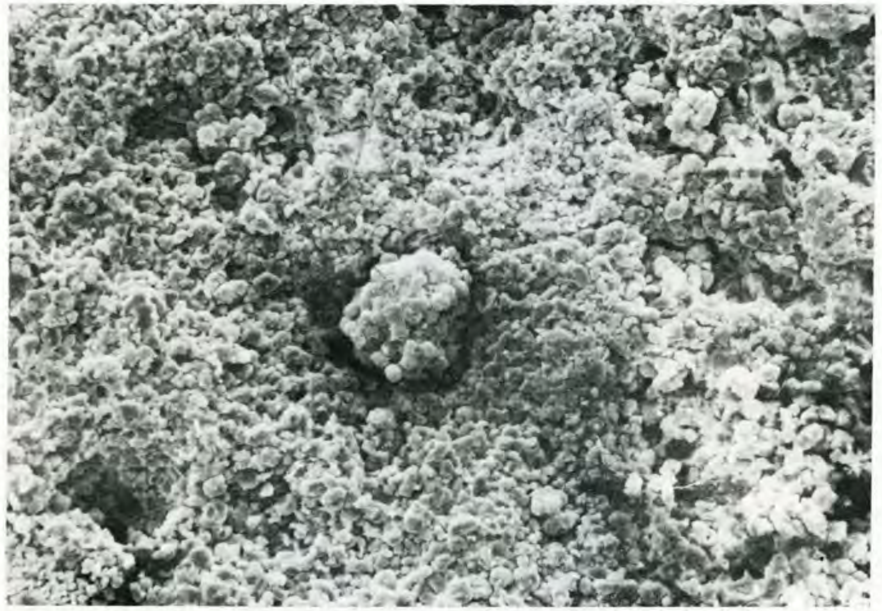

Fig. 25. *Biological attack. Marble "pitting" by black yeasts. The yeasts have a shape similar to Pentelic marble crystals and penetrate deep, sometimes also by hyphae formation. Theatre of Dionysus. (Scanning electron micrograph, Krumbein).*

The microflora growing on and in the marble were tested under laboratory conditions with biocidally active chemical substances. To test the effectiveness of the biocides and check the possibility of their potentially corrosive action on the Pentelic marble, a series of experiments were carried out on a large number of microorganisms taken directly from the marble and isolated in axenic cultures. It was obvious that no intervention to suppress and kill the microorganisms could be attempted unless a study was first conducted of the method's compatibility with Pentelic marble and unless the conditions of the macro- and the micro-environment were taken into account.

It is noted that intervention with biocides, without parallel concern for the cleaning and conservation of the marble surface, does not solve the biocorrosion problem on the Acropolis monuments. Moreover, the organic microfloral remains might possibly be used by new organisms. From the foregoing it is clear that the biological condition of the Acropolis marble must be checked at regular intervals both because of the unique nature of the monuments and because of their constant bombardment with the organic and inorganic pollutants characteristic of the area surrounding the Acropolis, at least for the present.

IV. GAMMAGRAPHY

L. Hatziandreou, G. Ladopoulos
National Scientific Research Centre "Democritus"

An examination using γ-rays was carried out on marble members of the Erechtheion and the Propylaea (entablature just above the Caryatids and coffered ceiling slab respectively). A Co^{60} (7.5 curies) radiation source was used. The method revealed information about internal cracks and hitherto unknown metal inserts (70).

Fig. 26. *Gammagraphy of a marble member.*

V. COMBATTING PLANT GROWTH

K. Cholevas, I. Giannopolitis
Weed Department
Benakeio Phytopathological Institute

Experimental applications of weed-killers were proposed to combat the various plants growing on the monuments and on the ground (71).

VI. KEEPING PIGEONS AWAY FROM THE MONUMENTS

I. Karakatsanis, PhD, Physicist
Microelectronics Institute
National Scientific Research Centre "Democritus"

A study was conducted on the effectiveness of using ultrasound to keep pigeons away from the monuments; a proposal was made to install special equipment to this end.

PART B

APPLICATION PROGRAMME

THE CONSERVATION PROGRAMME

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Ephorate of Antiquities, Ministry of Culture

Introduction

The term "conservation" refers to all interventions conducted on cultural heritage works or their environment which aim to prevent or arrest their deterioration. These interventions – according to the Venice Charter (72) – "aim to preserve them both as works of art and as historical evidence" without changing their form or texture.

Conservation work on the Acropolis monuments focuses on the surface of the marble and has, since 1986, constituted a separate progamme, conducted and coordinated simultaneously with the structural restoration programmes.

The conservation project which is being executed on the Acropolis monuments today includes *active conservation*, consisting of consolidation interventions on the monuments themselves or on detached members either in the site workshops or in the conservation laboratory of the Acropolis Museum; and *passive conservation*, consisting of interventions mainly of a preventive nature, such as transferring architectural sculptures from the monuments to the museum and placing some of them in an inert nitrogen environment (p. 29).

1. Condition of the monument surfaces

The Problems

Loss of marble cohesion and continuity

The isolated or combined action of mechanical, chemical and biological factors, in conjunction with the surrounding microclimate and the microstructure of the marble, cause the following forms of deterioration (73):

a) Cracking: Interruption in the continuity of the marble, which can lead to full-width cracks that result in the detachment of fragments.

b) Delamination: Formation of cracks parallel to the surface, accompanied by the imminent flaking of the marble (Fig. 27).

c) Exfoliation: Formation of marble flakes with reduced mechanical endurance.

d) "Sugaring": Intergranular decohesion and loss of marble crystals from the surface (Fig. 28).

