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Case Report

Spectral Imaging for Stone Surface Investigation: The Case of Horologion of Andronikos Kyrristos In Roman Agora, Athens, Greece

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Abstract

Horologion of Andronikos Kyrristos, also known as the Tower of the Winds, is an octagonal marble building dating from the 1st century B.C., located on the Roman Agora in Athens, Greece. The monument is still in good condition today and as one of the most important masterpieces of late Hellenistic architecture.

The present work refers to the application of modern non-destructive imaging techniques, such as visible, infrared and thermal imaging and symmetrical and raking light, in order to collect data useful for solving conservation problems and to document the different historical phases of the monument. The study focused on investigating the stone surface and decoration and on detecting color traces, engravings, graffiti and inscriptions associated with its historical phases and its use until more recent years. The research was carried out on all the interior surfaces of the building as well as on the upper zone exterior sculptures. Useful information regarding conservation status, surface morphology and archaeological history were extracted.

Keywords: Horologion of Andronikos Kyrristos; Stone; Spectral imaging; Raking light; Near infrared; False colour infrared; Condition; Epidermis

Introduction

Horologion of Andronikos Kyrristos is an octagonal marble building, located on the Roman Agora in Athens, Greece (Figures 1a & 1b). Different opinions about the date of construction can be found referring to either around 47 B.C. or, by some others, around the second century B.C. [1]. It is also known as the Tower of the Winds because its exterior upper zone is adorned with eight sculptures, each representing a different wind deity, one on each side wall of the octagon, that bear the name of the wind of the corresponding orientation: Boreas (North), Notos (South), Apeliotes (East), Zephyros (West), Kaikias (northeast), Evros (southeast), Lips (southwest) and Skiron (northwest).

Figure 1a: Left: Horologion in the Roman Agora [18].

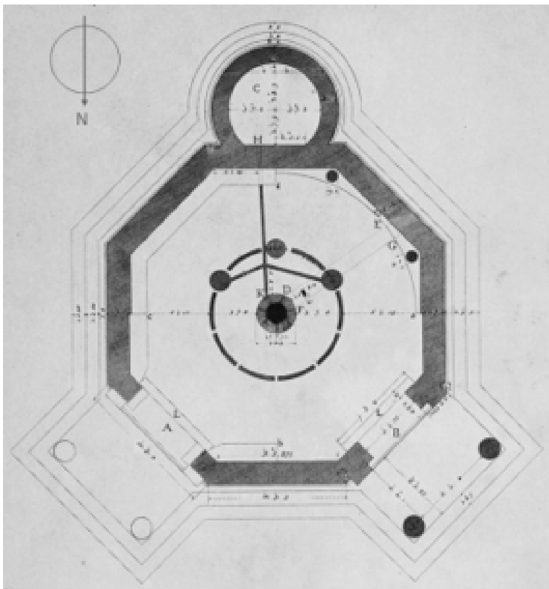


Figure 1b: Right: Plan of the Tower of the Winds (Horologion of Andronikos Kyrristos) in Athens [19].

The monument is still in good condition today and attracts particular interest as one of the most important masterpieces of late Hellenistic architecture. The monument's height reaches 13.5m and its maximum diameter is 8m. There is a semicylindrical annex attached on its south side. Andronikos from Kyrros, a town in Macedonia, was an astronomer who made good use of the era's science and technology and manufactured a mechanism that could indicate the time and other meteorological information [2,3]. Marks on the outer walls formed sundials for the sunny days, while a hydraulic mechanism inside the monument would be put to use on cloudy days. It is said that the tower was also used as a planetarium for astronomical purposes even though no mechanism survives to the present days [4- 9].

In the early Christian era, the monument was converted into a church or the baptesterion of a nearby church [10-16]. During the Ottoman occupation it was turned into a tekke [13], which describes a building dedicated specifically for Sufi residence, hospice, or lodge [17]. After the liberation of Greece in 1828, it was considered part of the antiquities of Athens and was used as a temporary museum [1].

In the recent years, the Horologion has been intensively and systematically studied from archaeological and astronomical angle of view. Furthermore, it participated in the National Strategic Reference Framework 2007-2013, 'Conservation and Valorization of the Horologion of Andronikos of Kyrros, at the archaeological site of the Roman Agora of Athens', initially by the A΄Ephorate of Prehistoric and Classical Antiquities followed by the Ephorate of Antiquities of Athens, Ministry of Culture and Sports. Within this framework, extensive conservation work on the surfaces of the monument took place both inside and outside, together with structural reinforcement and was completed a few years ago. In the same time, the ARTICON Lab: Conservation Promotion of Visual Arts, Books and Archival Material was entrusted with the systematic non-destructive physicochemical investigation of both internal and external wall surfaces. This was successfully carried out by the application of modern diagnostic physicochemical methods in order to collect data useful for solving conservation problems and to document the different historical phases of the monument.

The overall study focused on investigating the stone surfaces and the locally preserved decoration in visible and invisible radiation and on detecting color traces, engravings, graffiti and inscriptions associated with its historical phases and its use until more recent years. The research was carried out on all the interior surfaces of the building as well as on the exterior sculpture surfaces of the upper zone. Non-destructive testing was applied by means of imaging techniques in the visible and near infrared spectrum (Macro photography in normal and tangential illumination, Infrared Reflectography/SWIR Thermography, Hyperspectral Imaging (HSI) combined with False Colour Infrared (FCIR) and Spectral cube Spectroscopy). Since then, ample information has been collected on the Horologion, which resulted in several publications regarding the astronomical and historic use of the building [20] the detailed imaging of ship graffiti depicted in the interior stones [21], as well as the revelation of new ship graffiti enabled by the imaging techniques [22].

