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REVIEW

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The two-wavelength laser cleaning methodology; theoretical background and examples from its application on CH objects and monuments with emphasis to the Athens Acropolis sculptures

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Abstract

The two-wavelength laser cleaning methodology has been introduced and developed in order to meet demanding cleaning challenges in CH. The innovation lies on the combined use of two laser beams, allowing thus control of the laser ablation effective regimes towards an efficient and safe cleaning result. A series of studies on technical samples and real fragments aimed at defining and refining this methodology in order to ensure that the original surface, including its details and historic traces, will be safeguarded. In this paper related research and applications will be presented in an attempt to enlighten the associated laser ablation processes, as well as the potential cleaning applications in CH field. Laser-assisted removal of pollution accumulations from the Athens Acropolis monuments and sculptures is a unique highlight on the use of this methodology in practice. IESL-FORTH in collaboration with the Acropolis Restoration Service and the Acropolis Museum has developed an innovative cleaning methodology and a prototype laser cleaning system, which since 2002 have been introduced to the everyday conservation practice and will be presented in this paper.

Keywords: Two-wavelength laser cleaning, Pollution crust, Yellowing, Plaster, Acropolis sculptures, Parthenon West Frieze, Caryatids

Background

Laser cleaning relies on the ablation effect as a result of intense and short pulse irradiation at wavelengths that are strongly absorbed by the materials. The laser induced removal of unwanted material from unique Cultural Heritage (CH) objects and monuments is a complex process, closely dependent on the material properties and laser parameters [1, 2]. In fact selective and controlled material removal, with minimal thermal load or interaction to the substrate, can be achieved upon thorough knowledge of the materials involved and careful study and optimization of the related processes. In this framework a number of diverse cleaning challenges have been successfully tackled over the last 25 years, establishing laser technology as a fine, delicate and practical conservation tool in the service of conservators-restorers.

The laser cleaning project on the Athens Acropolis sculptures is a unique example of laser cleaning application in CH field. The selected and controlled removal of soot deposits and black encrustations from the surface of archaeological material has revealed the authentic surface of these fine-sculpted objects in all its detail and beauty. The multidisciplinary collaboration of the

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research team of the Institute of Electronic Structure and Lasers (IESL-FORTH), the Acropolis Restoration Service (YSMA) and the Acropolis Museum resulted into the development of a prototype laser cleaning system and an innovative cleaning methodology, which since 2002 have been introduced to the everyday cleaning practice of the conservators who care for these unique sculptures. The innovation lies on the combined use of two laser beams in spatial and temporal overlapping. This arrangement allows the control of the laser ablation effective regimes towards a safe and controlled cleaning result, ensuring that the original surface will be safeguarded.

This methodology was introduced in an attempt to overcome a number of potential complications, associated mainly with colour alteration observed onto the underlying original surfaces. Its successful application on the Athens Acropolis monuments influenced further work and new applications have been studied and optimised. These case-applications as well as a brief discussion on the methodology, its potential and restrictions will be discussed in this paper.

The two-wavelength cleaning methodology; background information and principles of operation

The discoloured appearance of laser cleaned surfaces, which may appear under certain conditions, poses limitations to the practice and wide application of laser technology in CH conservation and thus urges for thorough investigation. Laser-induced colour changes are directly dependant to the involved materials and can be distinguished as follows:

- Discoloration on stonework: yellowing alteration is mainly associated with the use of infrared (IR) radiation (1064 nm) of nanosecond (ns) pulse duration to remove pollution encrustations from stonework [3–6]. Revealing of pre-existing historic layers and/or patinas [3], 'staining' of the original surface (as a result of the migration of the yellowish fraction which is present within the pollution crust and originates from polar organic compounds) [7–9], and selective vaporization of the various dark-coloured airborne particles (which are embedded in the gypsum-rich matrix of the pollution crust) at rather low laser fluences [4, 10], were among the scenarios introduced to explain such undesired coloration. In parallel, discoloration into grey has been also reported upon use of ultraviolet (UV) radiation to treat pollution crusts [4, 11].
- Darkening phenomena observed on painted surfaces upon intense and direct laser irradiation. The sensitivity of most pigments to the direct exposure to laser irradiation is an important issue, which requires careful study and thorough approach. Relevant research [12–16] has pointed out that darkening or, in the worst case scenario, blackening of painted surfaces is a material related alteration which occurs upon direct exposure to laser radiation. Although initially it was believed that such undesired alteration is irrelevant to the binding medium as it affects both paints and pigments in raw form, recent studies on the basis of different ablative methodologies using lasers of various wavelengths and pulse durations, proved that the presence of a binding media that absorbs highly the employed laser wavelength may safeguard the pigment itself [16]. Therefore for cleaning applications that involve painted components or surfaces a number of parameters must be thoroughly considered.

Discoloration issues have been extensively and long studied and a number of publications have been focused on their understanding [3, 17–19], while emphasis has been also given to the development of eliminative and remedial approaches on the basis of careful choice and fine-tuning of the operative laser parameters (such as the laser wavelength [11, 18, 21–23] and pulse duration [17, 24].