Fig. 27. *Delamination. Detail from a Parthenon column.*

Fig. 28. *"Sugaring"*

e) Disintegration: Loss of marble cohesion in depth in the form of intergranular decohesion and/or a network of microfissures. (Fig. 29).

f) Pitting: Appearance of small semi-spherical holes (diam. 0,2 - 0,7 cm) either sporadically or in clusters (Fig. 30).

Fig. 29. *Disintegration of the marble in conjuction with deposits of soot and the formation of black crust.*

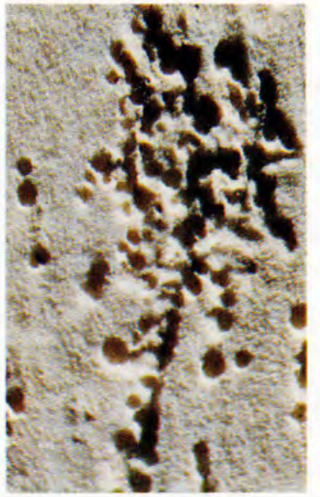

Fig. 30. *Pitting.*

g) Differential weathering: Non-uniform reduction of the marble surface, determined by the geological heterogeneity of the material (Fig. 31).

Fig. 31. *Differential weathering.*

Foreign non-calcitic inclusions (micas, feldspars, quartz, chlorite, titanite, iron oxides, and mineral sulphates, mainly of iron) existing in the Pentelic marble of the Acropolis constitute regions of heterogeneity. Certain of these are attacked more rapidly, break down and disintegrate, causing cavities and creating more fronts on which the marble can be attacked.

Microorganisms

Apart from their proven contribution to monument deterioration (68), the various epilithic (Fig. 32), endolithic and chasmolithic organisms hinder the successful application of conservation material and also geopardize the long-term effectiveness of the conservation treatment. More over epilithic and endolithic biota can cause chromatic alteration of the Pentelic marble.

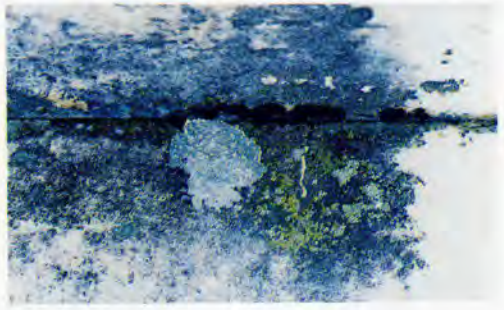

Fig. 32. *Epilithic and endolithic organisms on the north* crepidoma *of the Erechtheion.*

Deposition

The exposure of monuments to atmospheric pollutants and suspended particles modifies their colour in places which are not washed by rainwater. Deposits of dust and soot particles, in conjuction with the phenomena of calcium carbonate recrystallisation, create loose deposits, and cause black crust and black dendritic crust to form (Fig. 33).

Rust stains

Chromatic alteration on a smaller scale is caused by the corrosion products of steel elements.

Fig. 33. *Black dendritic crust on a Parthenon mutule..*

Pigeons

Pigeons can cause mechanical deterioration of the marble, while their droppings soil the monuments and can cause chemical decay (p. 46).

Vegetation

The roots of the various species of plants growing in cracks and joints can cause mechanical and chemical damage to the ancient marble and give the impression that the monuments are abandoned (p. 46).

Historical traces on the marble surfaces

Orange-brown skin

On the surface of the monuments, and frequently on the sculptures, an orange-brown layer of about 180 μm is observed. It consists chiefly of calcium oxalate, iron and phosphorus (56, 73). This layer is not merely a superficial coating, but penetrates into the intergranular regions. It may have been an ancient protective treatment of the surface, but the possibility of a biogenic origin cannot be ruled out (69) (Fig. 34).

Off-white coating

This term is used to describe the relatively uniform off-white (beige) layer about 70 μm thick on the Parthenon which has

Fig. 34. *Detail of orange-brown layer on the Parthenon.*

Fig. 35. *Engraved ship on a Parthenon column (graffiti).*

been observed on top of the orange-brown skin (p. 37). Its chemical analysis (calcium carbonate and gypsum) and the brushstroke traces it bears indicate that it is a subsequent protective lime wash (Fig. 35).

Painted decoration

Traces of ancient painted decoration are preserved today in a fragmentary form on the surface of the monuments (57, 74) (Fig. 36).

Fig. 36. *Egyptian blue can be discerned under the beige coating. A.TP. 13. Parthenon.*

Traces of red (hematite, Fe_2O_3) and blue (Egyptian blue) pigments have been recorded and analysed, while vestiges of engraved contour lines are still visible (p. 38).

In certain cases, the existence of decoration can be ascertained indirectly through the differential wear of painted and unpainted areas of marble.

Graffiti

Graffiti from different periods (names, designs, invocations, etc.) are preserved on the monument surfaces. These engravings constitute a source of historical data, mainly from the Christian era (75) (Fig. 35).

2. Historical data relative to the conservation of the Acropolis monuments

Systematic or preventive conservation works on the Acropolis monument surfaces have been executed in the past, within the framework of broader restoration interventions: the project undertaken by N. Balanos (1898 - 1940), interventions by the Restoration Service (1940 - 1960) and the Acropolis Ephorate (1960 - 1975) (73).

These interventions included re-attaching detached fragments, consolidating loose fragments, filling cracks and generally sealing cracks and joints to prevent vegetation and water penetration.

Mortars based on Meyer cement (inorganic magnesium oxychloride or Sorel cement) were primarily used to attach fragments and seal cracks; the percentage of aggregate added was dependent on the intended use.

