THE COMPOSITION AND STRUCTURE OF THE PATINA ON THE PARTHENON AND OTHER GREEK MONUMENTS

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By the term patina[1] we mean a thin layer formed on the surface of an object by the passage of time, which is the result of natural processes, human intervention or a combination of the two. It adheres to the material it covers, it is not harmful to it but on the contrary it protects it; it does not change the appearance of the object, in fact in contributes to its aesthetic appearance. The term was initially used to describe the superficial layers on metals, but its use has been extended to include other materials such as wood and stone. Such superficial layers on the stone of monuments are found all over the world. To understand the nature, the structure and the role of the patina on stone monuments and furthermore its origin, is a difficult task to which many scientists have contributed and are still contributing. Apart from the aesthetic contribution of the patina to the appearance of the monuments, its "chemistry" , using the wider sense of the word, is very important. The scientific examination of the film yields precious information about the monument, and traces of tools can be observed on the marble underneath the patina as well as traces of ancient pigments and other subsequent surface treatments. The knowledge of its composition and structure is significant for the choice of conservational methods, materials and procedures.

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[1] The term patina is today internationally accepted. It is of Latin origin, although its evolution of meaning is doubtful. It was introduced in the Greek language by the Venetians and it is often used in the modern Greek literature.

There are several kinds of patina and their variety does not permit a standard procedure concerning conservation treatments. So any individual case has to be tackled separately taking into consideration many factors such as the nature of the object, its position in the monument and the local climate.

Simple macroscopic observation of numerous Classical and Roman monuments in Greece and Asia Minor reveals that considerable part of their surfaces is covered by a characteristic orange-brown patina. The first chemical analysis was carried out by very famous scientists of the 19th century Liebig (Liebig J., 1853), Faraday (Donaldson D. L., Brandi C., 1951), Landerer (Rangabé A. R., 1842) using the limited means in their disposal. The international interest and the study of the patina revived in the early 1980s: the patina covering many Roman monuments in Italy, the "scialbatura", was studied by many Italian scientists and conservators. Similar scientific work has been carried out in Greece on the patina of the Parthenon. The almost parallel research activities on the superficial layers in Greece and in Italy led to some very interesting conclusions, raising more challenging questions about the nature and the origin of the patina. The oxalic nature of the patina covering most monuments in Italy was definitely confirmed and a discussion arose among scientists about the origin of these layers: some attributed the formation of this patina to natural causes (Del Monte M. Sabbioni C., 1987); others did not accept this generalisation of the origin and in some cases suggested the contribution of surface treatments to the formation of the "sciabatura". Although the research in Italy confirmed the oxalic nature of the patina on the monuments there, in Greece the chemical analysis of the orange-brown patina on the Parthenon indicated the systematic presence of phosphorus, while oxalates were only occasionally detected: clearly the orange - brown patina on the Parthenon was of phosphatic nature (Kouzeli K., Beloyannis N., Tolias C., Dogani Y., 1988). This bore out the results noted by M. S. Tite (Tite M., Middleton A.P., 1986) set out in his communication to the Committee for the Preservation of the Acropolis Monuments (see also Jenkins, I. and Middleton, A. 1988).

In Italy although some silicic and phosphatic superficial layers have been identified, the observations about the main patina “scialbatura” can be summarised as follows: the “scialbatura” is a homogenous and extensive layer coloured variously, over a variety of substrates, including stone (calcareous and non-calcareous), bronze, glass, paintings and wood as well.

It consists mainly of calcium oxalate (the monohydrated whewellite and the dehydrated weddelite). Iron oxides, gypsum, quartz and feldspars (as wind-born particles deposited on the surfaces) are frequently present (Lazzarini L., Salvatori O., 1989).

Some scientists attributed the formation of the oxalic patina to natural causes and especially to the action of encrusting lichens producing oxalic acid (Del Monte M., Sabbioni C., 1987), which reacted with the calcite of the marble to form the calcium oxalates present in this patina. This hypothesis was strongly disputed since it failed to provide an adequate explanation for all the cases. The systematic observation of the marble surfaces on the Parthenon reveals the presence of a variety of layers, of which the most widespread is the characteristic orange - brown patina.