The two-wavelength methodology has been introduced initially to overcome yellowing discoloration of sculpted marbles. The cautious "blending" of two laser beams, which overlap in space and time, has been suggested in an attempt to bridge the inefficient and unsuccessful cleaning result from the individual use of the two beams. An important parameter that must be taken into account in this methodology is the relative ratio of the intensity of the two beams, which has a decisive role as regards the prevailing ablation processes and thus the cleaning result. A brief description of background work that influenced the development of the methodology is highlighted in the following:

Laser-assisted encrustation removal using IR wavelengths (1064 nm) of ns pulse duration is a well established cleaning methodology for removal of dark-coloured over-layers from light-coloured substrates with numerous applications worldwide [1, 2, 11, 25, 26, 27, 28, 29] mainly on stonework. In this cleaning regime "photothermal" mechanisms (selective explosive vaporization and spallation) are responsible for material removal, while its success is attributed to its "self-limiting" nature based on the fact that the majority of encrustation usually encountered on stonework absorbs in this wavelength significantly higher than the stone substrate (typical absorption coefficients of pollution crusts in the 1064 nm are four times higher than the marble substrate ones). As a result the energy density (fluence, F) threshold value for encrustation removal is significant lower than the one for substrate/marble damage and thus selective and self-limiting cleaning is feasible. Typical F threshold values determined for 1064 nm ablation of black pollution crust and Pentelic marble are 0.8 and 3.5 J/cm^2, respectively [18].

Nevertheless, the use of IR laser beams both on technical samples simulating pollution encrustation, as well as on real marble fragments with pollution crusts, often resulted in surfaces discoloured to yellow–brown. A series of preliminary experiments, which took place on technical samples made of gypsum ($CaSO_4$ $2H_2O$) and 5–10 % wt of charcoal particulates (with size in the range of 50–150 μm) in a simplistic simulation of pollution crusts, aimed at studying the removal mechanisms of the pollution crusts in this IR regime (1064 nm, 30 ns). The irradiated surfaces appeared yellow, while it was evident that discoloration is more intense for higher charcoal percentages (10 %) [20]. Thus it was related with preferential charcoal particulate removal and consequently insufficient ablation of the bulk material (gypsum). Furthermore, the fact that IR irradiation of gypsum pellets without any particulates does not cause any colour or chemical (on the basis of Raman analysis [20]) changes suggest the thermal dissociation of the charcoal particulates as a reason for this alteration [20]. Indeed assessment of the treated surfaces under the optical microscope (OM) and the scanning electron microscope (SEM) pointed out the presence of voids/craters of various sizes without any significant damage to the gypsum crystals, indicating that at fluence values close to the ablation threshold of the crust, charcoal particulates, either individually or in clusters (Fig. 1a, c), are preferentially removed.

Similar results were also observed on real fragments bearing thin homogeneous pollution crusts which have been cleaned with 1064 nm of ns pulse duration. Evaluation of the treated surfaces pointed out that at F values slightly above the ablation threshold the crust is not totally removed and a thin layer of matrix material still remains on the surface (Fig. 2a, c). This layer, which has lost its initial dark colour and has a beige-yellow coloration, cannot be easily removed. Its removal is possible using significantly high fluence values, which are close to the ablation threshold of the marble and thus such an intervention cannot be considered "self-limited".

Conversely no yellow–brown discoloration is observed upon UV irradiation. Tests on the technical gypsum-charcoal samples using 355 nm with pulse duration of few ns [5, 6, 11, 21] resulted into relatively faded/bleached surfaces. Under the OM minimal void formation and relatively homogeneous surface relief is observed indicating that material removal takes place on the basis of the "layer-to-layer" ablation model and the whole structure (gypsum-charcoal) is gradually removed. It has to be noted that for effective material removal in this regime high fluence values are required, which may result into damaged gypsum crystals as confirmed with SEM (Fig. 1d).

On the other hand attempts to remove real pollution crusts from marble fragments using 355 nm were not satisfactory as regards the cleaning efficiency and the degree of control. Although thin and homogeneous crusts could be removed without yellow discoloration their cleaning rate was rather slow and inefficient, especially on areas with micro-relief. Furthermore thick and inhomogeneous pollution accumulations could not be eliminated satisfactorily resulting into irregular surfaces. It has to be noted that in the UV ablation regime the difference between the absorption coefficients of encrustation and substrate is not enough to ensure significant differences to the ablation thresholds of the two materials and thus a 'self-limiting' cleaning process [21].

To avoid discoloration and overcome the above issues the combined use of the two laser beams was suggested. Initially the attention was focused on their sequential (SQ) use with the intension to employ the UV laser beam to correct the discoloration induced by the IR beam [30]. The result was not satisfactory; the discoloration could be rectified to a certain degree, however the surface morphology appears seriously uneven under the microscope. This can be explained due to the fact that the "new" crust surface, which resulted upon the IR irradiation, shows different physicochemical properties to the untreated crust and the ablation effect with the UV beam is thus different from the one that has been reported on the crust itself. Similarly insufficient was the encrustation removal obtained when the IR beam was applied to rectify the effect of UV irradiation.