To reinforce attachments and consolidation interventions, copper wire in the form of staples was used up to the 1960s (Fig. 37); later, brass pins were used.

The major drawbacks of Sorel cement (water solubility, expansion force exerted on the marble, chloride content) (76) led, upon recommendation by CPAM, to its replacement by white Portland cement.

Fig. 37. *Detail from previous consolidation intervention in 1922 - 1933 with Meyer cement and copper rivets. Parthenon A.K. 2.11.*

Fig. 38. *Same region as shown in Fig. 37, after the delaminated piece has been detached. Parthenon A.K. 2.11.*

The use of visible metal reinforcements in the form of pins was also abandoned in 1975 in favour of the installation of invisible titanium dowels (3, 4).

3. Conservation treatment

The conservation of the monuments (Fig. 37 - 44)

The conservation of monuments generally entails three phases: *consolidation, cleaning* and *protection.*

The conservation work executed today on a broad scale on the Acropolis monuments centers on consolidation. This systematic task started on the Parthenon in 1988 and was extended as an organised programme to the Propylaea in 1990.

Consolidation consists of a series of interventions aiming at restoring the various manifestations of the marble's loss of coherence (73). Specifically:

a) Attachment: The fragments of marble which have become loosened or detached are cleaned on the broken surface and attached with white Portland cement. When the fragment is in good condition, the bond is reinforced with a titanium dowel. When spalls or small flakes are to be attached, a mortar of reduced strength is used consisting of a mixture of cement and lime with the addition of 6% $CaCO_3$. (54).

Fig. 39. *The delaminated area after cleaning of the broken surface. A.K. 2.11.*

Fig. 40. *After the reattacment of the delamination. Parthenon A.K. 2.11.*

b) Injection grouting: Wherever interior spaces are detected optically or acoustically, they are cleaned by air or water under pressure and hydrogen peroxide. They are then filled by injecting cement or a mixture of cement and lime, according to the strength required (Fig. 41).

c) Sealing: For shallow cracks, as well as after attachments or injection grouting, the joint is sealed with mortar made from a mixture of cement, lime and quartz sand. Pigment is added to the mortar to ensure its chromatic harmonisation with the ancient marble, together with 6% of the weight of the lime in calcium carbonate, to accelerate hardening of the mortar (54).

d) Impregnation: Wherever the marble exhibits intergranular decohesion (e.g. sugaring or microfissuring in depth) the marble is sprayed or impregnated with a solution or a suspension of lime in water, with the addition of 6% calcium carbonate (54) (Fig. 42).

Fig. 41. *Injection grouting of internal cavities. Propylaea. B–Δ.0.6.*

Fig. 42. *Impregnating disintegrated marble to restore the coherence of the crystals.*

To date, the *protection* of the monuments has been effected indirectly, by transferring the sculptures to the Acropolis Museum. There are no protective measures applied to the monuments themselves, since the known coating materials that have been in use up to the present are not guaranteed to be safe over the long-term so that we might use them on the Acropolis monuments. Research at the National Technical University of Athens continues, aiming to find a protection method based on the corrosion mechanism (45 - 50).

Finally, even though the research is almost complete (51, 59, 60) a *cleaning* programme has not yet been applied since it is directly linked with the application of some method of protection.

Fig. 43. In situ *preventive consolidation interventions on the Parthenon's west frieze before dismantling.*

The question of vegetation on the Acropolis monuments is dealt with by the periodic uprooting of the various plants and the sealing of cracks and joints, while a satisfactory solution has not yet been found for preventing soiling by pigeons.

The conservation materials

The conservation materials used are inorganic materials selected especially for the Pentelic marble of the Acropolis monuments (2, 3, 4, 54).

The cement used is white Portland cement with a low sulphate content. The addition of lime to the exterior sealing mortars increases the plasticity of the mortar and reduces its strength, while quartz sand has been selected as an aggregate on the basis of its inertia to acid pollutants (5, 6, 61, 62).

Wherever lime is used (in the injections, seals, lime water etc.) 6% (of the weight of the lime) calcium carbonate is added to the mixture to speed up its conversion to calcium carbonate and to increase its hardeness. (54)

Conservation of the sculptures

Passive conservation

Passive conservation consists in transferring the architectural sculptures from monuments to a museum environment and placing certain of them in an inert nitrogen atmosphere (19). So far, figures B, C and W from the west pediment and the metopes from the east side of the Parthenon, as well as the Caryatids from the Erechtheion have been transported to the Acropolis Museum. The transfer of the marbles from the west frieze of the Parthenon began in January of 1993, and was completed in July of the same year. Of these statues, the Cecrops - Kore group and the Caryatids are kept in a nitrogen atmosphere.

Active conservation on sculptures

The materials used to consolidate the surface of the sculptures in a museum environment are the same inorganic materials employed on architectural members exposed to the open air, but adapted to museum requirements. Intervention to consolidate

Fig. 44. *Horses from the Chariot of the Sun, from the east pediment of the Acropolis during conservation work.*

the surface in order to take casts were conducted on the Chariot of the Sun horses from the east pediment of the Parthenon (Fig. 44), and the block with the lion's head from the northeastern corner of its entablature.

Conservation of other movable objects

During the dismantling of a monument's architectural members, objects come to light which are associated with the structure and history of the monument in question.

Wooden *polos* and *embolio*

The polos and embolio (80) (wooden elements used for the centering of the column drums) which were found during the dismantling of the capital on the 5th column of the Parthenon's south side was morphologically intact, but split in several parts and wet. The *polos* presented shearing deformation. Directly correlated with the embolio were traces of the red pigment and marble powder used by the ancients to make the embolio fit into the marble joint.