The present paper refers to the results concerning the engraved images, the interior decoration, the state of preservation and the Epidermis of the monument. The successful implementation of the imaging methodology on the immobile monument Horologion of Andronikos Kyrristos and the overcoming of the challenges associated with it expanded the capabilities of the methods, improved material observation and assisted in revealing and interpreting elements that are often valuable but invisible to the human eye. These include the existence and highlight of engraved images on the stones, the confirmation of the Egyptian blue used as pigment in selected areas, the condition of the stones and the behavior of the Epidermis found on exterior blocks in different wavelengths. Consequently, this proved that modern non-destructive imaging techniques are rightfully considered as state-of-the-art technology in the diagnostics not only of artworks but also monuments.

Case presentation

State of the art

The aforementioned techniques have been widely used on easel paintings, wall paintings, paintings on paper and other materials diagnostics. It is worth noting that, in Greece, it was one of the first times these techniques were applied in a thorough and systematic manner to study large immobile stone surfaces for the diagnosis of conservation status, the study of morphology and the detection of historical data.

HSI and SWIR are both imaging techniques and they guarantee the safety of the investigated surfaces because they are non-destructive, exactly like photographic documentation. Hyperspectral imaging extends to both visible and near infrared regions, usually from 400 – 1000nm. It acquires images using an internal combination of filters and records the reflectivity response of surfaces at specific wavelengths, given by the manufacturer. This results to the acquisition of several singular images, each responding to a particular wavelength [23,24]. Hyperspectral imaging has a spectral resolution less than 10nm [25] and may record up to 36 or more distinct wavelengths [26], making the acquired data more specific and accurate [27]. In recent years, hyperspectral imaging reaches 100-200 spectral bands, an additional advantage compared to previous models, as this provides the opportunity to better discriminate the behaviour of paint layers. Even though in continuous images, such as the ones obtained by infrared reflectography, the contrast between the background and the surface does not always produce straightforward information, single wave images ensure that there will be at least one wavelength with efficient contrast to extract valuable information from. Hyperspectral systems enable also the acquisition of spectral cubes and false colour infrared images. Spectral cubes combine all spectral bands of the hyperspectral camera and can present the reflectance spectrum of every individual spot of the surface. In this way, reflectance spectra can be compared to those of known pigments from verified databases and identify them [28]. False colour infrared imaging (FCIR) is an invaluable asset in the hyperspectral toolbox. The combination of green (532nm), red (630nm) and near infrared (800nm) bands produces a coloured image bearing no similarity to the visible one regarding the colour, hence its name. False colours depend on infrared radiation being absorbed or reflected by the surface of objects i.e., usually pigments, therefore they provide useful information that may lead towards their identification or classification [29,30].

SWIR is usually armed with an Indium Gallium Arsenide detector (InGaAs). Detectors of this type were originally developed for military applications, but after their declassification, they were immediately adopted for a wide range of applications because of their infrared sensitivity [23,31]. InGaAs has the major advantage to exploit the short wave infrared, specifically between 900-1700nm; thus, it can provide information pertaining exclusively to the behaviour of surfaces in the near infrared, which penetrates to deeper layers of the material, revealing information coming from non-visible layers of the surface. Furthermore, due to this penetration, superficial visible information could become be invisible in the infrared and in this way could help producing higher contrast to highlight the information coming from below.

Apart from the conventional use of these two methods for the study of icons [32,33], paintings [34] and manuscripts [35], they have been employed for other kinds of archaeological materials as well, such as papyrus [29,36], marble pyxis [37], ancient lekythoi [29] and ceramics [38].

HIS systems are usually employed in cases of paintings and movable objects, both of which have dimensions that can be covered either entirely by the camera's frame or by a small grid. In cases of non-movable, large sized murals, especially when they are located inside or outside monuments and require dedicated artificial illumination systems remote-sensing hyperspectral imaging is used instead [39]. However, the present case study, a large-scale monument, was one of those pilot cases to apply the know-how of those methods on non-conventional materials such as large stone surfaces and obtain remarkable results. In the international bibliography there are mentioned only a few cases regarding the use of hyperspectral/multispectral imaging for studying archaeological or historical buildings and stone surfaces [40,41]. Furthermore, it was one of the first times in Greece that these techniques were applied systematically and comprehensively for the diagnosis of conservation status, the study of morphology and the detection of historical data, on stone surfaces in a case such as the Horologion. This expanded the potential of the methods, improved the possibilities of observing the material, assisted in the discovery, approach and interpretation of aspects invisible to the human eye. By providing all these valuable information, modern non-destructive documentation techniques prove once again to be the cutting-edge technology in the diagnosis of works of art and monuments [39,42].

Materials, methods and instrumentation

As stated before, all the applied techniques were non-destructive. The modern diagnostic methods were applied in situ. The obtained data were in form of images and spectra. The employed techniques were active Short Wave Infrared Thermography (SWIR), Hyperspectral Imaging-Spectral Cube acquisitions (HSI SC) and Infrared False Colour Imaging (FCIR) assisted by macrophotography under normal and tangential visible and infrared illumination.

For the Hyperspectral Imaging, the Spectral Cubes and the Infrared False Colour Imaging (FCIR), the hyperspectral detector MuSIS HS model 2009 (Forthphotonics Hellas S.A. now Dysis) equipped with a CCD 1/200 Progressive Scan sensor (1600x1200 pixels, 8 bits, 15 fps) with 34 selectable spectral bands in the range of 400-1000nm for B&W and colour imaging, was used. It has the ability of sequential spectral image storing (spectral cube) and calculation of a full spectrum per image pixel as well as False Colour Infrared Imaging. Its standard illumination sources were two Dr.Fischer Halogen Lamps 500W with colour temperature 3200 K.

