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Lasers in the Conservation of Artworks

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Colour changes in Galician granitic stones induced by UV Nd:YAG laser irradiation

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ABSTRACT: Laser cleaning has become a high profile and accepted specialized cleaning technique for most stone types. Given that local natural building stone in our region, Galicia (North West of Spain) is granite, our interest was focused on the response of this stone type to laser cleaning. The aim of this work is to determine the change in colour as index of the response of galician granites to UV-Nd:YAG laser exposure. For this purpose samples of commercial granites from different quarries were irradiated at increasing fluences. Colour changes were determined through the analysis of digital images and expressed in the *L*a*b** and *L*h*C** colour models. The results enable the establishment of application limits of laser cleaning to these materials.

1.1.1 *Colour changes in Galician granitic stones induced by UV Nd:YAG laser irradiation*

2 INTRODUCTION

Laser cleaning of stones has become a high profile and accepted specialized technique in restoration. The majority of the reported laser stone cleaning has been for limestone and marble and to a lesser extent for silicate rocks such as sandstone; experience with granite and other crystalline stones is rare at present (Fotakis et al. 2007). Given that Galicia (North West of Spain) has a rich heritage of buildings and monuments constructed from locally obtained granite, our interest was focused on the response of this stone type to laser cleaning. Besides, the current development of transport and construction techniques has led to the widespread use of granite in facing tiles, even in areas located far away from the product source, which enlarge the interest on this topic.

Because of the wet climate in Galicia, the granite is almost permanently damp, which made it highly bioreceptive. Biological colonization and blackening of exterior surfaces can be observed in many buildings (Prieto et al. 1999, Aira et al. 2007); the main objective of the cleaning process is the removal of biological contamination.

The effects of laser cleaning on stone depend on the laser parameters, the type of the stone and the characteristics of application. Between the undesirable effects, changes in colour have been observed for different stone types at different working parameters (Klein et al. 2001, Lee et al. 2001). In the case of granites, changes in coloration of "Rosa Porriño" under 1064 nm Nd:YAG laser irradiation, and different Scottish granites under 1064, 532 and 355 nm were reported (Wakefield et al. 1997, Esbert et al. 2003, McStay et al. 2005, Grossi et al. 2007).

The aim of this work is to determine the change in colour of Galician granites under UV laser exposure. For this purpose samples of commercial granites showing different colours were irradiated with a Nd:YAG laser source at the wavelength of 355 nm and different fluences. The colour changes were determined through the analysis of digital images of the irradiated and non irradiated samples. The results can help to establish the application limits of the laser cleaning technique for different types of Galician building granites.

3 EXPERIMENTAL

3.1 *Materials*

The stone types used in this study are specifically those of Galician origin and comprised samples of pink (Rosa Porriño), pinkish-gray (Mondariz), and gray (Albero, Gris Morrazo) granites. All of them are commercial stones being Rosa Porriño, one of the most marketed ornamental stones in Spain and outside Spain.

Fresh samples from stores were cut in tablets of around 10×10 cm^2. Surface finishes were polished for all the samples except for Albero which was sew. Table 1 summarizes some relevant characteristics of these stones (Quiroga-Calviño et al. 1998).

Table 1. Granites analyzed in this work.

Granite	Classification	Macroscopic Description
Porriño	Biotite granite	Pink colour due to the coloration of the feldspars. Medium to coarse grained.
Mondariz	Biotite granite	Pinkish-gray with mega-crystals of feldspar.
Albero	Muscovite granite	Light gray, with a yellow to brown shade, medium-grained, rich in muscovite.
Morrazo	Biotite granite	Gray, fine-grained.

3.2 *Laser irradiation*

Experiments were carried out using a Q-switched Nd:YAG laser source; operating at the third harmonic, 355 nm, 10 Hz repetition rate, spot diameter around 8 mm; pulse duration 6 ns and maximum pulse energy varying between 10 and 60 mJ.

The samples were irradiated at different fluences between 0.18 and 1.03 J/cm^2. The energy density was calculated from measured energy data and the spot size of the laser beam on heat sensitive paper.