From the moment of its discovery until its conservation, the embolio was kept in aseptic conditions with relative humidity of 60 - 70% at a temperature of ± 18°C. To consolidate it, a synthetic resin was used (copolymer of ethyl methacrylate and methyl acrylate). The embolio is kept in the Acropolis Museum.

Steel junctions

The ancient junctions which were removed from the monuments have been stored in the Acropolis Museum in a low humidity environment to prevent further deterioration (81, 82).

4. Documentation

In accordance with article 16 of the Venice Charter, "all phases of the consolidation works... as well as all the technical and morphological facts ascertained during the works should be recorded in detail...".

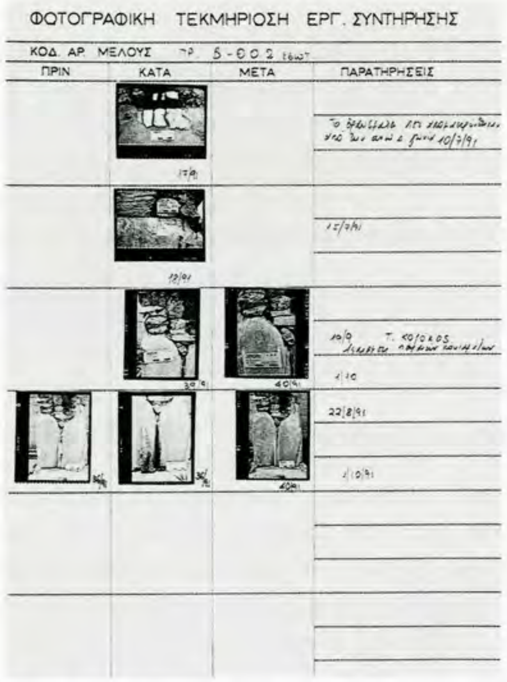

Fig. 45. *Photographic documentation card.*

For practical reasons, owing to the size of the monuments, the basic unit of documentation adopted was the architectural member. The documentation includes (73, 77):

Photographs: Each member is photographed before, during and after conservation works; thus a photographic record is created for each member (Fig. 45).

Mapping: On a drawing of the member (scale 1:10) the following data are mapped in various colours: the monochromatic surface layers/polychromy, the deposits, the past conservation interventions and the present interventions (Fig. 46).

Fig. 46. *West frieze of the Parthenon. Block X. Ancient surface layers. Comparison over time 1910 to 1992. (Mapping A. Galanou, Y. Dogani).*

Each group of data is mapped on a separate transparent sheet so that, by overlaying the sheets, one has a complete picture of the conservation status of the member.

The above documents (photographic reports, mappings) are kept in files (one for each architectural member).

Journal

A journal is kept of the conservation works in which the interventions are described in detail. In some cases, the extent of the preserved surface layers, the painted ornamentation and the graffiti are recorded on transparent sheets of PVC on a 1:1 scale.

It is planned that the above documents will be computerized for easy access and processing.

5. Technical infrastructure

The technical infrastructure deemed necessary for the conservation task includes:

a) Scaffolding (Fig. 47) and special tool kits for *in situ* work on the monuments.

b) On site workshops

Fig. 47 *View of scaffolding on east side of Parthenon.*

Fig. 48. *View of the conservation laboratory in the Acropolis Museum.*

c) A fully equipped conservation laboratory in the Acropolis Museum for the conservation of the sculptures (Fig. 48).

6. Personnel

The conservation works are being carried out on the Parthenon by conservators Y. Dogani, A. Galanos and A. Panou and by specialist marble masons I. Kladios, K. Dimopoulos, I. Skalkotos and A. Lyritis.

Work on the Propylaea is being conducted by conservators A. Moraitou and M. Papadimitriou and specialist masons T. Kozokos and L. Michalakos, and on the Temple of Athena Nike by conservator A. Babanika.

In the Museum laboratory, the conservation of statues is conducted by conservators G. Paganis and D. Maraziotis.

Mrs E. Papakonstantinou, chemical engineer, is coordinating the conservation work while the programme as a whole is under the scientific direction of Prof. Th. Skoulikidis, Professor of the

NTUA and member of the CPAM, and the administrative responsibility of the Acropolis Ephorate.

Periodically, apprenticeships are undertaken by students from the Conservation of Antiquities and Works of Art Department of the Athens Technological Educational Institute (TEI) upon assignment by the Acropolis Director.

BIBLIOGRAPHY AND REFERENCES

1. Th. Skoulikidis, Th. Tassios: *"Corrosion des armatures du béton et leur protection par un nouvel additif"*. 1st Intern. Congress on Marine Corrosion and Fouling, Cannes, 1964, Proc. p. 225.
2. Th. Skoulikidis: *"Να αντικατασταθούν τα 'σιδηρά δεσίματα' των Μνημείων της Ακρόπολης"*. (*"The 'steel junctions' in the Acropolis Monuments should be replaced"*). Interview in the periodical "Nea Politeia". 8 August 1971.
3. Th. Skoulikidis: *"Détérioration des matériaux de construction et notamment des marbres par la corrosion d' acier incorporé. Cas de l' Acropole"*, ler Colloque Intern. sur la Détérioration des Pierres en Oeuvre, La Rochelle, 1972, Comptes-Rendus, p. 41.
4. Th. Skoulikidis: *"Attaque atmosphérique (Coujon en acier), et mesures à prendre"*, 2ème Colloque Intern. sur la Détérioration des Pierres en Oeuvre, Athènes, 1976, Comptes-Rendus, p. 347.
5. Th. Skoulikidis, K. Sarropoulos, G. Batis, D. Theodoropoulos, M. Androulakis, J. Kalogyrou: *"Standardisation des éprouvettes en béton armé sur la base des mesures dans l' eau douce et l' eau de mer avec ou sans protection cathodique. Mesure du potentiel de corrosion; courbes potentiostatiques"*, Corrosion Marine-Fouling, **1**, 25 (1976).
6. Th. Skoulikidis, G. Batis, J. Kalogyrou, J. Kaselimis, D. Theodoropoulos: *"Standardisation des éprouvettes en béton armé sur la base des mesures dans l' eau douce et l' eau de mer avec ou sans protection cathodique. Mesure du potentiel et de la perte de poids des armatures; courbes potentiostatiques"*, Corrosion Marine-Fouling, **1**, 35 (1976).