For the Short Wave Infrared Thermography (SWIR), the SWIR detector Goldeye G1 P-008 Cool Allied vision, model 2015, equipped with an InGaAs AVT sensor (320x256 pixels, 118fps spectral response at 900-1700 nm) was used. It is combined with CCTV 16mm/f1.4 and 50mm/f1.4 KOWA lenses as well as with NIKON micro NIKKOR 60 mm f/2.8D. Images were recorded both in greytones and pseudocolour. Pseudocolours depict the change of the object's temperature, starting from the lowest blue up to the highest red colour, being cool and hot respectively, while white signifies that the hottest point is off scale. The selection of colours is given by the camera's software and the scale can be adjusted manually so that off grid spots are avoided.

Photographic images were acquired with a Nikon D800 FX-format with a CMOS censor 36.3 megapixels (59.4 x 84.1 cm/ 200 dpi) and micro NIKKOR 60 mm f/2.8D and NIKON AF-S NIKKOR NANO CRYSTAL ED 24-70 mm lenses. The same illumination system as with MuSIS HS was used.

The majority of images were acquired with the position of lights at such an angle to provide uniform illumination (symmetrical lighting). However, after careful examination of the surface, scratch marks were located and it was decided to acquire extra images in all techniques also in tangential light, in order to record any further information that might be revealed. Furthermore, in order to record the stone blocks with an adequate resolution, it was decided the detectors would be up to 1.5 m away from the surface, meaning no image could cover their entire surface. Therefore, depending on the size each stone block, a grid comprising four, six, or nine areas, was drawn on paper facilitating the acquisition of images and their respective grouping and categorization. Recordings at specific wavelengths (420, 500, 600, 700, 80, 900 and 1000nm, vis and FCIR) were carried out in all grid sections. All images were stored on digital media.

The processing of the acquired images was carried out with Adobe Photoshop 2020 (v21.2.10.118) and consisted of brightness/contrast enhancement, sharpening edges, crop images and manual application of drawing lines with brush tool.

Discussion

The application of the imaging techniques to the internal and external walls of Horologion revealed much information about the stones and what was on them in a very wide sense of the meaning. Instead of being confined to pigment detection and identification, the combination of data from the different imaging techniques led to new sets of results regarding several aspects of the stones.

Engraved images

Photography in the visible region is a standard procedure before, during and after any conservation treatment. In the case of the Horologion, the photographic documentation would provide reliable high resolution images for the project. However, during the photographic sessions of the interior level 1, and while moving the light sources from one position to the next, the angle of the light changed in such a way that scratches became clearer to acknowledge. These sketches were engraved on the stone surface and normal light could not reveal their existence as the marks were very finely scratched. After careful examination of the stone surfaces, it was discovered that those were not coincidental scratches, but parts of sketches engraved on the stones. It was therefore immediately decided to apply tangential illumination to all internal wall surfaces and check whether those marks were random or formed sketches. All marks were located up to a height of 2m, the average maximum height that a man might reach to paint or sketch on a wall.

Most of the engraved images were located in the interior surfaces, on the southeast wall/Evros (orientation of the stone/ wind deity of the outer wall) and especially on stone 344, which is situated on the second row from the ground (Figure 2). The development of the lowest rows of the internal stones of the building and the assigned numbers of the stones are presented in one of the author's previous articles [21]. The dimensions of the stones on this row are approximately 173cm x 108cm, making them ideal for use as a painting canvas. Indeed, on most of these stones there are graffiti sketches. Stone 344 is directly opposite the north-west entrance and parallel to the north-east entrance. This makes it an excellent surface for marking, as light comes behind the "artist" to help him see, while, when time passes, the raking light from the north-east entrance enhances the visibility of his engraving. However, unless someone stands at the correct time for the light in front of the sketches, they are hard to discern.

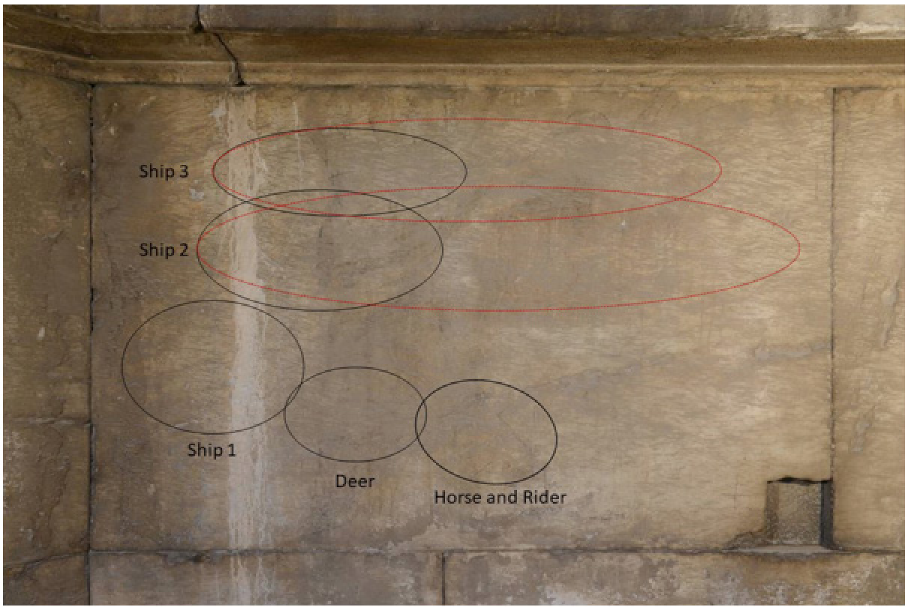


Figure 2: Evros wall (SE), stone 344. VIS. The black circles depict the position of each of the engraved sketches captured by raking light. The red circles mark the entire topic, which could not be shot at once.