The synchronous (SN) use of the two wavelengths in spatial and temporal overlapping was then tested [10, 30, 31]. Tripled QS Nd:YAG lasers emit simultaneously in 1064 nm, as well as their 2nd (532 nm), 3rd (355 nm) etc. harmonic frequencies and thus offer a convenient basis to exploit the possibility to combine the different cleaning mechanisms (in this case the IR at 1064 nm and UV at 355 nm). Key feature is the adjustment of the energy density ratio of the two beams (F_{IR}/F_{UV}) and thus the regulation of the contribution of the individual ablation mechanism for different encrustations and substrates. Moreover, another important aspect that must be taken into account is the total F value ($F_{total} = F_{IR} + F_{UV}$). In order to avoid damaging effects upon cleaning the sum of the F values of the two beams must be lower to the ablation threshold of the underlying original surface, while for ensuring an efficient cleaning the total F must be higher to the IR ablation

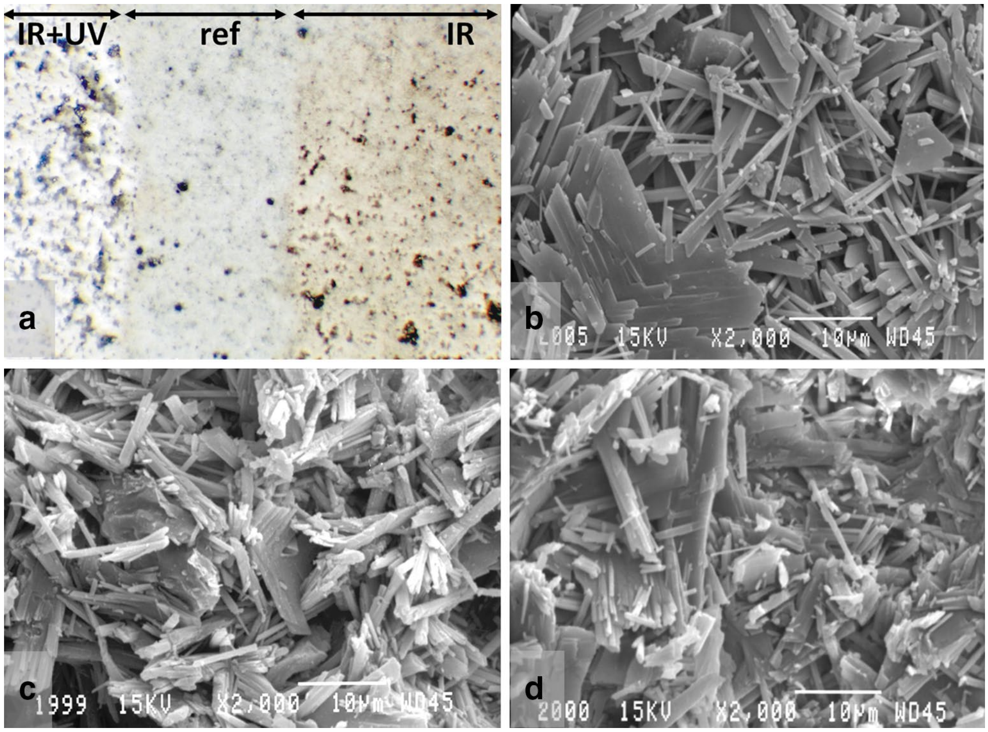

Fig. 1 **a** surface photo of a gypsum-charcoal technical sample irradiated with 1064 nm (10 pulses at $F_{IR} = 1.5$ J/cm^2) and a combination of 1064 nm and 355 nm (10 pulses at $F_{IR} = 1.5$ J/cm^2 and $F_{UV} = 0.9$ J/cm^2). The width of the reference stripe is 5 mm. **b**–**d** SEM photos of reference-untreated **b**, IR **c** and UV **d** irradiated technical samples at the above-mentioned parameters

threshold for dark pollution encrustation removal (i.e. $F_{IR\_crust} \sim 0.8$ J/cm^2).

An illustrative example of the different effects upon laser ablation of pollution crusts from individual, sequential and synchronous use of the two wavelengths is shown in Fig. 3. In this Figure a series of laser irradiation experiments on a real fragment of marble is shown, which was added as a corner complement to replace missing elements and reinforce the Parthenon Frieze blocks during their restoration intervention in the 1960s. This piece of new marble of the same origin to the ancient marble pieces (Pentelic quarry) shows the same encrustation to the rest of the Parthenon Frieze and thus could be used for the purpose of this study. Previous studies [32, 33] have determined the ablation threshold values for the thin pollution crust in the IR and UV regime to be respectively $F_{IR\_crust} = 0.8$ J/cm^2 and $F_{UV\_crust} = 0.6$ J/cm^2, while the corresponding values for damaging the marble are $F_{IR\_marble} = 3.5$ J/cm^2 and $F_{UV\_marble} = 1.2$ J/cm^2. The fragment was treated dry with 20 pulses of various laser beams and combinations as shown in the schematic of Fig. 3.

Irradiation with the IR laser beam at 1064 nm (left column, areas 1, 2 and 3) shows yellow discoloration. Treatment at F values close ($F_{IR\_2} = 0.8$ J/cm^2) and below ($F_{IR\_3} = 0.4$ J/cm^2) the ablation threshold of the crust shows insufficient crust removal while the final surface is yellow. For F above the ablation threshold ($F_{IR\_1} = 1.5$ J/cm^2) cleaning is efficient but the marble surface has still a slight yellow hue. Similar insufficient result is obtained upon irradiation with the UV laser beam at 355 nm (second to the left column, areas 4, 5 and 6). In this case for F values in the range of 0.1–0.2 J/cm^2 the crust appears rather discoloured into grey, while at F slightly higher ($F_{UV\_4} = 0.4$ J/cm^2) damage of the marble substrate is visible as broken shiny marble crystals are revealed.