Samples were mounted onto a computer-controlled X−Y translation stage. Each sample was submitted to 3 scans at a scan speed of v = 2 mm/s. Under these conditions the average degree of overlapping given by the relation $(d\ f / v)$ was 40 laser pulses in each scan, being f the frequency, d the diameter of the laser beam and v the speed of scan. Then, an average of 120 laser pulses was delivered over each point of the sample surface.

3.3 *Colour measurements*

Although the measure of colour used to be performed by conventional spectrophotometric techniques; at present available commercial colorimeters measure colour only over a very few square centimeters, and thus their measurements could not be very representative in heterogeneous materials such as granite items. For this reason, in order to quantify the colour changes induced by laser irradiation, a simple method based on computer vision techniques was applied (Yam et al. 2004, Thornbush et al. 2004, Leon et al. 2006). This method uses a digital camera to capture the colour image of the granite tablet under proper lighting. The captured image is a bitmap image consisting of many pixels; each pixel assign a specific location and colour (RGB) value which can be transformed into different colour coordinates by means of the adequate software (Westland and Ripamonti 2004).

The digital camera was a Nikon D100 with exposure times ranging from 30 s to 1/4000 s and an objective Nikon micro 60/2.8. The CCD of the camera consists of 6.1×10^6 pixels and presents an active area of 23.7×15.6 mm^2. The images were stored in non-compressed file (TIF format) to avoid loss of image quality. The standard light source D65 (http://www.cie.co.at/) which mimic variations of daylight and with a colour temperature of 6500 K was used.

The position of the camera, sample, and light sources was arranged in order to capture the diffuse reflection responsible for the colour, which occurs at 45° from the incident light, and to ensure a uniform distribution of light intensity over the sample surface. A standard colored chart GretagMacbeth ColourChecker was used to calibrate and verify the experimental settings prior to actual measurements. The digital images were taken out of focus to obtain a fuzzy image which simulates the effect of the standard CIE viewing angle geometry (http://www.cie.co.at/).

4 RESULTS AND DISCUSSION

In order to quantify the colour changes, digital images of all the samples irradiated were analyzed and colour measurements were expressed using the CIE $L^*a^*b^*$ system. Here L^* is the variable lightness or luminosity, which varies from 0 (black) to 100 (white); a^* and b^* are the chromatic coordinates. The attributes of chroma (C^*_{ab}: saturation or colour purity) and hue (h^*_{ab}: referring to the colour wheel) can be calculated by the equations: $C^*_{ab} = (a^{*2} + b^{*2})^{1/2}$ and $h^*_{ab} = \tan^{-1}(b^*/a^*)(180/\pi)$. Colour differences ($\Delta L^*, \Delta a^*,\ \Delta b^*, \Delta C^*_{ab}, \Delta h^*_{ab}$) were calculated and the total colour change (ΔE^*_{ab}) was estimated by the expression: $\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$.

The colour of the granite stones results from a combination of colours of the granite rock-forming minerals; thus, the selected stones present different colour coordinates, which are summarized in Table 2. Different responses to UV-Nd:YAG laser irradiation of these stones are appreciable under naked eye examination showing changes in colour especially in the case of Rosa Porriño in which a clear loss of pink colouration was observed. Gris Mondariz, as well as Albero, present more subtle variations, however in the case of Gris Morrazo no changes were noticed. On the whole, colour changes seem to be higher at higher laser fluences.

Data of color variations, in terms of colour coordinates, as a function of the laser fluence are discussed below for each granite type:

Table 2: Values of colour coordinates of granites.

Granite	Albero	Morrazo	Mondariz	Porriño
L^*	44±2	47±3	45±6	46±4
a^*	1.0±0.9	□0.1±0.6	0.6±1.0	5.7±3
b^*	4.7±1.0	1.0±0.8	3.4±1.4	8.7±3
C^*	4.8±1.0	1.2±0.8	3.5±1.4	10.5±4
h^*	79±11	68±59	80±19	58±8