The study of the engraved images revealed the figure of a deer, a horse and his rider and parts of at least two ships. The figure of the deer is elegant, its feet risen in gallop, its head adorned with antlers (Figure 3a). At first, it was thought that the outline of a horse was seen but after careful study of the engraved lines, the form of a rider's leg was discerned. The horse is decorated with a zig-zag strap. The rider wears a long cloth. No upper body or head could be distinguished (Figure 3b). The style the two animals were created i.e., the curve of the front necks and the angles of the front and back legs indicate that it might have been the same artist who created them. Furthermore, their proximity, the deer being left of the horse and rider and the fact that all of them face left, could indicate that they belonged together and were part of a hunting scene.

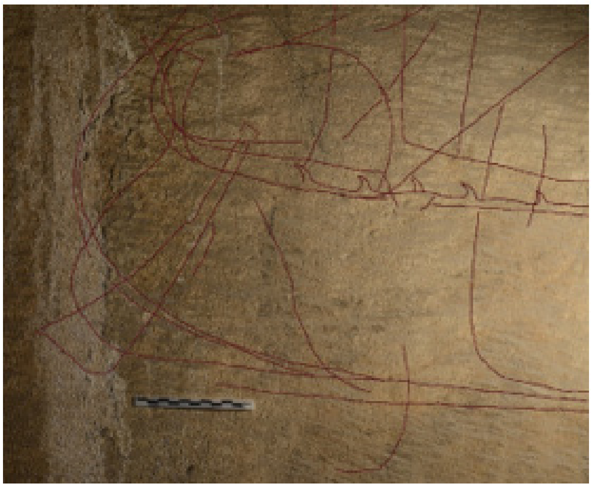
3a

3b

Figure 3: Evros wall (SE), stone 344. VIS, raking light. (a) Left: the figure of a deer. (b) Right: the figure of a horse and rider. Both images have been digitally processed to highlight the outline of each figure in red color.

Apart from that, at least three ships could be recognized engraved on this stone. One (ship 1) is smaller than the other two and seems to be unfinished (Figure 4a). The other two (ship 2 and ship 3) are bigger in size (Figure 4b). They cover almost the entire length of the stone and therefore, imaging under raking light was impossible to be carried out at once. Attempts have been made to acquire continuous images, the raking light source accompanying the camera as it moved, but the overexposure on the same one side of each of the three images it took to photograph the entire vessels deterred the photomerge. Nonetheless, images were autonomously acquired and even though they could not be pasted together in a single image, information could be retrieved. Damianidis [43,44] in his study of the ship graffiti of Horologion mentions that "recording these graffiti during the fieldwork turned to be easier than recording the charcoaled graffiti", without hinting the method he used to record them. A standard procedure for highlighting engraved writings and/or decorations is the use of rubbing pencil or coal on tracing paper fixed upon the area under investigation. The result is a life-size copy of the original. In this case, and provided the applier was meticulous, the life-size scale would produce a very accurate reproduction of the image carved on the stone. However, access to cultural heritage artefacts does not always guarantee permission to handle or touch them given the fact that many of them are very sensitive and could be irreversibly harmed. In such cases, the application of non-destructive imaging methodologies can provide reliable and precise images without endangering the artefacts.

4a



4b

Figure 4: Evros wall (SE), stone 344. VIS, raking light. (a) Left: ship1 and (b) right: ships 2 and 3. Both images have been digitally processed to highlight the outline of each figure in red color.

In the case of both the hunting scene and the ships' figures, after the acquisition of the images, mathematical processing was applied and, in high magnification, the engraved images were traced manually, under high magnification, with the brush tool of Photoshop.

Moreover, several other inscriptions were located on the stones such as names or the symbol of the cross [20]. They are either very finely inscribed or roughly carved on the marble. In order to remove any visible obstacles that might hinder the highlight of the carvings, spectral images were obtained at 1000nm. Indeed, the marble is presented clear of discoloration and in the same time, the surface morphology and carvings can be observed more easily.

The interior decoration of the building

Stepping inside the monument, the visitor is overwhelmed by the height and the surrounding walls consisting of huge slab stones. Entrance is accessible by two oversized gates at the northwest and northeast sides. As seen in the architectural section (Figure 5), there must have been at least four levels, different in height and shape. There are no stone steps that might indicate the existence of a staircase. The levels are separated from each other by different styled cornices now seen as protruding geisons. The first level has a simple geison. The second level has a more elaborate geison with molding, soffit and curved consoles. The third is a smooth circular band. The fourth level contains eight small sized columns, each of them standing at the interior corner of the octagon building. The columns have no base and bear Doric capital. The entablature above the columns consists of two smooth bands. On the upper band of the entablature, painted on several stones such as 52, 46 and 48, anthemion figures can be found (Figure 6).

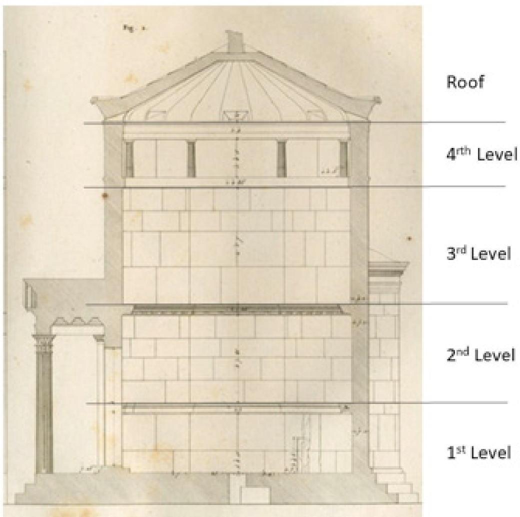
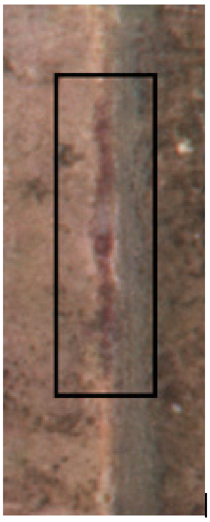


Figure 5: Section of the interior of the monument can be separated in four distinct levels and the roof [49].