The SQ use of the two beams has been also comparatively studied and is shown in Fig. 3 (the two columns on the right). Areas 10, 11 and 12 have been irradiated initially with the IR laser beam (at the same conditions to 1, 2 and 3) and then, following a ~5 mm shift to the right for comparison purposes, with the UV beam (at the same conditions to 4, 5 and 6). It is obvious that the result of the SQ irradiation varies significantly to the SN one on every aspect (colour-wise and efficiency).

The synchronous (SN) use of the two wavelengths in spatial and temporal overlapping is shown in the middle column (areas 7, 8 and 9). In this case the exact parameters of the individual IR and UV beams have been combined effectively with the aim to reach an optimum

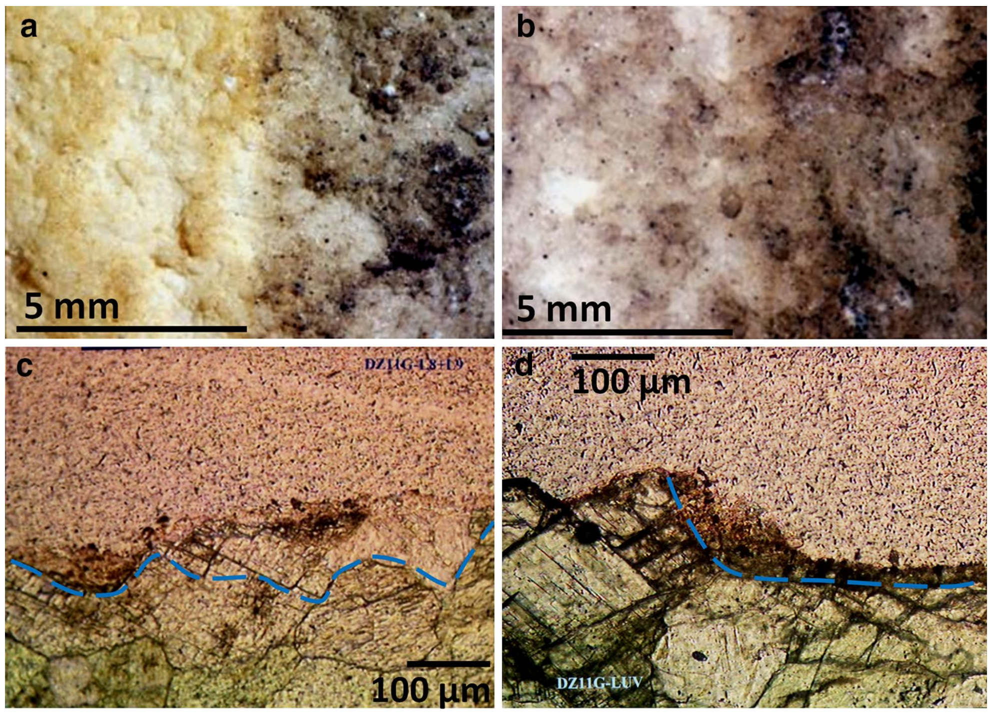

Fig. 2 OM photographs (**a** and **b**) and cross-sections (**c** and **d**) of real fragments of marble with thin pollution accumulations irradiated with 50 pulses at 1064 nm ($F_{IR} = 0.85$ J/cm^2) (**a** and **c**) and 355 nm ($F_{UV} = 0.35$ J/cm^2) (**b** and **d**). *Dark areas* on the right in **a** and **b** are reference/untreated areas, while *dashed lines* in the cross sections **c** and **d** indicate the *border* between the marble structure and the crust

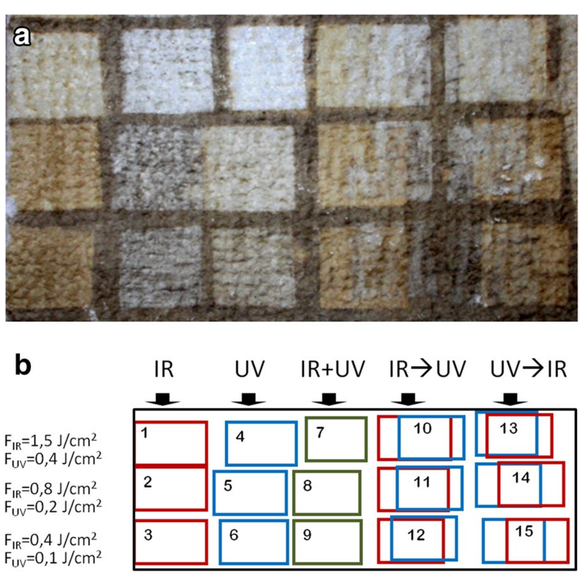

Fig. 3 Series of laser irradiation experiments to remove thin pollution crust from marble in single, sequential and synchronous use of the two wavelengths (IR at 1064 nm and UV at 355 nm). Each *square* has been irradiated with four pulses and its dimension is about 2 × 2 cm