7. Th. Skoulikidis: *"La détérioration des monuments et des statues anciens par les polluants atmosphériques et leur protection. Pollution atmosphérique–La détérioration des monuments de l' Acropole et leur protection"*, International Seminar, Thessaloniki: International Protection of the Environment at a Regional Level, Thessaloniki, 1980, Proc. 1982, p. 349. Guest lecturer.
8. Th. Skoulikidis: *"Atmospheric Corrosion of the Concrete Reinforcement and of the Limestones and Marbles of Ancient Monuments and Statues"*. Intern. Symposium on Atmospheric Corrosion, Electrochemical Society, Hollywood, Miami, Florida, 1980, proc. p. 825.
9. Th. Skoulikidis: *"Preservation of the Monuments of Greek Antiquity"*. The Naval Research Laboratory, Chapter of Sigma-XI, The Scientific Research Society, Washington D.C., 1980. Guest lecturer.
10. Th. Skoulikidis: *"The Deterioration and Protection of the Acropolis Monuments"*, University of Tampa, Tampa (Florida), 1980. Guest lecturer.
11. Th. Skoulikidis, G. Batis, D. Marinakis: *"Corrosion and Protection: Studies in Sea Water of the Reinforcements of Concrete Using Normalized Specimens"*, 5th Inter Congr. on Marine Corrosion and Fouling, Barcelona, 1980, proc. p. 57.
12. Th. Skoulikidis: *"Effects of Primary and Secondary Air Pollutants and Acid Depositions on (Ancient and Modern) Buildings and Monuments"*, Symposium on Acid Deposition-A Challenge for Europe, Karlsruhe, 1983, Proc. p. 193, Guest lecturer.
13. Th. Skoulikidis, N. Gudev, G. Batis, A. Ganeva: *"L' Influence de différents inhibiteurs sur la corrosion d' armatures du Béton"*, Matériaux de Constr. et Industrie de Silicates, **6,** 12 (1983).
14. Th. Skoulikidis, A. Tsakopoulos, A. Moropoulou: *"Protection of Rebars with Needle-Diodes: Use of the Atmospheric Electricity"*, Intern. Symp. on the Corrosion Effect of Stray Currents and the Techniques for Evaluating Corrosion of Rebars in Concrete, Williamsburg, Virginia, 1984. A.S.T.M. Special Publication 906, p. 15, 1986.

15. Th. Skoulikidis, D. Marinakis, G. Batis: *"Terra Theraic and MgO with Induced Defects as Additives in Concrete for the Protection of Rebars"*, ibid, 1984, A.S.T.M. Special Publication 906, p. 118, 1986.
16. Th. Skoulikidis, D. Marinakis, G. Batis: *"X–Ray Permeability of Corrosion Products as a Measure of the Rate of Corrosion of Rebars and of Prediction of Concrete Cracking"*, ibid, 1984, A.S.T.M. Special Publication 906, p. 108, 1986.
17. Th. Skoulikidis, G. Batis, P. Vassiliou, N. Gudev, A. Ganeva: *"L' évaluation critique de l' aptitude des courbes potentiel/temps et des courbes potentiostatiques et potentiodynamiques de polarisation comme méthode de prévision de l' évolution de la corrosion de l' armature dans le béton"*, Matériaux de Constr. et Industrie de Silicates, **8,** 10 (1984).
18. Th. Skoulikidis: *"Διάβρωση και Προστασία του Σιδηροπλισμού του Οπλισμένου Σκυροδέματος", (The Corrosion and Protection of the Steel in Reinforced Concrete).* Commemorative edition in memory of NTUA Prof. A. Deligiannis, p. 244, Fig. 6, 1990.
19. Th. Skoulikidis, P. Papakonstantinou, D. Charalambous: *"Attaque atmospheric (marbres) et mesures à prendre"* 2me Colloque Intern. sur la Détérioration des Pierres en Oeuvre, Athènes, 1976. Proc. p. 327.
20. Th. Skoulikidis, D. Charalambous, P. Papakonstantinou, N. Beloyannis: *"Le mécanisme de la sulfatation des marbres par action de SO_2"*. 3me Congrès Intern. sur la Détérioration et la Préservation des Pierres en Oeuvre, Venice, 1979, Proc. p. 439.
21. Th. Skoulikidis, D. Charalambous, P. Papakonstantinou: *"Restaurations d' anciens objets d' art en marbre détérioré: Inversion de la sulfatation–Utilisation de $CaSO_4 \cdot 2H_2O$ et transformation en $CaCO_3$"*, 2me Colloque Intern. sur la Détérioration des Pierres en Oeuvre. Athènes, 1976, Proc. p. 171.
22. Th. Skoulikidis, N. Beloyannis: *"Inversion de la sulfatation du marbre: reconversion du gypse formé sur les surfaces des Monuments et des Statues"*, International Symposium on Conservation of Stone, Bologna, 1981, Proc. p. 545.