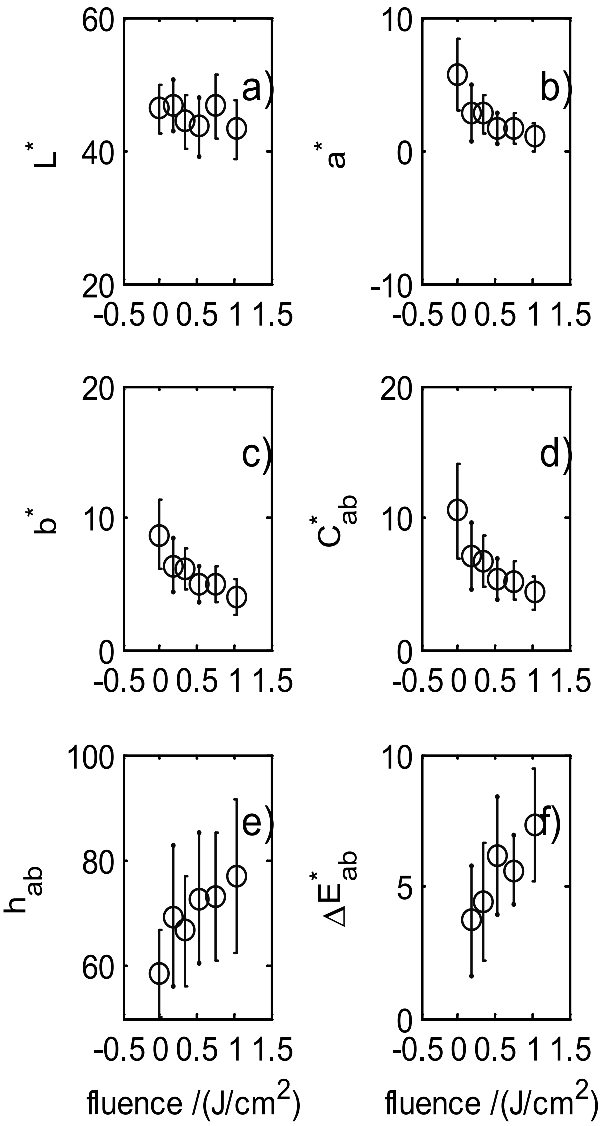

Figure 1: Rosa Porriño L^*, a^*, b^*, C^*, h^* and ΔE^*_{ab}.

Rosa Porriño

As can be appreciated in Figure 1a and Figure 1b, there are strong changes in chromatic coordinates a^* and b^* even at the lowest value of laser fluence. As a consequence, the chroma C^* (Fig. 1c) decreases showing a higher rate of change at the lower values of fluence (between 0 and 0.5 J/cm^2). This decrease in C^* indicates that the colour of the surface was approaching the values corresponding to gray colouration. At the same time, the increase in hue h^* (Fig. 1d) indicates a separation from the red-green axis; i.e. a loss of red colouration. Finally, from the measurements of L^* (Fig. 1e), no discernible trend can be appreciated confirming that the loss in red colouration was not accompanied by a corresponding lightening or bleaching of the stone surface which was measurable using the L^* component.

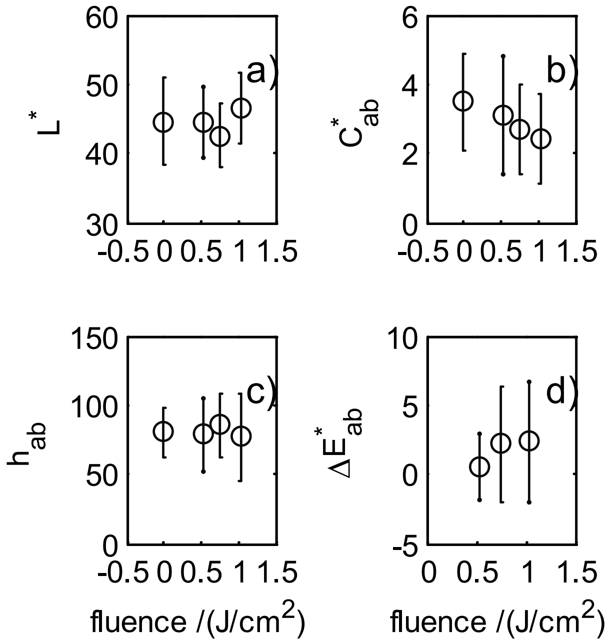

Figure 2. Mondariz L^*, C^*, h^* and ΔE^*_{ab}.

