

Towards the understanding of the two wavelength laser cleaning in avoiding yellowing on stonework: a micro-Raman and LIBS study

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Abstract

The synchronous use of Infrared (IR at 1064nm) and Ultraviolet (UV at 355nm) wavelengths of a Q-Switched Nd:YAG laser has been shown to efficiently confront the issue of discoloration, which may be observed upon laser ablation of environmental encrustation from marble surfaces, and thus this methodology is effectively employed in various laser cleaning applications. In order to further investigate the mechanisms that influence this result, a series of tests were undertaken on fragments of marble with environmental homogeneous compact crust. Through a number of irradiation tests applying a variety of laser parameters (individual use of IR and UV beams, as well as, their synchronous use) the different ablative processes have been investigated. In this paper, micro-Raman and Laser Induced Breakdown Spectroscopy (LIBS) were employed in order to examine the role of each laser beam, as well as their combination, and so to approach the reasons that induce yellow discoloration. The results of the above studies will be presented with the aim to further describe the two wavelength laser cleaning methodology and its principle, thus elucidating its effectiveness.

Keywords: Laser cleaning, pollution encrustation, yellowing, double wavelength, laser spectroscopy

1. Introduction

1.1. The yellowing effect

Outdoor Cultural Heritage (CH) monuments made of stone (marble, limestone etc.) are susceptible to a number of harmful environmental factors such as micro climate, acid rain, humidity and airborne particles from exhaustions of cars and factories. Due to these compounds a hard, dark-coloured crust is often developed on their surface. In

an effort to remove the crust from the surface of the marble IR lasers were used but yellowing of the treated surfaces often appears as an undesirable side effect.

The discoloration effect has been extensively studied and a number of hypotheses explaining its origin have been developed through the last years [1–9]. A brief presentation of the prevailing explanations upon the yellowing hue on the irradiated surface is given here:

- The revealing of pre-existing layers: According to this hypothesis, IR radiation removes the encrustation layer and reveals coloured pre-existing layers or “patinas”. These layers may be either intentionally applied (i.e. to protect the original surface and/or as a preparation layer before the application of paints) or they may have been developed naturally (due to weathering effect). In both cases they are considered historical and must be safeguarded as they may contain valuable information, as for example sculpted details and tooling traces, as well as historical evidence about materials and techniques used (traces of colours/pigments etc.) [10].

- The change of the original colour of the stone surface; this alteration may be caused due to the migration of water soluble organic compounds from the encrustation to the underlying stone, which is favoured in environments with high humidity and rain. As a result, the surface revealed upon laser cleaning show a colour different to the expected one [11, 12].

- The chemical transformation of iron components after the irradiation with IR. According to this hypothesis, although the percentage of iron oxides in the encrustation is indeed very low (~0.6% [13]), their chemical transformation may result into yellowing of the treated surfaces, which can be significant. Studies performed by different research groups have detected the presence of nanospheres rich in iron on the surface of technical samples containing hematite and graphite, after irradiation with IR [14], or the reduction of iron components present in pollution crusts, such as Fe_2O_3 , into magnetite (Fe_3O_4) [15]. Recently it has been suggested that both hematite (Fe_2O_3) and goethite ($\alpha\text{-FeO(OH)}$) exist at the encrustation [9] and that yellowing can possibly be attributed

to the transformation of hematite (Fe_2O_3) to goethite ($\alpha\text{-FeO(OH)}$) or maybe maghemite ($\gamma\text{-Fe}_2\text{O}_3$).

- The selective vaporization of black components and the preservation of a gypsum matrix on the marble’s surface after the irradiation at 1064 nm below the ablation threshold. The dark coloured particles highly absorb the IR radiation and are removed from the surface leaving behind a gypsum matrix with very small holes in their place. The incident, on the surface, light is then differentially scattered (according to Rayleigh scatter) causing a shift to the cleaned surface towards yellow [16].

In order to approach this delicate issue, namely the discoloration of the treated surface of polluted marble following irradiation with IR laser beams, research efforts have been focused on the identification of the composition of the environmental encrustation [13, 17] in relation to the series of cleaning tests at different laser parameters [5, 9, 18]. Physicochemical analyses and evaluation of the treated surfaces and/or the material removed [7, 12, 15, 19] were also employed to further investigate the yellowing issue.