Figure 6: Skiron wall (NW), stone 46. VIS. Anthemion figure on the upper band of the entablature.

Color traces

7a



7b

Figure 7: Zephyros wall (W), stone 187. Macro photos of a console. (a) left: VIS and (b) right: IRFC, where the purple false color of Egyptian blue can be observed.

8a

8b

Figure 8: Roof, stone 10, macro photos: (a) left: VIS, small area of blue pigment and (b) right: IRFC image of the blue area which produces a dark color unlike the bright red false color of the Egyptian blue.

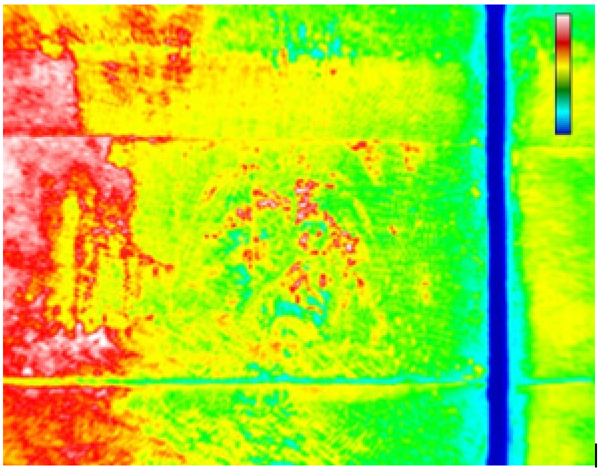
The structure of the roof has an impressive umbrella shape. Kienast (2014) [6] believes that the stone pieces were put into place in specific order because they were marked with Greek alphabet letters that indicated following a specific sequence. They were held in place by the middle stone. This structure is now visible while inside the monument, but closer examination revealed much more. Traces of color have been located in several areas of the 24 stone pieces of the roof. Panou and Alexopoulou (2022) [20] support that the 24 stone pieces of the roof represent the celestial sphere and the blue color traces enhance this interpretation. In antiquity the astronomical observations were based on the Geocentric model and the celestial sphere was divided into 24 equal parts for providing better astronomical observations. Kienast (2014) [6] regards that the interior of the roof was covered by a dark blue color that symbolized the night sky and on it there might have been stars perhaps of silver or gold paint. He supports that when the light came into the building, it would be reflected by the Pendelikon marble it was made from and guided to the roof, where the painted stars would supposedly shine on the dark blue sky. However, the building originally had no windows or openings that would allow light in the interior. Kienast (2014) [6] mentions the existence of small slits at the joints of the Winds relief stones but this is not verified by the technical report of the Ministry of Culture [1]. When it was turned into a tekke, the level of the ground was very high due to centuries of aggradation. At that time, it is said that the three windows that now exist were opened [1]. While decoration can be observed at the entablature, traces of blue colour have also been detected in other areas of the inner stone walls of the monument. Blue areas under the moldings, consoles and soffits at the second level geison, such as on stone 187, produce a bright purple false color, similar to that encountered in the study of funerary masks and is indicative of Egyptian blue (Figure 7a & 7b) [45]. The presence of Egyptian blue is mentioned both by Kienast (2014) [6] and by Papastamatiou & Photopoulou (2011) [1] and is based on the analysis of the specialized laboratory “Kentro Lithou” that attributes the color to Egyptian blue ($CaCuSi_4O_{10}$). The false color from the blue pigment in the areas on the interior roof that were examined by the aforementioned techniques is rather similar to blue false color while the surrounding area produces a magenta false color (Figure 8a & 8b). Azurite produces a dark blue false color due to the absorption of the near infrared radiation [46,47]. Both Egyptian blue and azurite ($Cu_3(CO_3)_2(OH)_2$) were used at that era for painting the blue color [48]. So, the use of neither Egyptian blue nor azurite can be excluded. Indigo, an organic pigment, also produces a red false color but so far there has been no mention of it found on monument decorations.

As mentioned before, the aggradation at the monument had risen the floor level. During the Ottoman occupation, a wooden floor was constructed and placed at the first level geison. A mihrab was chiseled at stones 212, 213, 237,239, 261,262, 288 and 289. The walls of the second level and the mihrab were coated with mortar. The mihrab was painted with red and green paint and on its right side an inscription in Arabic alphabet can be seen. The numeration starts from the stone above the north west entrance on the roof level and proceeds downwards and clockwise.