cleaning result without discoloration or other alterations. As seen in Fig. 3 areas irradiated with the synchronous beam are less discoloured to the ones treated with the individual beams. For example the colour of area 9 (which is the combination of the beams that treated areas 3 and 6) is closer to the colour of the untreated crust. Indeed, the final surface of area 9 appears less yellow to area 3 ($F_{IR\_3} = 0.4$ J/cm^2) and less grey to area 6 ($F_{UV\_6} = 0.1$ J/cm^2), although it has to be mentioned that all three areas are considered under-cleaned. In this example area 8 appears to have an optimal cleaning level and final surface (judging on its colour and surface morphology) while area 7 is undoubtedly over-cleaned.

The irradiated areas shown in Fig. 3 illustrate the superiority of the two-wavelength laser cleaning methodology as regards the final colour, surface morphology and homogeneity of the cleaned areas, while indicating the limitations of the individual IR and UV cleaning regimes, as well as of their SQ use. The methodology has been thoroughly tested through a series of studies, both on technical samples and real fragments [18, 30, 31], in order to determine the optimal conditions for its application.

These results have allowed its adaptation and fine-tuning for the cleaning challenges of the Athens Acropolis Sculptures and Monuments with success. However it must be underlined that the choice of the laser parameters and cleaning methodology relies strongly to the materials involved and the specific conservation challenge. The combinative use of the two beams is an option that may answer difficult and demanding cleaning issues. A couple of such examples is highlighted in the following including its application on the Athens Acropolis.

Case applications

Acropolis of Athens

Cleaning interventions on the Sculptures and Monuments of the Athenian Acropolis aimed at the removal of dark deposits and encrustations accumulated on their surface mainly due to environmental pollution. The Athenian Acropolis is a unique complex of monuments located on a hill in the centre of Athens. These fine-curved architectural elements made of fine white Pentelic marble, are exposed to the environmental conditions and weathering for about 2500 years now. Their surface condition has been further and significantly altered within the past 70 years due to the rapid industrialization of Athens, which increased significantly the pollution rates and resulted to the deposition of soot and suspended particles on the monuments. As a result extensive layers of soiling crusts were formed, disfiguring the marble surface while hiding historical details. Their analysis [34] indicated the presence of soot and heavy metals such as copper (Cu), lead (Pb), iron (Fe), zinc (Zn) etc. in their bulk. Moreover the presence of sulphur dioxide in the atmosphere led to the formation of a gypsum layer on the marble surface, which up to a certain thickness preserves details of the relief and therefore must be safeguarded [35].

On the basis of their morphology, thickness and composition these encrustations were classified as follows [32–34]:

1. Loose deposits. Rich in gypsum, organic compounds and traces of minerals loose deposits form a rather uniform veil that obscures surface details. They are the thinnest deposits layers observed on the monument with their thickness reaching up to 100 μm.
2. Homogenous compact crusts. Thicker layers (up to 150 μm) of accumulated deposits well adhered to the marble hiding any surface traces and details.
3. Dendritic black crusts; "Stalagmitic" formations of significant thickness consisting of re-crystallized and re-precipitated calcium carbonate and a mixture of gypsum and other atmospheric particles. Their thickness may be significant and their removal necessary.

In late nineties the Committee for the Conservation of the Acropolis Monuments (ESMA) indicated that these encrustations should be removed from the archaeological material in order to reveal the original surfaces. The decision on the cleaning level relied on a thorough understanding and study of the stratigraphy of the original surfaces. Preliminary studies under the scientific guidance of late professor Th. Skoulikidis [36] investigated the surface condition underneath the pollution crusts and tested a number of cleaning methodologies.

Furthermore, the presence of two monochromatic surface layers preserved on the marble was pointed out:

1. 'Epidermis' (skin) which forms the lower surface layer. This thin (30–100 μm) orange-brown layer, rich in calcium oxalates, calcium phosphates and iron oxides [32] is well-adhered to the marble surface and often encountered on many Classical and Roman monuments.
2. 'Coating'; this artificial outer layer (80–120 μm thick) of beige colour covers the epidermis and is composed mainly of calcium carbonate.

Both of these surface layers [37] which cover a significant part of the sculpted surfaces (especially on the Parthenon West Frieze) indicate the presence of historical details (colour and original tooling traces) and thus should be preserved upon cleaning.

With the aim to safeguard these historic layers and reveal the original surface a number of conservation methodologies were tested as regards their efficiency and result and the following four were shortlisted for further study: (1) absorptive poultices, (2) micro-blasting, (3) inversion of gypsum layer into calcite and (4) laser cleaning. The superiority of laser cleaning over the other three conventional methods was confirmed, as the majority of stonework encrustations could be removed effectively and selectively, however scepticism as regards yellow coloration effects documented on the treated surfaces urged for further studies.