1.2. The double wavelength methodology

With the aim to overcome the challenge of laser induced yellowing, a laser cleaning methodology has been developed [20], in which two wavelengths from the same laser system are used simultaneously to effectively remove the encrustation from the marble’s surface without changes to its colour, chemistry or delicate structure. The success of this methodology relies on the blending of an IR and a UV beam, at a specific ratio and fluence values, which provides the opportunity to efficiently remove the encrustation.

To further investigate the yellowing effect and understand the mechanisms of the two-wavelength blending, a series of studies were undertaken. They involved tests using different laser parameters (wavelengths, laser pulse duration, fluence values etc.) on technical samples simulating black crusts, as well as on real fragments.

It should be noted that pollution accumulations on outdoors stonework are particularly complex systems and their composition, morphology and stratigraphy may vary among monuments of different materials; located in different countries (depending on their climatic conditions, pollution level and history) and representing various historic eras. This is an important parameter to take into account when studying laser cleaning and interpreting analytical data for evaluation purposes.

This research has been focused on the investigation of fragments of minor historic value taken from the Athenian Acropolis. Analytical techniques provided the chemical and molecular composition of the samples before and after laser irradiation in order to understand the physicochemical processes taking place while using two laser wavelengths separately or simultaneously.

2. Materials and methods

2.1. Samples

Irradiation tests were performed on a marble fragment with real environmental homogeneous thin compact crust. The fragment is part of a freshly-cut marble complement added onto the Parthenon Frieze in Athens, Greece, during the restoration actions by Balanos in 1960s. During this restoration marble pieces (of the same quarry in Pentelic mountain) have been added to replace miss-

ing or damaged parts of the sculpted Frieze blocks. These complements bear the same accumulations with the rest of the Frieze and thus have been chosen for the purpose of this study [4].

2.2. Experimental parameters

The laser irradiation tests were performed with a Q-Switched Nd:YAG nanosecond (ns) laser (a customised system of Spectron, series SL850) emitting in the first and third harmonic wavelengths, in the infrared (IR, 1064nm) and ultraviolet (UV, 355nm) respectively. The laser provides the opportunity to emit each of the wavelengths separately and simultaneously. When the two beams are used simultaneously, the operator has the opportunity to select the fluence (F , measured in J/cm^2) output of each beam in order to get different ratios of the fluence of the IR (F_{IR}) and the UV (F_{UV}) beams. Thus it is possible to select a final output ratio $F_{IR}/F_{UV} = 1/4$ or $4/1$ and therefore get a different cleaning result. It should be noted that the decision on the ratios presented in this paper is the result of extensive past studies [5].

A marble fragment covered with environmental homogeneous thin compact crust was irradiated in a variety of laser parameters (fluence value, number of pulses for each beam, as well as their combination). Three clearly distinctive in colour and effectiveness, cleaning results have been chosen for this study and are indicated in Fig. 1. Specifically, the area on the left side of Fig. 1 was irradiated at 1064 nm with 5 pulses of fluence $F = 0.8 J/cm^2$. The middle area was irradiated with the same number of pulses at 355 nm and $F = 0.2 J/cm^2$. A combination of the two beams (in synchronous mode) in the same fluence values (in ratio $F_{UV}/F_{IR} = 1/4$) was used for the area shown in the right side of

Fig. 1. The fluence values shown correspond to the cleaning thresholds of this crust in both wavelengths. The tests were performed in dry conditions and the laser was operating in low repetition rate (3 Hz).

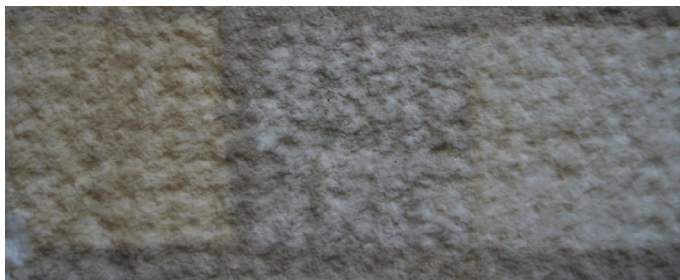


Fig. 1. Detail of marble fragment with environmental homogeneous thin compact crust after laser irradiation tests: (left) 1064 nm, $F=0.8$ J/cm², (middle) 355 nm, $F=0.2$ J/cm² and (right) their synchronous application, $F_{UV}/F_{IR}=1/4$ (each square is $\sim 2 \times 2$ cm²).