This adheres to the marble almost perfectly protecting it as if it were its skin (Corres E., Bouras C., 1983). This monochromatic layer is more apparent on protected areas of the monument, to a lesser but still considerable extent on the south side, whereas its presence is very limited on the north side, where the weathering effects are intense. A further layer, whitish, is present to a lesser but still noticeable extent. It covers traces of ancient pigments as well as the orange-brown patina when they co-exist, which is why the term "covering" has been adopted.

From the existing references since the 19th century we can deduce that these layers were responsible for the optical impression that the monuments gave to the visitor: Chateaubriand (Chateaubriand, 1811) describes the colouration of the monuments as resembling the golden colour of wheat, while a French art historian describes this colouration as the "yellow-brown colour of a rotten peach". Greek writers also commented on the colouration of the marble surfaces. Among the many colours of the Athens' plains Emmanuel Roides (Roides E.) remarked on the wheat-coloured hues of the ancient monuments. Painters of the 19th century depict the monuments as having an orange colouration, which we know does not originate from their personal desire to add warm colours to their paintings, but from simple representation of reality. Figure 1 shows a water-colour by Stiling (1865).

Early photographs dating back to the late 19th and the early 20th century show these layers covering much larger areas than they do today (figure 2). Mapping of these layers on the metopes of the east side as well as of the west Doric frieze of the Parthenon using old photographs gave us an idea of their reduction during the 20th century, which can be attributed to acid rain. Various methods were used for the examination and the study of the composition and structure of these layers: Optical Microscopy, Polarising Microscopy, Scanning Electron Microscopy combined with X Ray Microanalysis and Energy Dispersion System, X Ray Diffraction, Atomic Absorption Spectroscopy as well as microchemical tests.

The covering (i.e. the whitish layer which covers traces of ancient pigments and very often the orange-brown layer (when they co-exist) is of relatively uniform thickness (figure 3). It is better preserved on protected areas and the shorter sides of the monument, where the weathering effects are less intense. It flakes off more easily than the orange-brown patina. According to the results of the analysis the thickness of the covering is about 80-100 microns. It consists mainly of calcite and contains large quantities of gypsum. It is an artifical layer, probably applied to the Temple during some reconstruction. It covers Byzantine graffiti of which the most recent is one of 947 A.D., but it does not cover graffiti of the western occupation (1204-1458 A.D.), though its absence could be due to its removal because of the weathering effects. We can be fairly certain that this film is the result of a surface treatment (using mainly lime) (Kouzeli et al., 1988).

The orange-brown patina (figure 4) according to detailed macroscopic and in situ microscopic observation in most of the cases showed two or three layers: a whitish one in contact with the marble, followed by another very thin orange-brown one, which is sometimes followed by another darker film. This orange-brown skin of the marble is very smooth, when the surface it covers is smooth too (following the details of the under-lying marble). It is also better preserved on protected areas, on the shorter sides of the monument (east and west), to a lesser but still considerable extent on the south side and its presence is very limited on the north side, where the weathering effects are more intense.

The image of the orange-brown patina under the optical microscope, parallel to the surface (figure 5) and in cross section (perpendicular to the surface) as well as of thin cross-section under the polarizing microscope (figure 6) gave us the first objective information about the structure of the patina, which was accomplished through observation under the Scanning Electron Microscope and X Ray Microanalysis of the same area. In order to achieve a better and more comprehensible presentation of the results of the examination under the Scanning Electron Microscopy and of X Ray Microanalysis a combination of Scanning Electron Image of the cross-section of the sample and of the X Ray Images at the same place was undertaken (figures 7,8). The well-known X Ray Images (white spots on black font, where high density of the white spots corresponds to high content of the chemical element under analysis) have been inverted resulting in an image consisting of black spots on white font and coloured (giving each element a different colour). Then the inverted and coloured images of X Ray Microanalysis were transferred on the Scanning Electron Image giving us detailed information about the existence and the distribution of the chemical elements on the sample. In figures 7 and 8 the cross-section of a sample of marble covered by the orange-brown patina (the upper surface corresponds to the external surface) and the distribution of the main chemical elements detected is presented (phosphorus, iron, silicon and aluminum are indicated by red, yellow, green and purple respectively). According to the results of the analysis (Kouzeli Keeper., Beloyanis N., Tolias C., Dogani Y., 1989,Kouzeli et al, 1996):

The orange-brown patina is of a relatively uniform thickness of about 150 microns.