Taking into account the cleaning requirements and the nature of encrustations and substrates stratigraphy, as well as the results of previous studies on technical samples and real fragments, IESL-FORTH suggested the combination of the two mechanisms in an attempt to reach an optimum cleaning result. The simultaneous use of two laser beams of different wavelength, in an arrangement in which both laser-beams were temporally and spatially overlapped has been introduced and optimised for the materials and crusts involved on the Acropolis monuments conservation needs. Preliminary tests on all the possible substrates and encrustations present on the surface of the Acropolis monuments determined the optimum cleaning parameters such as the energy fluence and the appropriate number of pulses for a desirable depth of cleaning. Additionally, the optimum ratio of UV to IR contribution to achieve a satisfactory cleaning was determined.

According to this research a prototype hybrid portable laser cleaning instrument was developed (Fig. 4) on the basis of a Q-switched Nd:YAG system emitting at the fundamental (1064 nm) and the third harmonic (355 nm), with the option of using the two laser beams individually or in combination and in various ratios. The maximum energy density in the IR does not exceed the 1.8 J/cm^2 (for "dendritic"-type encrustation) while working fluencies in the synchronous operation lie in the range of 0.3–0.8 J/cm^2 for the IR and 0.1–0.2 J/cm^2 for the UV and the optimum ratio for the F values of the two combined laser beams is $F_{IR}/F_{UV} = 4/1$ [32].

The Parthenon West Frieze was the first assemblage from the Acropolis to benefit from this laser cleaning methodology (2002–2005). The aesthetic value of the sculptures was thus restored, while ancient monochromatic surface layers, as well as other historic information, such as tool-marks and colour traces that have survived on the surface of sculptures, were revealed. Upon the completion of the Parthenon West Frieze blocks, the laser cleaning methodology has been employed for the cleaning of a number of sculptures from the Parthenon, the Erechtheion and the Temple of Athena Nike. In the period 2006–2010 a total of seventeen metopes from the north and east sides of the Parthenon, along with four pedimental sculptures (the Kekrops and Pandrosos group and the horses of Helios and Selene), the upper body of Caryatid "F" and four blocks from the Frieze of the Temple of Athena Nike were restored.

Following the opening of the new Acropolis Museum (in 2009) and the transfer of the exhibits to their new location in 2010, the Acropolis Museum commenced a conservation project for the Caryatids (the lady figures supporting/holding the Erectheion porch) after their removal from the monument in 1979. To avoid any risks entailed in an additional transportation it was decided not to move the Caryatides from the Museum galleries and perform any preserving activities in situ at their exhibition area. For this purpose a temporal, but at the same time advanced laser laboratory has been set-up on the visitors' floor where the Caryatids are exhibited. The cleaning procedure took place inside a specially designed platform that "embraces" and isolates one sculpture at a time (Fig. 5a, b). This arrangement brought the visitors of the Acropolis Museum in contact with the conservation interventions that until now were limited inside restricted access laboratory environments. Following the completion of the laser cleaning interventions of the Caryatids in 2014, the project continues with other sculptures in the Acropolis Museum.

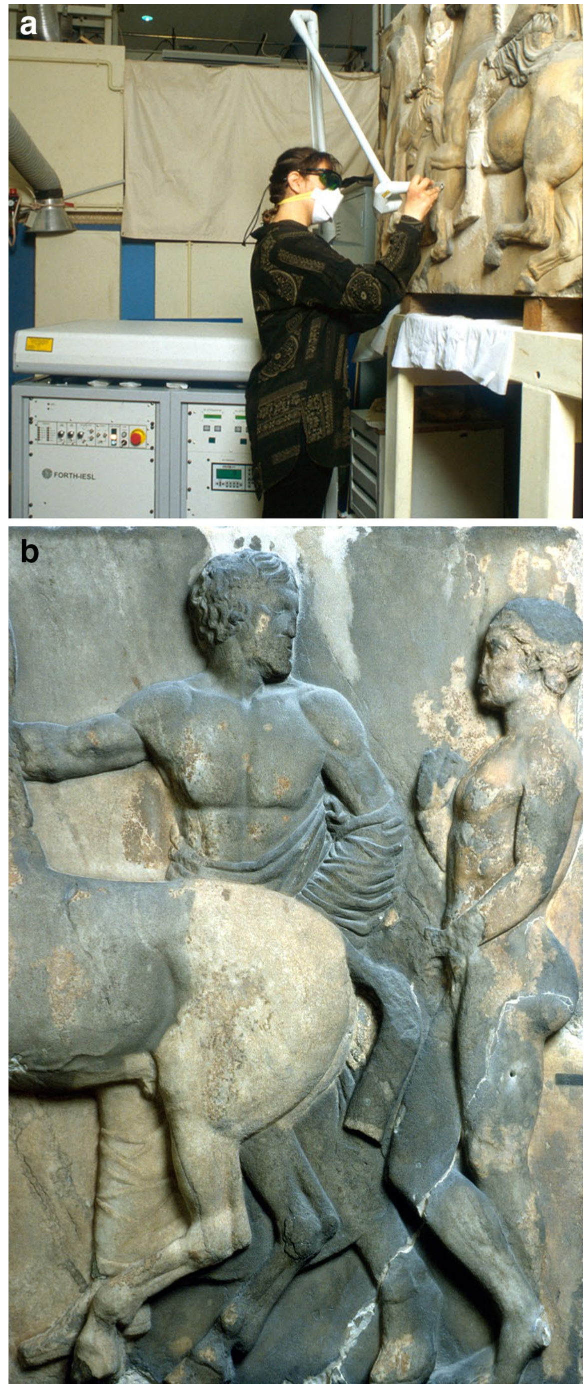

Fig. 4 **a** The prototype laser system in action cleaning the Parthenon West Frieze and **b** Detail of the Parthenon West Frieze block III, in which the back-side and the legs of the horse have been laser-cleaned