Gris Mondariz

As in the case of Rosa Porriño, a loss of pink colouration is appreciable at all the fluences analyzed giving a decrease in C^* with increasing fluence (Fig. 2b). Values of L^* and h^* do not show an appreciable trend (Fig. 2a and 2c).

Albero

This granite presents a light gray colour with a shadow of yellow-brown. Changes in colour were discernible by eye at the higher fluences but they are very subtle. Figure 3b shows appreciable changes in C^* for fluence values of 0.5 J/cm^2 onwards. Coordinate h^* shows a subtle decrease (Fig. 3c). Values of L^* do not evidence lightening or bleaching caused by the UV laser irradiation.

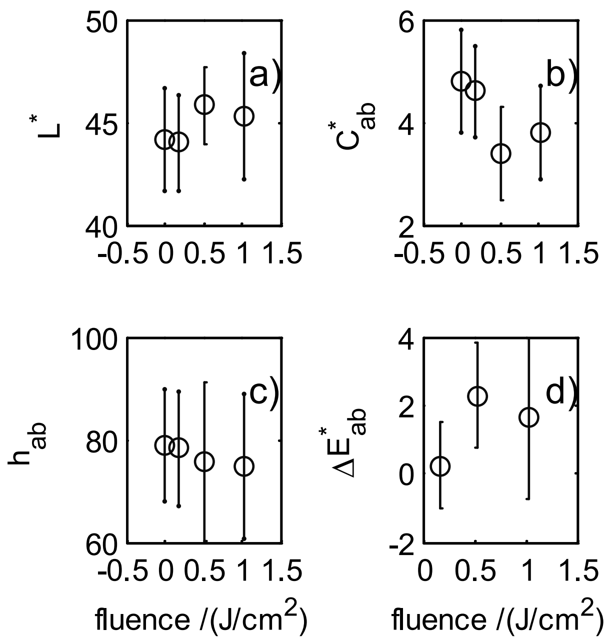

Figure 3: Albero L^*, C^*, h^* and ΔE^*_{ab}.

Morrazo

This gray granite does not show changes in colouration caused by the laser irradiation.

Then, UV-Nd:YAG laser irradiation has caused colour changes in pinkish granites (Rosa Porriño and Gris Mondariz) even at the lowest fluences applied, probably associated to changes in the pink feldspars which contain iron oxides. In the case of Albero, gray granite with a yellow-brown shadow, changes were appreciated when the laser fluence reaches around 0.2 and 0.5 J/cm^2. In all cases chroma, i.e. C^* coordinate, is sensitive to the laser fluence, showing a clear decrease when the fluence increases. This decrease indicates a progressive approach to the gray axis in $L^*C^*h^*$ space. The lightness, L^*, does not show any trend indicating that no bleaching is produced by the laser. The behavior of hue, h^* coordinate, under laser irradiation depends on the granite type but does not exhibit a great variation with laser fluence. As a result, colour difference ΔE^*_{ab} shows a clear increase with increasing fluences for all the granites analyzed, giving a maximum value of 5 for Rosa Porriño and around 2 for Mondariz and Alberto.

5 CONCLUSIONS

Different coloured granite stones were exposed to irradiation of a Q-switched Nd:YAG laser in the UV range (355 nm) at different energy densities to determine the effect of the laser on the colour of fresh stone surfaces. Except for the case of gray granite Gris Morrazo, a loss of colour with increasing fluence is visible with the naked eye.

In order to obtain quantitative values of changes in coloration, a method based on the analysis of digital images was used, and coordinates of the $L^*C^*h^*$ space were selected for quantification. The more sensitive coordinate to the laser energy density was the chroma C^* which decreases with the increase of laser fluence. For granites containing red colored minerals such as Rosa Porriño and Gris Mondariz, colour loss occurred at the lowest fluence applied, 0.18 J/cm^2. Exposure of these stone types to UV causes a loss in pink coloration from the feldspar grains which turn gray. In the case of gray granites, Albero, a light gray stone with a yellow-brown shadow, changes occurred at values around 0.5 J/cm^2, probably associated to changes in the minerals responsible of the yellow-brown shadow.

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