It is of phosphatic nature: phosphorus is always detected (as calcium phosphate) and uniformly distributed (figure 7). This phosphorus-containing patina enters the intercrystalline regions and forms an almost intermediary layer, where the marble crystals are both slightly reduced in size and subtly changed in shape and surrounded by calcium phosphate, which is responsible for its adherence to the marble.

Oxalates have been detected occasionally, in small amounts and their presence is associated with dark and humid conditions.

Gypsum has been detected.

The colour of the patina must be mainly attributed to the presence of iron oxides, contained in aluminosilicate depositions in the outer layer (figures 7 and 8).

Considering all the detailed information about the composition and the structure of the orange-brown patina given by the microscopic examination and the physicochemical analysis, it becomes clear that in most cases removal of this patina leads to a consequent removal of marble crystals leaving it naked and more susceptible to the process of deterioration.

The extended presence of the orange-brown patina, which was noticeably more widespread in the past, the detection and the uniform distribution of phosphorus, the absence of this patina on later constructions in the Parthenon (i.e. the minaré) and the completely different composition of the orange-brown layer existing on freshly quarried pentelic marble all support the hypothesis that the orange-brown patina (the skin of the marble) can be attributed to some extent to human factors (it could possibly be considered as the result of a surface treatment with a phosphorus - containing material, e.g. yolk or bone glue). However the participation of biological factors in the formation of this phosphatic patina can not be excluded.

Graziu C., Jenkins I. and Middleton A. analyzed the orange-brown patina on sculptural and architectural marble surfaces of the Mausoleum of Alicarnassus, which also proved to be of phosphatic nature and its structure was found to be very similar to that of the Parthenon, a fact that reinforced the already existing conclusions about the patina of the Parthenon. According to their opinion, these results seem to imply some superficial treatment peculiar to the Greek culture or that the nature of the orange-brown patina is probably related to the climatic conditions of the area. Almost simultaneously a major exception in Italy was discovered: the dark brown patina, which covers the pentelic marble base of the Arch of Titus in Rome was found not to contain oxalates or other inorganic crystalline compounds. The presence of very large amounts of phosphorus and silicon characterized the layer. It is the major example in Italy of a patina almost identical to that of the Parthenon and its presence has been associated with old protective treatments (probably in this case with a phosphorus or silicon-based compound).

After much extensive scientific investigation and discussions, speaking about patina of phosphatic nature has become increasingly common. This issue has raised questions about the origin of the orange-brown patina linking it to some old specific surface treatment techniques and/or to biological factors favoured by the climatic conditions in the area. Consequently the study was extended to the nature of the patina covering the marble surfaces of other monuments in Greece (Classical and Roman), which according to extensive examination appear to bear strong similarities to that on the Parthenon and analysis was carried out on samples from several monuments:

The Hephaisteion (in Athens)
The Olympian Zeus Temple (in Athens)
The Propylae of the Athens Acropolis
The Arch of Hadrian (in Athens)
The Stoa of the Athenias (in Delphi)

In the Hephaisteion (the most complete Classical Temple) extended areas of the surface are still covered by the orange-brown patina, which is of phosphatic nature.

In the Olympian Zeus Temple in Athens, which was mainly constructed during Roman times, the orange-brown patina covers large areas of the marble surface. According to the analysis the patina is similar to that covering the Parthenon surfaces. Oxalates have been detected only occasionally (Kouzeli K., 1991, Kouzeli et al, 1996).

The results of the analysis for the Propylae are analogous. (Kouzeli et al, 1996).

The patina on the Arch of Hadrian in Athens is also of phosphatic nature and oxalates have been only occasionally detected. A great variety of colourations of this patina are exhibited on the monument.

The combination of the results of Scanning Electron Microscopy and X Ray Microanalysis on the same place of all the above-mentioned samples leads to the same conclusions as for the patina on the Parthenon. Unfortunately due to printing limitations it is not possible to present the combined results of Electron Scnaning Microscopy and X Ray Microanalysis.

In the Stoa of the Athenians in Delphi, the orange-brown patina covers very limited areas. Phosphorus is mainly present In this case the layer is thinner (80 microns) and less coherent to the marble (Kouzeli et al, 1996).