23. Th. Skoulikidis, N. Beloyannis: *"Inversion of Marble Sulfation–Reconversion of Gypsum Films into Calcite on the Surfaces of Monuments and Statues"* Studies in Conservation, **29,** 197 (1984).
24. Th. Skoulikidis, E. Georgopoulou, P. Adamopoulou: *"Oriented Inversion of Gypsum on the Surface of Ancient Monuments back into Calcium Carbonate"* 2nd ASMOSIA Meeting, Leuven. Belgium, 1990.
25. Th. Skoulikidis, E. Georgopoulou, P. Adamopoulou: *"Oriented Inversion of Gypsum on the Surface of Ancient Monuments back into Calcium Carbonate"* 3rd ASMOSIA Meeting, Athens, 1993.
26. Th. Skoulikidis, M. Koui, A. Kostoudi: *"A New Non-Destructive Method to Differentiate in situ Marble from Gypsum and $CaCO_3$ from Inversion of Gypsum: use of Liquid Crystals"*, Mol. Cryst. Liqu. Cryst., **206,** 117 (1991).
27. Th. Skoulikidis, P. Papakonstantinou-Ziotis: *"The Mechanism of Sulfation by Atmospheric SO_2 of Limestones and Marbles of the Ancient Monuments and Statues. I. Observation in situ and Measurements in the Laboratory; Activation Energy"*, Br. Corros. J. **16,** 63 (1981).
28. Th. Skoulikidis, D. Charalambous: *"The Mechanism of Sulfation by Atmospheric SO_2 of Limestones and Marbles of the Ancient Monuments and Statues. II. Hypothesis and Proofs of the Rate Determining Step: Galvanic Cell Model"*, ibid, **16,** 70 (1981).
29. Th. Skoulikidis: *"The Influence of Air Pollution on the Deterioration of Ancient Monuments"*, Inter. Congr. on Pollution of Environment, Thessaloniki, 1981, Proc. p. 32. Guest lecturer.
30. Th. Skoulikidis: *"Présentation des méthodes de protection des marbres contre la pollution atmosphérique"*, 3èmes Journées de l' Industrie Minérale, Bruxelles, 1981, Proc. p. 839. Guest lecturer.
31. Th. Skoulikidis, D. Charalambous, P. Papakonstantinou-Ziotis: *"Preuves supplémentaires pour le modèle de la pile galvanique valable pour la sulfatation des marbres"*, 4th Intern. Congress on the Deterioration and Protection of Building Stones, Louisville, 1982, Proc. p. 307.

32. Th. Skoulikidis: *"Mechanism of Sulfation of Marbles by Atmospheric SO_2"*, Symposium on Chemistry and Biology in Service of Research and Preservation of Cultural and Historical Inheritance, Sofia, 1983, Proc. p. 45. Invited paper.
33. Th. Skoulikidis: *"Pollution atmosphérique et corrosion de la surface du marbre du Parthénon. Observations et propositions"*, 2nd Intern. Meeting for the Restoration of the Acropolis Monuments-Parthenon, Athens, 1983, Proc. p. 56.
34. Th. Skoulikidis: *"Επίδραση της ρύπανσης στα υλικά", (The effects of pollution on materials) from the Conference on "Environmental protection within the context of the country's technological development through the NTUA's study and research programmes»* celebrating the 150th anniversary of the founding of the National Technical University of Athens (NTUA). Athens, 1988.
35. Th. Skoulikidis, D. Charalambous, P. Papakonstantinou-Ziotis: *"Mechanism of Sulfation by Atmospheric SO_2 of the Limestones and Marbres of the Ancient Monuments and Statues. III. Further Proofs for the Galvanic Cell Model"*, Br. Corros. J., **18,** 200 (1983).
36. Th. Skoulikidis, D. Charalambous: *"Preuves pour le modèle de la pile galvanique du mécanisme de la sulfatation des marbres"* Vth Intern. Congress on the Deterioration and Preservation of Stone, Lausanne, 1985, Proc. p. 547.
37. Th. Skoulikidis, D. Charalambous, M. Kyrkos: *"Further Proofs for the Mechanism of Sulfation (Galvanic Cell Model) of Marbles and Orientation for Their Protection"* Conference on the Recent Advances in the Conservation and Analysis of Artifacts, University of London, Institute of Archaeology, London, 1987, Proc. p. 383.
38. Th. Skoulikidis: *"General Guidelines for the Protection of Ancient Monuments and Especially of the Acropolis Ones"* Intern. Symposium on Engineering Geology as Related to the Study, Preservation and Protection of Ancient Works, Monuments and Historical Sites, Athens, 1988, Proc. p. 1975. Guest lecturer.
39. G. Bell, J. Coulthard: *"Stone Preservation with Illustative Examples from the United Kingdom"* ibid, Proc. p. 883.