2.3. Analytical Documentation

Raman spectroscopy

Raman analysis was applied before and after laser irradiation on the real marble samples with the aim to detect possible variations on the molecular composition of the surface. The mobile Raman spectrometer (HE 785, Horiba-Jobin Yvon, France) was employed with excitation at 785 nm provided by a cw (continuous wave) diode laser coupled to an optical head ([21, 22]). A light-emitting diode (LED) and a high resolution colour camera (video microscope) are also part of the optical head and offer a very clear view of the area under investigation, necessary for positioning the beam on individual areas. The scattered radiation is collected through the objective lens, passes through an edge filter that cuts off Rayleigh scattering, and finally is focused into an optical fiber that is fed into a compact spectrograph, equipped with a concave grating, which provides spectral coverage in the range of 120–3395 cm⁻¹ at a spectral resolution of about 10–15 cm⁻¹. The detector, a Synapse TM CCD (1024 × 256 pixels), is Peltier-cooled and features

high sensitivity with low dark counts. The objective lens used for these analyses was $\times 20$ and the beam power on the sample was adjusted at 30 mW. Typical exposure time on the CCD was 30 s per scan and the spectra

recorded correspond to an average of 2 consecutive scans of the same point.

LIBS Spectroscopy

Laser induced breakdown spectroscopy (LIBS) was used aiming to detect and analyse the chemical composition of the samples surface before and after the laser treatment with a variety of parameters. The mobile LIBS spectrometer (LMNTII+), developed and constructed at IESL-FORTH, was used for this study [21, 22]. The instrument uses a compact passively Q-switched Nd:YAG laser emitting pulses at 1064 nm (10 mJ/pulse, 10 ns). Pulses are focused by means of plano-convex lens ($f = +75$ mm) on the surface of the object. The plasma emission is collected through the same lens and transmitted via an optical fiber that splits it into a dual spectrometer unit (Avaspec-2048-2-USB2, Avantes) that records emission spectra across a wavelength range extending from 200 to 660 nm, with resolution of about 0.2–0.3 nm. The laser along with necessary optics and a miniature CCD camera are integrated in a light-weight optical probe head. The camera offers a magnified view of the object surface

during the analysis and permits accurate aiming of the laser beam with the aid of a cross-hair indicator superimposed on the image. All LIBS spectra were collected with a time-delay of 1.3 μs with respect to the laser pulse and for an integration time of 1 ms. A nearly circular spot with a diameter of about 150–300 μm is probed by the laser beam.

3. Results and discussion

3.1. Visual evaluation

Visual observation of the sample shows that the areas treated with IR irradiation appear yellow, areas treated with UV irradiation are grey while the ones treated with both beams, simultaneously, are closer to the colour expected in this case.

3.2. Raman evaluation

Upon microRaman analysis calcite (CaCO_3 –157, 285 and 1088 cm^{-1}) and/or gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ – 1009 cm^{-1}) were detected on the homogeneous thin compact crust as well as on all the surfaces treated either with IR and UV, separately or simultaneously. An intense fluorescent signal (Fig. 2) was observed on the crust and the area irradiated at 1064 nm, though this is clearly reduced on areas irradiated at 355 nm or with the combination of 1064 and 355 nm. The origin of the fluorescence can be attributed to organic compounds previously detected on the homogeneous thin compact crust [6]. Indeed, studies on pollution accumulations (on marble and limestone) by means of GC–MS detected a number of components, part of which show intense fluorescence.

The presence of these fluorescent compounds indicates that either these com-

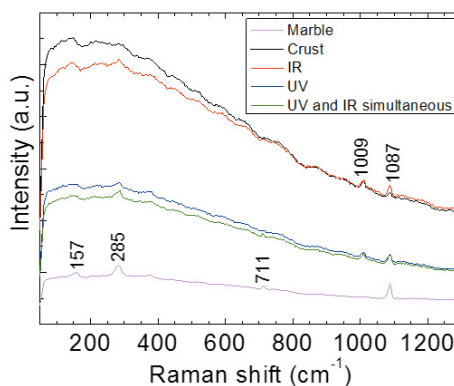


Fig. 2. Raman spectra acquired from the marble fragment presented in Fig. 1. Crust and areas treated with IR exhibit an intense fluorescence, while areas irradiated with UV or the combination of the 2 beams have a lower fluorescence, which is closer to the one of marble.

pounds were not affected, and thus they were not removed, upon IR irradiation, or they could possibly be induced by the laser beam as indicated by Oliveira et al. in their study [18]. Further analysis is currently performed in order to respond to this question. Among the arguments that support the first hypothesis (fluorescing compounds not removed by the IR laser beam) is that the fluorescing signal was detected on the sample prior to its irradiation/cleaning and the intensities of the Raman spectra recorded from the IR treated and reference areas are comparable. No additional fluorescence signal was detected after the IR radiation and thus the hypothesis that the detected fluorescence is due to IR laser irradiation seems unlikely for our samples. On the other hand, the reduction of the fluorescence after UV irradiation implies the removal of this fluorescent material from the surface of the sample. This difference in the Raman spectra of the irradiated areas suggests that the ablation occurs in a different and probably preferential/selective way for the two wavelengths.