State of preservation

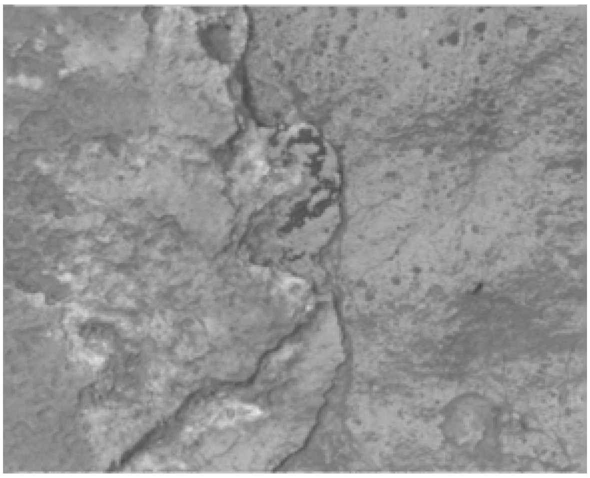
Thermal imaging provided useful information for the state of preservation of the stones. The monument was built without the use of binding mortar between the stones. One of the structural problems that was observed is the slight separation between some of the stones. This could have been induced either by natural phenomena such as earthquakes or during works applied in later times, such as the opening of the three windows. No matter the cause of the phenomenon, intermittent gaps contribute to the further deterioration of the stone surface because the inflow of the water in those areas causes leaching of the material. Using the pseudo color mode of the thermal imaging camera, the stones were recorded and some of them presented distorted images, indicating either their displacement and/or the existence of humidity. In the case of stones [47-48] (Figure 9a & 9b), the gap between the stones is visible but the important information the thermal image provides is that both stones are in a rather good condition (green, yellow colors), without humidity or water inflow having affected them, as it would have shown as blue-black color. In the case of stones covered with mortar, such as stone 199 (Figure 10a & 10b), in the visible the condition of the material is not clear – there may be successive layers. However, looking at the thermal image, it is evident that the mortar has deep cracks depicted by dark blue color. On the other side, stones like 256, surrounded by 257 on its left and 279 under it, present a perfect condition (Figure 11a &11b). The joints are almost not observed indicating not only the quality of the artisans who placed them but also the lack of any signs of humidity. In this example, it must be noted that a black paint inscription is also observed producing a deep blue color. One could argue that its absorption could be strong enough to diminish the existence of humidity signs between the stones. However, this is not the case, because for each recording local calibration takes place and such an anomaly would have been noticed. In this case, the deep blue color refers to the absorption of the infrared radiation by the specific pigment. Furthermore, in cases of humidity existence, the extreme lack of heat always shows as dark blue color. A good example is the black color of the ottoman inscription. The joints of the stones bearing the inscription (stones 256, 257, 25, 259, 260) present humidity as dark blue, so the inscription is depicted by dark blue, light blue and green. This can be observed on all stones that bear the black ottoman inscription (Figure 11b & 12b). The black used for the writing shows consistently high absorption in the infrared indicating a carbon black or bone black material [47].

9a

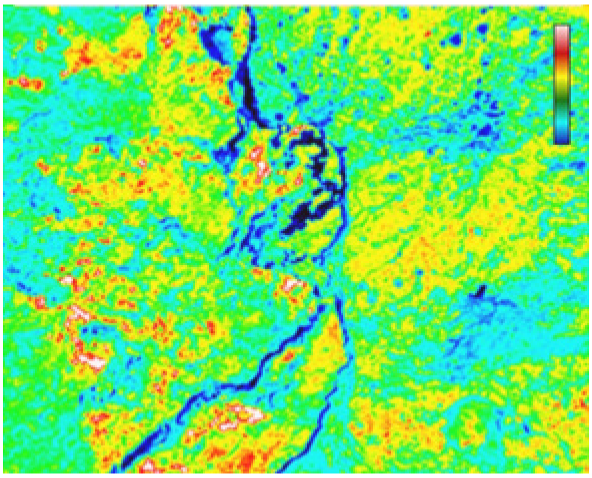


9b

Figure 9: Zephyros wall (W), stone 47. (a) Left: b&w image. (b) pseudo color image. While the vertical gap between the stones is visible, no trace of incoming humidity can be observed.

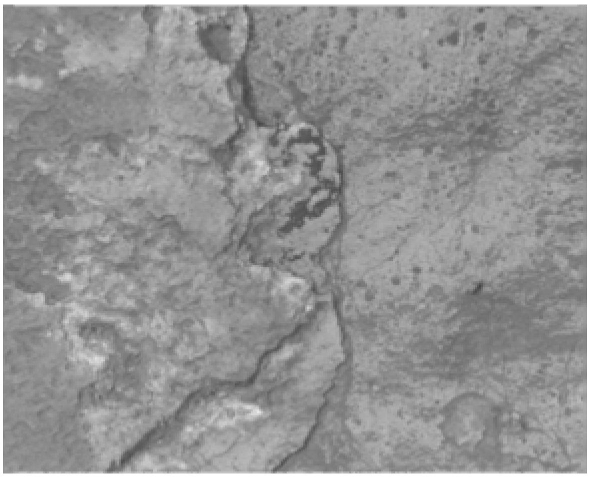


10a

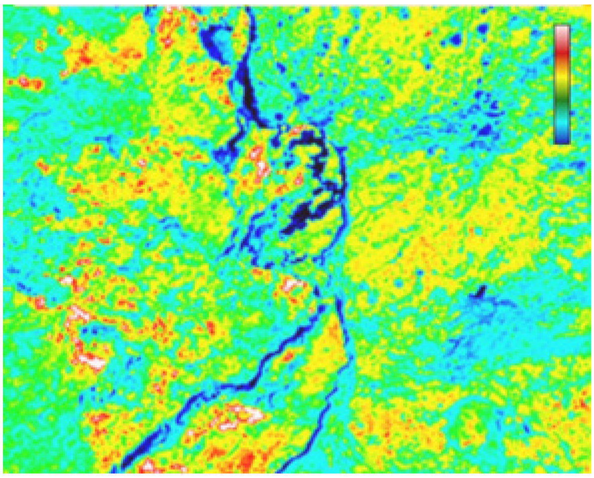


10b

Figure 10: Boreas wall (N), stone 199. (a) Left: b&w image. (b) pseudo color image. Pseudo colors highlight the existence and depth of cracks in the mortar.