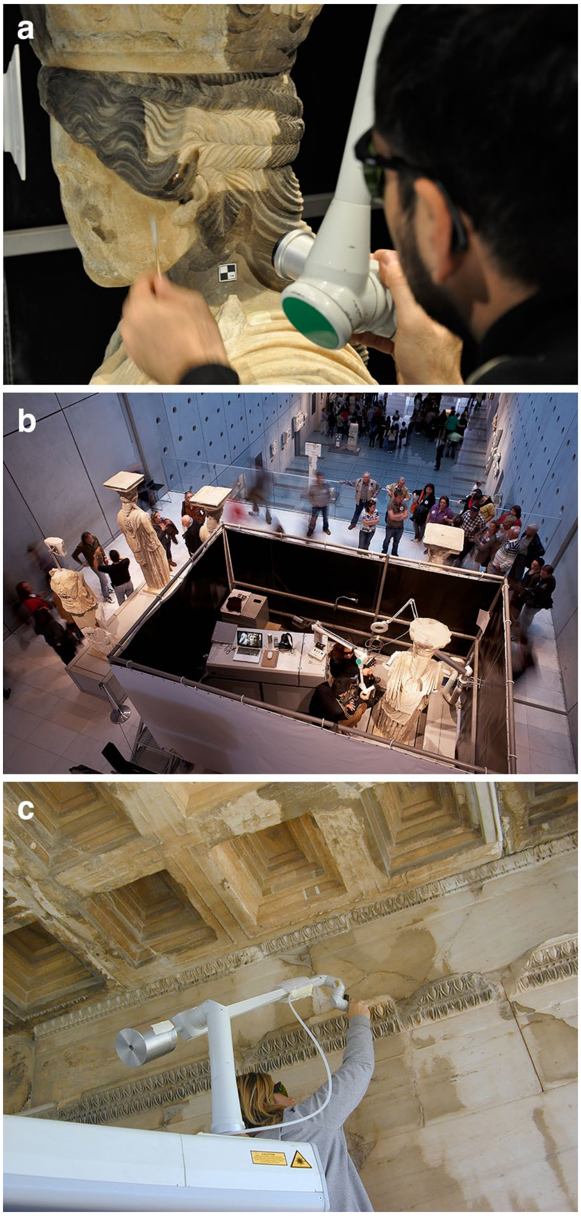

Fig. 5 **a** Laser cleaning of Caryatid "A" inside the in situ laser laboratory **b** at the Acropolis Museum and **c** The Laser cleaning system in action on-site in the Erechtheion Porch

At the same time, during the period 2008–2010, another laser cleaning project was undertaken on the Acropolis hill; a second prototype laser system was accommodated inside the Caryatids' porch in the Erechtheion with the aim to clean the coffered-ceiling of the porch (Fig. 5c). This intervention was particularly demanding from the technical point of view, as the coffered structures were located to the ceiling of the temple and necessary ergonomic measures should be taken for an efficient work. Furthermore, this challenging laser cleaning project involved along to the pollution accumulation the removal of soot (from fires) and a number of unconventional materials (from past unsuccessful restorations i.e. cement). The project was completed in 2010 and a number of analytical measurements has proven the efficiency of the cleaning intervention.

Dark soiling on plaster objects

Another cleaning challenge that has been effectively approached with the two-wavelength laser cleaning methodology is the removal of dark over-layers from plaster objects. Models (moulds) for three dimensional objects are often prepared with plaster and through the years they found covered with dark crusts. This is a rather composite problem as this crust may have soiling particles (internal dust), organic materials (from casting processes), as well as biological organisms. Given the sensitivity of gypsum [38–39], as well as its solubility to water, cleaning interventions on such objects are particularly demanding.

Initial tests (Fig. 6) with 1064 nm (ns pulse duration) resulted into cleaned but discoloured (yellow) surfaces [19] while the 355 nm laser radiation could not efficiently remove the crust leaving behind dark spots which are mainly located to in-homogeneities and micro-relief of the gypsum surface. Their combination was investigated (Fig. 6b) with encouraging results. Experiments applying sequentially the two beams (Fig. 7a, b) were not completely satisfying, while their synchronous use could reach the optimum cleaning level without surface or colour alterations (Fig. 7c). In this case the chosen operative laser irradiation parameters are $F_{IR}/F_{UV} = 2/3$. Raman analysis [20] supported the results as it was proven that the chosen laser parameters do not cause any change to the hydration state of the cleaned gypsum surface as no peaks indicating de-hydration states of the calcium sulphate hemi-hydrate were detected.

For the purpose of this cleaning challenge (thin soiling on plaster) the two-wavelength methodology was found to be able to remove the unwanted over-layer without damage or discoloration to the very sensitive gypsum surface. In this case the F ratio chosen favours the dominant contribution of the UV laser beam as the aim is the "layer-by-layer" removal of such thin and homogeneous crust. The contribution of the IR beam is minor and aims mainly to the removal of particulates trapped inside the surface micro-relief. On-going research aims to confirm the above results to other similar objects with the same type of crusts in order to establish this methodology for the laser conservation needs of plaster objects.