3.3. LIBS analysis

LIBS analysis on the same areas of the sample detected the presence of a number of elements with most important Ca, Al, Fe, Mg, Si and Na. Characteristic spectra from these measurements are presented in Fig. 3. In order to detect and investigate the possible alterations in the elemental composition of the laser irradiated areas, either separately or simultaneously, the ratio of the chemical elements Fe and Ca was studied. The major components of the encrustation are Fe, Si and Mg [17, 23] but on the basis of previous research indicating that Fe holds a significant role in laser yellowing, our study was focused on the Fe concentration and behaviour for different irradiation parameters. In order to

achieve accurate results, the detected signal intensity of the Fe peak was normalized with another element that exhibits a constant concentration. The selected component was Ca since its presence is homogenous among the sample. Therefore, data analysis was performed by investigating the ratio of Fe/Ca for each irradiation parameter.

The proper selection of spectral lines was very important for achieving accurate results. The spectral lines chosen for this study are Fe 438.354 nm and Ca 445.478 nm. Calcium (Ca) exhibits a number of emission spectral lines but 445.478 nm was chosen because it originates from a highly excited state with big excitation energy and therefore low self-absorption possibility. The available

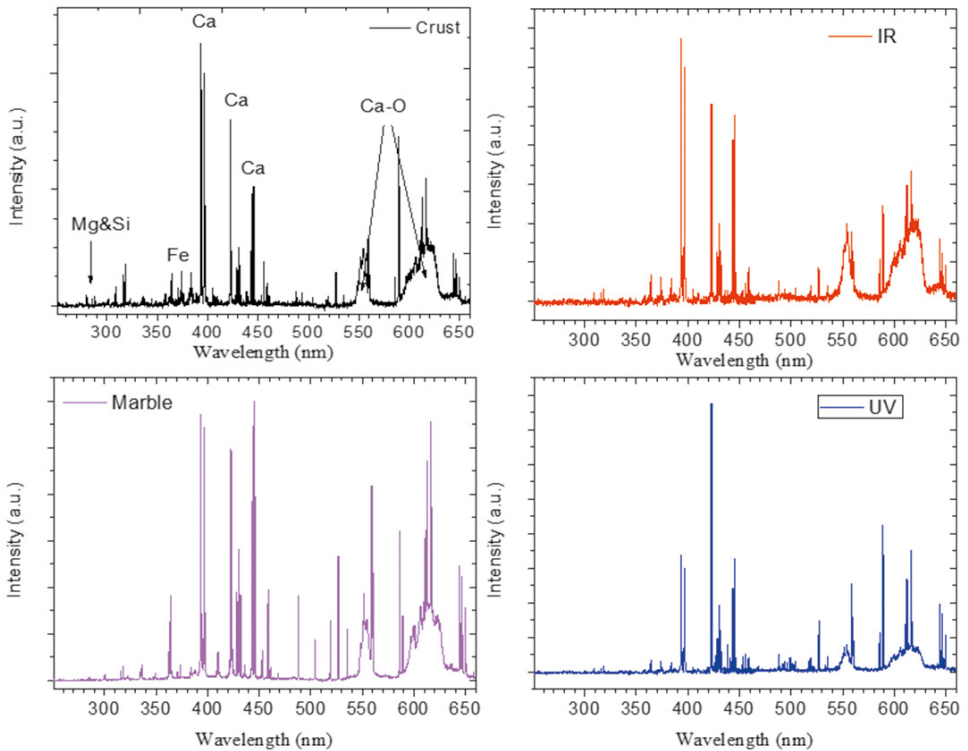


Fig. 3. LIBS Spectra obtained from the marble fragment prior (crust and marble reference) and after laser irradiation (with IR and UV beams).