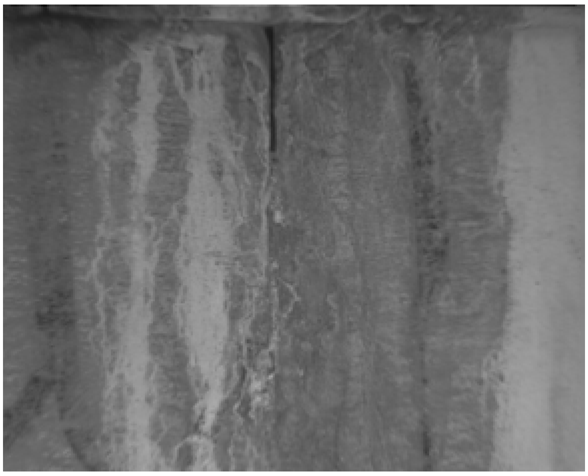
11a



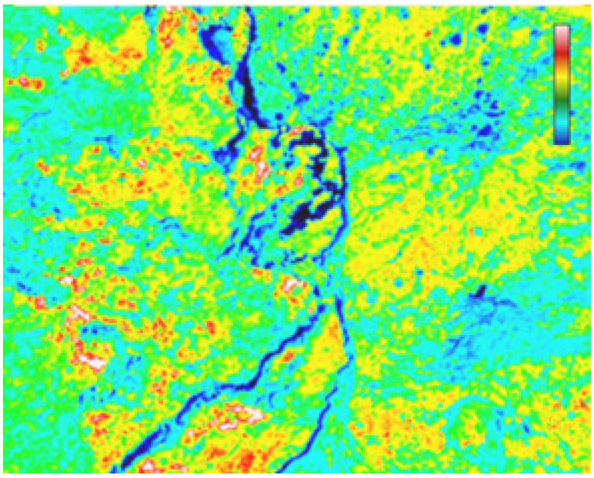
11b

Figure 10: Lips wall, (SW), stone 256. (a) Left: b&w image. (b) pseudo color image. The Arabic writing can be observed in black colour.

Another phenomenon can also be observed on the interior stones of the monument. As previously mentioned, the inflow of water deteriorates the stone surface. The incoming water has washed off the patina and the material itself of the affected stones leaving those areas exposed to the atmosphere. It is presented as visible stains on the stones. Thermal imaging applied on these stones has recorded not only the condition of the marble, but also the extent of the area of deterioration, as seen in stones 47 (Figure 9a & 9b) and 258 (Figure 12a & 12b). In this case, the yellow, red, and white colors depict the areas affected. The lighter the color the more severe the deterioration of the material. In the visible and infrared images, the deterioration can be easily detected but it is with the help of the thermographic camera that the severity of the phenomenon and its actual extent can be observed and recorded.



12a



12b

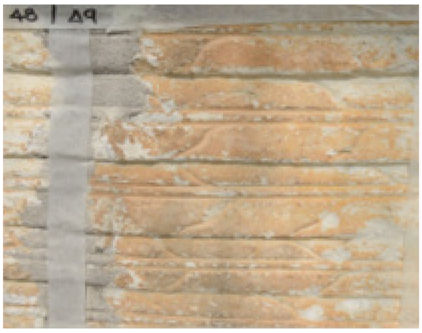
Figure 12: Notos wall (S), stone 258. (a) Left: b&w image. (b) pseudo color image. The severity and extent of the humidity on the wash off on the stone is clearly observed.

The Epidermis

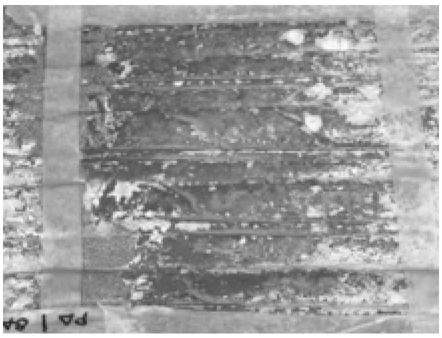
On the exterior walls of Horologion, an orange color layer can be observed. Close-up observation reveals the existence of a thin layer or crust on top of the marble blocks, decoration and sculptures. In some cases, the orange surface gives the impression of having brushstrokes as if the brush marks of the artisan were imprinted on the marble. This patina is called scialbatura, a phenomenon widely encountered on stone and marble monuments and sculptures in the Mediterranean basin for example in Greece, Italy, Portugal and other countries [50] and is also associated with pitting phenomena of the material [51]. It forms mainly on the exterior surfaces, which means areas that come in contact with the atmospheric air, the weather phenomena and exposure to direct or indirect sunlight. There are only a few mentions of this patina be preserved while an artefact was kept in interior circumstances for a long period of time, such as the one on the Parthenon frieze inside the British Museum [51]. Scialbatura consists usually of calcium oxalates, usually whewellite, the monohydrated calcium oxalate and weddellite, the dehydrated calcium oxalate. Gypsum, quartz and iron oxides (ochres) from veins of impurity inside the marble [51] or embedded airborne dust particles [52], could also be present and accountable for its reddish coloration. Up to the present, its origin is still debated and refers to different biogenic or chemical processes. The possible biogenic culprits include the metabolic activity of encrusting epilithic lichens [50]. Human origination may attribute to fumes from the exhaust of vehicles and from factories in the industry [54], with environmental reasons, such as volcanic eruption of Vesuvius, also contributing to the phenomenon [55]. Lazzarini and Salvadori (1989) [51] suggest that a layer, such as calcium caseinate, could have been applied on the marble surfaces or the sculptures, for either decorative or protective reasons, which has actually responded to the given conditions and produced the colored patina. They mention that calcium caseinate might form either by microorganisms later deposited on the surface, such as bacteria, or by microorganisms already present in the medium. Obviously, combination of the aforementioned reasons could apply.