40. Th. Skoulikidis, D. Charalambous, P. Papakonstantinou: *"New Protective Coatings for Marble against Pollution"* ibid, Proc. p. 871.
41. Th. Skoulikidis, P. Vassiliou: *"New Anticorrosive Paints"*, 3rd Intern. Congr. on Marine Technology, Athens, 1984, Proc. p. 535.
42. Th. Skoulikidis, P. Vassiliou: *"New Anticorrosive Paints"*, 6th Inter. Congr. on Marine Corrosion and Fouling, Athens, 1984, Proc. p. 335.
43. Th. Skoulikidis, P. Vassiliou, N. Diamantis: *"Red Mud can be used as Pigment for Steel Anticorrosive Paints combined with Cathodic Protection"* 5th Intern. Congr. on Marine Technology, Athens, 1990, Proc. p. 155.
44. Th. Skoulikidis, D. Charalambous, E. Kalifatidou: *"New Protective Coatings for Marble Against Pollution"* VIth Int. Congress on Deterioration and Conservation of Stone, Torun, Poland, 1988, Proc. p. 534.
45. Th. Skoulikidis, E. Kritikou: *"Protection of Marbles of Ancient Monuments; Method of Doped Semiconductors"* 2nd Inter. Congr. for the Conservation of Monuments in the Mediterranean Basin, Geneva, 1991, Proc. p. 389.
46. Th. Skoulikidis, E. Kritikou: *"Protective Coatings for Marble and Stones using n-semiconductors as Pigments"*, Intern. Congress STREMA (Structural Studies, Repairs and Maintenance of Historical Buildings), Seville, 1991.
47. Th. Skoulikidis, E. Kritikou: *"Protective Coatings for Marbles and Stones Using Polymers Pigmented with Doped n-Semiconductors"*, 7th Int. Congr. on Deterior. and Cons. of Stones, Lisbon, 1992.
48. Th. Skoulikidis, P. Vassiliou, D. Charalambous, P. Papakonstantinou, E. Kalifatidou, S. Vlachos, E. Kritikou: *"Protection of Steel and Marbles from Pollution based on their Similar Mechanism of Decay"*, 1st Inter. Exhib. and Confer. of Environ. Technology for the Mediterranean Region, HELLECO, Athens 1993, Proc. p. 106.
49. Th. Skoulikidis, E. Kritikou: *"Protective Coatings for Marble and Stones Using n-Semiconductors as Pigment"*, 3rd Inter. Conf. STREMA 93, Bath, U.K., 1993, Proc. p. 241.

50. Th. Skoulikidis: *"Protective Treatment of Marbles and Stones based on the Mechanism of Decay"*, 2nd Inter. Course on Monument Conservation, C.U.M., Crete, 1993.
51. Th. Skoulikidis, P. Papakonstantinou: *"Stone Cleaning by Inversion of Gypsum back into $CaCO_3$"*, Stone Cleaning Inter. Conf., Edinburgh, 1992, Proc. p. 155. Invited paper.
52. K. Lal Gauri, L. Parks, J. Jaynes and R. Atlas: *"Removal of Sulphated-crust from Marble using sulphate-reducing Bacteria"*, ibid, Proc. p. 160.
53. Th. Skoulikidis, P. Papakonstantinou, E. Kritikou, G. Tsangalidis: *"Production of Artificial Patinas on the surface of New Marbles used for the Restoration of Ancient Monuments and on the Surface of White Cement Copies of Statues"*, Inter. Congr. UNESCO-RILEM, Paris, 1993, Proc. p. 644.
54. Th. Skoulikidis, D. Charalambous, D. Dramali: *"Ways to increase the Mechanical Resistance of Lime* [$CaO \xrightarrow{H_2O} Ca(OH)_2 \xrightarrow{CO_2} CaCO_3$] *used for Conservation and Restoration of Ancient Monuments"*, Int. Symp. on the Deter. of Building Materials, ASESMO, La Rochelle, 1991, Proc. p. 177.
55. Th. Skoulikidis, P. Vassiliou, E. Kritikou K. Tsakona: *"Stress Corrosion Cracking of Untreated Pentelic Marble or Artificially weathered or treated with Pigmented or Unpigmented Polymer"*, 3rd Inter. Conf. STREMA '93, Bath, U.K., 1993, Proc. p. 241.
56. K. Kouzeli, N. Beloyannis, Ch. Tolias and Y. Dogani: *"Monochromatic Layers with and without Oxalates on the Parthenon"*, Int. Symp: the Oxalate Films, Origin and Significance in the Conservation of Works of Arts, Milano, 1989.
57. K. Kouzeli, Y. Dogani, N. Beloyiannis: *"Study of the Remaining Colouring on the Architectural Surfaces of the Parthenon"*, Superfici dell' Architettura: Le Finiture, Bressanone, 1990.
58. Unpublished Report: N. Beloyannis, P. Theoulakis, Chr. Tolias: *"The aluminosilicate veins in the marble of the Acropolis Propylaea"*, CPAM Archives, No. 210, 1985 and Proceedings of 3rd Int. Meeting on the Restoration of the Acropolis Monuments, Study for the Restoration of the Parthenon, Athens, 1989, p. 189.

59. Unpublished report: K. Kouzeli, Y. Dogani: "*Δοκιμαστικές εφαρμογές μεθόδων επιφανειακού καθαρισμού για την απομάκρυνση της μαύρης κρούστας*", *(Trial applications of surface cleaning methods for black crust removal)*. CPAM Archives, No. 326, 1990.
59a. K. Hempel, "*The biological pack*", UNESCO–RILEM, Alteration et Protection des Monuments en Pierre, Paris 1978.
60. K. Kouzeli: "*Black Crust Removal Methods in Use. Their Effects on Pentelic Marble Surfaces*" 7th Inter. Cong. on Deterioration and Conservation of Stone, Lisbon, 1992, Proc. p. 1147
61. Ch. Lazari: "*Σύνθεση και μελέτη ιδιοτήτων κονιαμάτων, που περιέχουν τσιμέντο, υδροξείδιο του ασβεστίου και αδρανή για συγκολλήσεις μικρών απολεπίσεων, για σφραγίσματα, ενέματα για την πλήρωση ρωγμών σε πεντελικό μάρμαρο σε αστικό περιβάλλον*", *(Composition and study of the properties of mortars containing cement, calcium hydroxide and aggregate for attaching small delaminations, for sealing and injections, for filling cracks in Pentelic marble in an urban environment"*. Athens 1991. Undergraduate thesis, Technical Educational Institute [TEI] Athens.
62. Unpublished report: K. Kouzeli, A. Moraitou: "*Παρασκευή και μελέτη ιδιοτήτων κονιαμάτων καταλλήλων για χρήση στο πεντελικό μάρμαρο σε αστικό περιβάλλον*", *(Preparation and study of the properties of mortars suitable for use on Pentelic marble in an urban environment)*, 1994 CPAM Archives, No 2.
63. S.B. Curri: "*The Microbiological Attack on the Surface of Fidia's Statue Cecrops and Pandrossos: I-Preparation of the Antibiograms and Results of some Biological and Biochemical Analyses*". Biochemistry and Experimental Biology vol. XV, n.2, 1979 σ. 203-207.
64. S.B. Curri: "*The Microbiological Attack on the Surface of Fidia's Statue Cecrops and Pandrossos: II-Evaluation of the Activity of some Biocides on the polluted Marble*", Biochem and Exper. Biology vol. XV, n° 3, 1979, σ. 299-304.