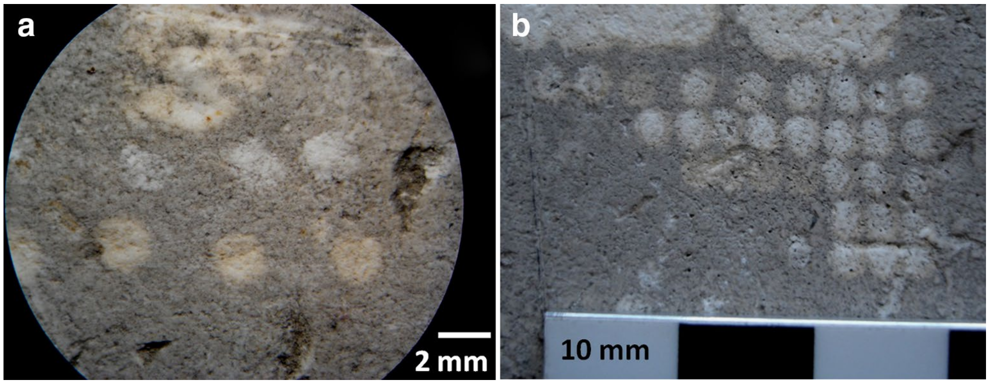

Fig. 6 **a** Series of 1064 nm (*lower line*) and 355 nm (*upper line*) of spot irradiation tests to remove dark over-layers from plaster (1 pulse at various F), **b** Series of spot irradiation tests using the two laser beams simultaneously (1 pulse at various F_{IR}/F_{UV} ratios)

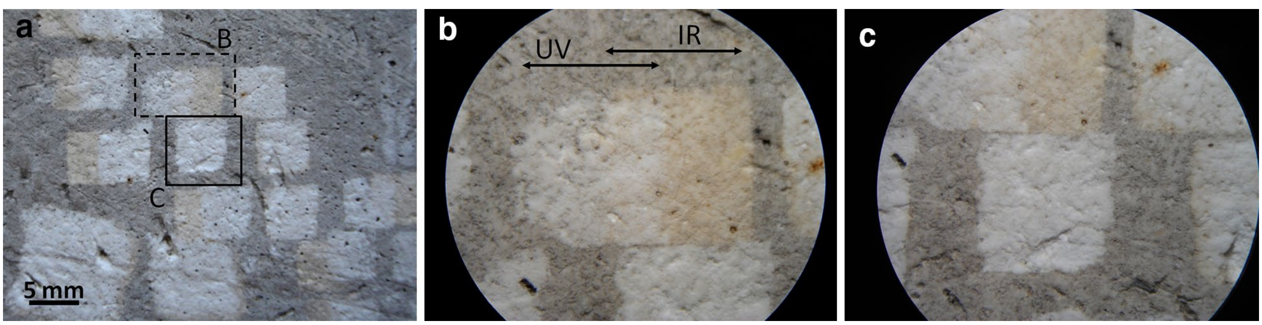

Fig. 7 **a** Series of SQ and SN irradiation tests to remove dark over-layers from plaster, **b** SQ irradiation (four pulses at $F_{IR} = 0.4$ J/cm^2 and following 5 mm shift to the *left four* pulses at $F_{UV} = 0.6$ J/cm^2) and **c** SN irradiation (four pulses at $F_{IR} = 0.4$ J/cm^2 and $F_{UV} = 0.6$ J/cm^2)

Conclusions and prospectives

Laser radiation is a unique conservation tool enabling the conservators to remove unwanted layers and materials in a highly controlled way, ensuring selectivity, precision and no harmful or uncontrolled by-products. Its application within the past 20 years in a number of cleaning challenges was proven able to restore the original surfaces while revealing fine details, historical tool-marks and traces of colour, information valuable for the CH historic research. Along these lines the two-wavelength methodology was suggested and developed aiming to address a number of conservation challenges and side-effects; yellowing discoloration of stone surfaces being the most characteristic. The methodology allows the regulation of different laser material ablation regimes and thus can be adapted to different cleaning issues with emphasis to cases in which conventional laser cleaning methodologies (i.e. using IR wavelengths) are not effective or successful. As a general rule for the combination of the 1064 and 355 nm their relative ratio is determined on the basis of the composition and morphology of the material to be removed. In order to remove relatively thick and inhomogeneous crusts the contribution of the IR beam (which is highly absorbed by the bulk of the crust) must be dominant, while for thinner soiling layers UV favoured ablation is recommended. Another important limitation is the cautious choice of the F value of each of the two beams and/or their sum, in order to operate below the threshold F values for damaging the substrate.

Fine-tuning of the two-wavelength methodology on a number of technical simulation samples and real fragments allowed its optimisation and implementation to the cleaning needs of Athens Acropolis sculptures where it has been operating for the past twelve years. Work in progress aims at the investigation and study of the combination of different laser wavelengths with encouraging results, as for example the combination of 1064 and 532 nm, which has been found particularly promising for the removal of biological encrustation from stonework.

Authors' contributions
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