Macroscopic and in situ microscopic observations were carried out on Greek and Roman monuments in Ephessus, Miletos and Didyma in Asia Minor: an orange-brown layer, which according to our observations is similar to the phosphatic patina extensively present in Greece, covers large surfaces of the monuments there.

The examination of stand-alone statues in museums (Archaic, Classical Greek and Roman), showed limited or extended presence of the orange-brown phosphatic patina on their surfaces.

The opportunity to examine the Parthenon marbles at the British Museum contributed to our knowledge and has enriched the existing information on this matter. The remains of the patina on the slabs of the Parthenon frieze and on the East pediment sculptures, according to our observation are very similar to the patina on the Parthenon. It can be categorised according to its macroscopic and in situ microscopic appearance into three groups:

The typical orange-brown patina consisting of two or three sub layers: a whitish film in contact with the marble, a very thin orange-brown film on this, sometimes followed by a third orange-brown one).

A dark brown patina, often with a rather shiny appearance.

The colouration of some areas of the surface revealed after the “cleaning” suggests a preexisting patina, the third kind where iron seems to have been evenly distributed.

These three groups of patina are also observed on marble monuments in Greece and their examination is still under progress.

Parallel to the analysis, systematic efforts have been made by many scientists to reconstruct in the laboratory a patina of oxalic or of phosphatic nature on the marble. Although some proposed methods and mechanisms on the patinas’ formation are extremely interesting, no fully acceptable results have been achieved yet (Chiari G., 1996 et al, Graziu C.

and Melucco-Vaccaro A., 1989, Rossi-Manaressi R. et al, 1989).

The presence of the orange-brown patina, which gave the ancient monuments their characteristic appearance was and is familiar to the Greek people who have lived close and with the monuments for thousands of years. The term “ancient rust” is indicative that the patina was considered an integral part of the monuments.

Today the composition and structure of the orange-brown patina has been clarified. After the results of the physicochemical analysis were published and accepted, various interpretations were proposed with or without laboratory evidence: some considered its formation to be linked to some extent to human intervention without excluding the contribution of biological factors, others attributed it solely to natural causes and even a direct correlation with the ancient treatment of ganosis or the encaustic technique described by Plinius has been put forward (despite its presence on marble surfaces broken in Byzantine times).

But what ever its origin, the phosphatic patina must be recognized as being very closely related to the original marble surface; in fact it is the most authentic surface we have. It contains in all probability transformation products of the original marble surface as well as depositions (iron-containing aluminosilicate in the outer layer from the environment etc) Its removal usually leads to actual loss of the marble itself.

Since scientific observation, study and discussion are our only reliable tools to enrich our knowledge and to contribute to the preservation of our cultural heritage, as far as our current scientific methods and equipment allow, all the existing data leads to the conclusion that the preservation of the orange-brown patina must be one of our major concerns, when making conservation decisions.

Finally I would like to thank the British Museum for its kind invitation to give during the 26th Colloquium on Cleaning the Parthenon marbles the speech presented in this paper.

REFERENCES

Brandi C., Bolletino del Instituto di Restauro, vol. 5-6, pp 3-8, 1951.

Chateaubriand F.R.,: "Itinéraire de Paris à Jérusalum",,ed. Garnier, 37, 39,Paris, 1811.

Chiari G., Gabrielli N., Torraca G.: "Calcium oxalates in internal exposure. Sistine Chapel and others", Proceedings of the II International Symposium "The oxalate films in the conservation of works of art", PP 179-188, Milan, 1996.

Del Monte M., Sabbioni C.: "A study of the patina called scialbatura on imperial roman marbles", Studies in Conservation 32, PP 114-121, 1987.

Donaldson D.L., RIBA Transactions 1st Series (1837-1842), no 1, pp 106-107.

Corres E., Bouras C. : Study for the Restoration of the Parthenon. P. 309, Athens, 1983.

Jenkins, I. and Middleton, A.: “Paint on the Parthenon Sculptures”, The Annual of the British School of Archaeology at Athens volume 83, pp 183-207, 1988.