65. S.B. Curri: "*Microbiological Aspects of Weathering of the Caryatids*", Bioch. & Experimental Biology, vol. XV n° 3, 1979 σ. 294-297.
66. S.B. Curri: "*Biocide Testing and Enzymological Studies on damaged Stone and Frescos Surfaces: Preparation of Antibiograms*", Bioc. & Exp. Biol., Vol. XV n° 1, 1979. σ. 97-104.
67. K. Anagnostidis, A. Economou-Amilli, M. Roussomoustakaki: "*Epilithic and Chasmolithic Microflora (Cyanophyta, Bacillariophyta) from Marbles of the Parthenon (Acropolis-Athens, Greece)*", Nova Hedwigia-Band XXXVIII. Braunschweig, 1983, σ. 227.
68. Unpublished report: W.E. Krumbein, A. Pantazidou, C. Urzi, "*The Biodeterioration of Marbles of the Acropolis. The Choice of Biocidal Treatments and of the Biological Status of some of the Sculptures in the Acropolis Museum*", Aug. 1992, CPAM Archives.
69. C. Urgi, W. Krumbein and T. Warscheid: "*On the Question of Biogenic Colour Changes of Mediterrenean Monuments*", 2nd Inter. Symp. on the Conversation of Monuments in the Mediterranean Basin, Geneva, 1991, Proc. p.p. 397-420.
70. L. Hatziandreou: "*Gammagraphy*", 2nd Inter. Symposium on the Deterioration of Building Stone. Athens, 1976. Proc. p. 309-317.
71. Unpublished report: D.H. Cholevas: "*Καταπολέμηση ζιζανίων στα μάρμαρα του Παρθενώνα*", *(Combatting plan growths on the Parthenon marble)*. Benakeio Phytopathological Institute report, 18/8/88. Archives, 1st Ephorate of Prehistoric and Classical Antiquities, Prot. No. 2709.
72. Venice Charter: "*Architectural issues*", **9**, 1975, p. 108 (in Greek).
73. Th. Skoulikidis, P. Theoulakis, K. Kouzeli, N. Beloyannis, E. Papakonstantinou, D. Charalambous, Y. Dogani, A. Moraitou: "*Το μάρμαρο του Παρθενώνος και η συντήρησή του*", *(The Parthenon marble and its conservation)* in "Μελέτη Αποκαταστάσεως του Παρθενώνος", (Study for the Restoration of the Parthenon), Vol 2a, Athens 1989, p. 181.

74. I.D. Jenkins, A.P. Middleton: *"Paint on the Parthenon Sculptures"*, The Annual of the BSA at Athens, vol. **83,** 1988, p. 183.
75. A.K. Orlandos, L. Vranoussis: *"Τα χαράγματα του Παρθενώνος"*, *(The Parthenon graffiti)*, Athens Academy, Athens 1973.
76. Unpublished report: A. Moraitou: *"Η αρνητική επίδραση της κονίας Meyer σε γλυπτά του Μουσείου της Ακρόπολης"*, *(The adverse effects of Meyer cement on the sculptures in the Acropolis Museum)*. CPAM Archives. March 1991, No. 106.
77. Y. Dogani, A. Moraitou, A. Galanos: *"Case Study: Conservation Work at the Parthenon"*, Proceedings of the 7th International Congress of the Deterioration and Conservation of Stone, Lisbon, Portugal, June 1992.
78. A.M. Korres, H. Bouras: *"Μελέτη Αποκαταστάσεως του Παρθενώνος"*, *(Study for the Restoration of the Parthenon)*, Athens, 1983.
79. C. Zambas, M. Ioannidou, A. Papanicolaou: *"The Use of Titanium Reinforcement for the Restoration of Marble Architectural Members of the Acropolis Monuments, Case Studies in the Conservation of Stone and Wall Paintings"*, IIC Bologna Congress, 1986, p. 138.
80. A. Orlandos: *"Η αρχιτεκτονική του Παρθενώνος"*, *(The architecture of the Parthenon)*, Athens 1977.
81. Unpublished report: A. Moraitou: *"Συντήρηση και προστασία σιδερένιων συνδέσμων"*, *(Conservation and protection of steel junctions)*, Athens 1988. Archives of the First Ephorate of Prehistoric and Classical Antiquities, Prot. No. 3962.
82. G. Varoufakis: *"Πώς άντεξαν στην διάβρωση τόσων αιώνων οι σιδερένιοι σύνδεσμοι και γόμφοι των ναών της Ακρόπολης"*, *(How the steel junctions and clamps on the Acropolis temples have withstood so many centuries of corrosion)* Archaeologia, 45, 1992.

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