spectral lines for iron are at 302.064, 371.994, 374.556 and 385.991 nm in the UV range and 438.354, 440.475 nm in the visible region of the LIBS spectrum. The spectral lines at 371.994, 374.556 and 385.991 nm coincide with the molecular emission band of the CN, and thus cannot be used. Furthermore, the line at 302 nm is too weak to provide reliable results. Therefore, the line at 438 nm has been used for the analysis because it has a higher intensity than the one at 440 nm. Of significant importance is the average value, taken from 10 different spots/points on the studied areas, of the ratio corresponding to the first LIBS pulse of each irradiation condition. It was decided to take into account for our measurements only the first LIBS pulse as, due to ablation, any additional pulse will represent a different/altered surface. Figure 4 shows the average value of Fe/Ca ratio for each irradiation parameter (described before in the caption of Fig. 1). A significant proportion of iron (Fe) to calcium (Ca), and therefore a greater concentration of iron, is

tion than the area treated simultaneously with IR and UV. In addition, the reference marble has the lowest proportion of Fe/Ca and it is comparable to the area treated with IR and UV simultaneously. The above lead to the conclusion that IR radiation removes preferentially the iron compounds, and thus that the ablation occurs in a selective way. On the other hand, the selective removal of the iron compounds does not occur upon UV irradiation, while the simultaneous use of both wavelengths shows the most efficient iron removal and results into a surface very similar, in iron concentration, to the one of the marble.

4. Conclusions

In summary, analytical investigation on a marble fragment with thin environmental homogeneous compact crust, which was irradiated with different laser beams and parameters, allows us to further under-

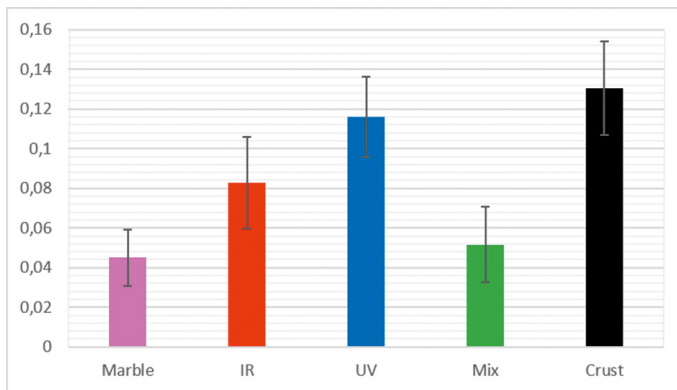


Fig. 4. The average Fe/Ca ratio obtained from the first pulse of the LIBS spectra accumulated from 10 different spots for each of the irradiated areas. The error bars correspond to the standard deviation of the Fe/Ca ratio.

detected in areas with crust deposits and areas treated with UV radiation. Furthermore, the area treated with IR presents a lower ratio value, compared to the one irradiated with UV or the crust, but higher iron concentra-

stand the ablation mechanisms that can be significant upon irradiation with different laser wavelengths. Optical observation confirmed the different ablation processes that take place upon irradiation with IR and

UV wavelengths, and/or their combination, and thus to the final colour of the treated surface. Raman spectroscopy showed reduced fluorescence on the areas treated with UV wavelength (or where UV was involved), suggesting a selective removal of organic/fluorescing compounds from the surface of the sample in this laser ablation regime. On the contrary ablation with IR, at the fluence values employed in this study, does not remove the bulk of the crust and possibly these fluorescing particulates that are trapped therein. The hypothesis that this ablative regime may cause the presence of these types of fluorescing has been also examined. In addition, LIBS analysis detected a lower Fe concentration in the area treated with IR suggesting the selective removal of iron particles from the marbles surface, in contrast with areas irradiated with UV wavelengths.

Taking all the above into account, it is suggested that the ablation mechanisms occurring during the irradiation of environmental homogeneous compact crust from stonework are closely dependant to the beam wavelength. On the basis of the different absorption properties of the involved materials to the applied laser wavelength, it has been shown that different removal processes vary significant in each case. Our hypothesis is that upon UV irradiation organic fluorescing components are preferentially removed while upon IR irradiation Fe-rich particulates are effectively ablated, as shown by our LIBS measurements. By combining the two beams simultaneously dark coloured particles and organic/fluorescing compounds are equally removed from the crust, resulting thus into a homogeneous and efficient cleaning procedure. Of course, the ratio of the two beams is an important parameter in the whole process.

It has also to be noted that in our experiments the aim was to understand the ablative mechanisms rather than clean our samples. Therefore, for the purpose of our study it was important to irradiate the crust, but not remove it totally, in order to have a base for investigation. This remaining material, of different colour and composition, was analysed and studied. Further experiments are in progress, focused on the study of different ablation parameters through technical simulation samples and real marble fragments, in order to elucidate the ablation mechanisms and processes.

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