Gratziu C., Jenkins I.D., Middleton A.P.: “Dati preliminari sulle relazioni fra patine e polycromia nei fregi del Mausoleo di Alicarnasso”, Proceedings of the International Symposium “The oxalate films: origin and significance in the conservatin of works of art”, pp 317-326, Milan 1989.

Jenkins, I, Gratziu C., Middleton, A., “The Polychromy of the Mausoleum”, Jenkins I. and Waywell, G. (eds.) Sculptors and Sculpture of Caria and the Dodecanese, 35-39, London, 1997.

Gratziu C., Melucco Vaccaro A.: Patine ad ossalato di calcio; un problema scientifica”, Proceedings of the International Symposium “The oxalate films: origin and significance in the conservation of works of art”, pp 163-193, Milan, 1989.

Kouzeli K.,Beloyannis N., Tolias C., Dogani Y.: Study of the superficial layers on the Parthenon, Athens, 1988, Archives of the Committee for the Preservation of the Acropolis Monuments.

Kouzeli, K.,Beloyannis N., Tolias C., Dogani Y.: “Ancient and Byzantine Treatments on the Parthenon”, Proceedings of the 6th International Congress on the Deterioration and Conservation of Stone, pp 687-694, Torun, 1988.

Kouzeli K.,Beloyianni N, Tolias C, Dogani Y.: “Monochromatic layers with and without oxalates on the Parthenon”, Proceedings of the International Symposium “The oxalate films: origin and significance in the conservation of works of art”, pp 327-337, Milan, 1989.

Kouzeli K.:Study of the Composition and structure of the orange-brown layers on the Olympian Zeus Temple in Athens, Athens, 1995.

Kouzeli K.Tolias C.: Structure and Composition of superficial orange-brown layers from different classical, Hellenistic, Roman and Byzantine monuments of Greece, Proceedings of the II International Symposium “The oxalate films in the conservation of works of art”, pp 69-80, Milan, 1996.

Kouzeli K.Lazari C., Economopoulos A., Pavelis C.: Phosphatic Patinas on Greek Monuments (Acropolis of Athens and other ancient and Byzantine monuments): general discussion and further documentation on the presence of oxalates, Proceedings of the II International Symposium “The oxalate films in the conservation of works of art”, pp 83-93, Milan, 1996.

Liebig, J.: Annal d. Chimie und Pharm., LXXXVI, pp. 113-115, 1853.

Lazzarini L., Salvatori O.: A reassessment of the formation of the patina called scialbatura, Studies in Conservation, 34 (1), pp. 20-26, 1989.

Paccard A: Paris-Rome-Athènes. Le voyage des architectes français au XVIIIème et au XIXème siècle. Mémoire explicatif de la RESTAURATION DU PARTHENON,PP 365-368, Rome, 1845.

Plinius, XXXV, XLI, 149.

Rangabé, A.R., Antiquités Hélleniques, pp 63-64, Athènes, 1842.

Rossi Manaressi R., Grillini G.C., Pinna D., Tucci A.: La formazione di ossalati di calcio su superfici monumentali: genesi biologica o da trattamenti?", Proceedings of the International Symposium "The oxalate films: origin and significance in the conservation of works of art", pp 113-125, Milan, 1989.

Tite M.S., Middleton A.P.: Report on the analysis of superficial layers in the Research Laboratory of the British Museum. 10/10/1986.

Figure 1: The East Side of the Parthenon (water-colour by Stiling, 1865)

Figure 2: East Doric Frieze of the Parthenon (photograph of the early 20th century)

Figure 3: The whitish layer (covering) on the triglyph between the sixth and seventh metope. It covers traces of blue ancient pigment (Egyptian blue).

Figure 4: Orange-brown patina on the base of a column (East side of the Parthenon)

Figure 5: Marble covered by orange-brown patina under the optical microscope (parallel to the surface)

Figure 6: Thin section perpendicular to the surface of marble covered by orange-brown patina under the polarising microscope (parallel prisms). The upper surface corresponds to the external surface.

Figures 7 & 8: Marble covered by orange-brown patina (cross-section). Combination of the results of Scanning Electron Microscopy and X-Ray Microanalysis on the same place of the sample. The existence and the distribution of the main chemical elements detected is presented (Phosphorus, Iron, Silicon and Aluminum are indicated by red, yellow, green and purple respectively).