Ding et al. (2022) [52] and Kawamura and Kaplan (1987) [54] support that calcium oxalates may be derived from car emissions, which due to incomplete combustion of aromatic hydrocarbons they produce diacids. These acids are polar and, if combined with moisture, could react with calcareous stone and form calcium oxalates. This could be an explanation, as Athens had a massive problem of car fumes especially after 1975 and until recently. However, written testimonies of scholars visiting Athens in the nineteenth century mention the orange, orange-brown or honey-hue color of the Parthenon monument [56] which indicates that there must have been another reason that initiated the formation of the patina. Galanos and Doganis (2003) [56] have studied the orange patina, found on the Parthenon calling it Epidermis (which in Greek means the outer layer of the skin), and so has Maravelaki-Kalaitzaki (2005) [57] who studied both black and orange patinas and verified that the latter consisted of calcium oxalate, calcite and other elements. It is also supported that it was an applied layer, which has actually protected the polychromy and the original relief of the sculpture. The Parthenon was built between 448-437 BC and the Horologion, as stated above, varies between the 2nd century BC and around 47 BC. Both monuments were constructed from Pentelikon marble [1, 6, 57] and despite the time gap between them they both present Epidermis. Furthermore, Epidermis was found on several monuments in Italy, some of them made from Pendelikon marble, such as the Arch of Titus [51]. It is known that Pentelikon marble was imported in the Roman Empire as building material since 130BC [58]. In a time when, from the Hellenistic period, the Roman Empire emerged and thrived, it is only logical than any knowledge on monumental building would be adopted and evolved. So, if the protective layer was already common knowledge in ancient Greece, it would have been transported and used in Italy as well, not only on the Pentelikon marble, but on marble generally, regardless its origin and, after eons passing, it would turn into what we now call Epidermis or scialbatura.

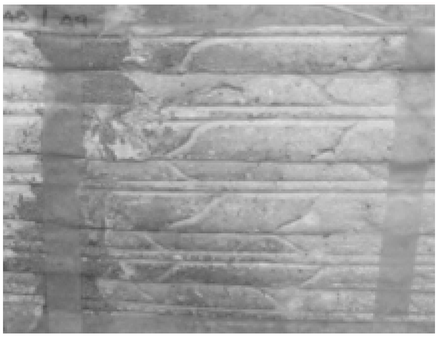
The orange color found on the sculptures of Horologion produces fine images. In the visible, the Epidermis on the Horologion marbles has a light orange color (Figure 13a, 14, 15a). The images at 460nm present areas of high absorbance where the patina is formed, enabling the recording of the boundaries and extent of this phenomenon more accurately (Figure 13b & 15b). On the other hand, in the infrared, the Epidermis is highly transparent. Apart from pigments that reflect infrared radiation such as cinnabar, most pigments and especially earth pigments that might have been employed for the decoration of the monument usually have high absorption in the infrared region [47]. However, in this case, the transparency of the layer proves that it regards to Epidermis and not a paint layer containing iron based or earth pigments. At 1000nm, in all areas that were examined, the marble is depicted in a very fine white tone with high reflectivity (Figure 13c & 15c). Traces of pitting of the material are visible thus helping in a more in depth validation of the condition of the marble. The relief decoration of the areas was highlighted and could be observed more easily. Further chemical analysis is need to verify the existence of calcium oxalate and traces of pigment on the sculpture.



13a



13b

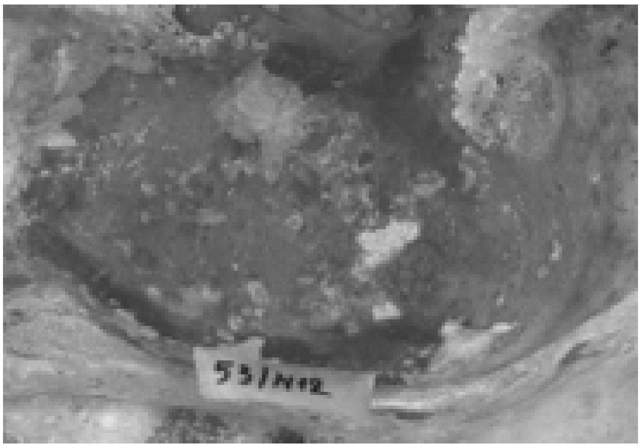


13c

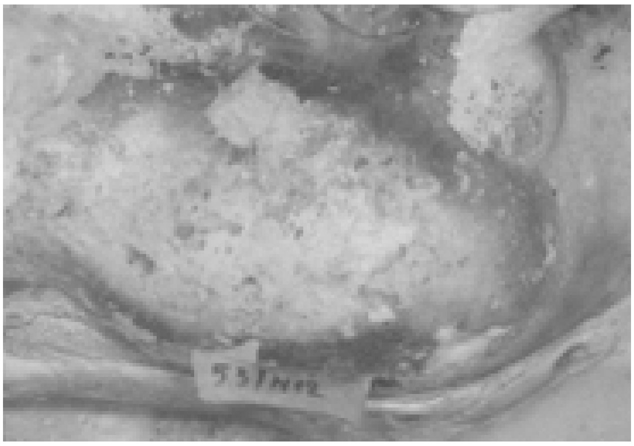
Figure 13: Zephyros wall (W), exterior stone 48/Δ9. (a) visible, (b) 460nm and (c) 1000nm.

Figure 14: Apeliotes wall (E), exterior stone 53/N12. VIS, Sculpture of Wind Deity Apeliotes, the east wind, who brings a gradual gentle rain.

15a



15b



15c

Figure 15: Apeliotes wall (E), exterior stone 53/N12. Sculpture of Wind Deity Apeliotes, the east wind, who brings a gradual gentle rain. Detail of the shoulder (a) VIS, (b) 460nm and (c) 1000nm.

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Declaration of interest statement

The authors report no conflict of interest.

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