# Colour changes by laser irradiation of reddish building limestones

C.M. Grossi[1] & D. Benavente[2]

1.- School of Health Sciences, University of East Anglia, Norwich NR4 7TJ, UK[1]

2.- Department of Earth and Environment Sciences. University of Alicante. 03690 Alicante (Spain)

**Abstract**

We have used X-ray photoelectron spectroscopy (XPS) as a novel method to investigate the causes of colour changes in a reddish limestone under irradiation by a Q-switched Nd:YAG 1064nm laser. We irradiated clean dry and wet surfaces of *Pidramuelle Roja*, a building stone frequently used in the Asturian heritage, at fluences ranging from 0.12 to 1.47 $Jcm^{-2}$. We measured the colour coordinates and undertook XPS analysis of the state of oxidation of iron both before and after irradiation. Visible colour changes and potential aesthetic damage occurred on dry surfaces from a fluence of 0.31 J $cm^{-2}$, with the stone showing a greening effect and very intense darkening. The colour change on dry surfaces was considerably higher than on wet surfaces, which at the highest fluence (1.47 J $cm^{-2}$) was also above the human visual detection threshold. The use of XPS demonstrated that the change in colour (chroma and hue) is associated with a reduction in the iron oxidation state on dry surfaces during laser irradiation. This points out to a potential routinary use of XPS to analyse causes of colour changes during laser cleaning in other types of coloured building stones.

**Keywords:** Q-switched Nd:YAG 1064nm laser, heritage red limestones, X-ray photoelectron spectroscopy, iron oxidation state, colour variation

[1] Corresponding author: c.grossi-sampedro@uea.ac.uk

**Highlights**

- This is the first time that XPS is used to determine the cause of colour change in coloured stones when cleaned with laser at 1064 nm
- We demonstrate that the colour change in red limestones is due to a reduction in the state of oxidation of iron, in this case present as hematite.
- XPS could be routinely used to analyse causes of colour changes during laser cleaning in other types of coloured building stones.

## 1. Introduction

The pulsed mode solid-state "Nd ions - Yttrium Aluminum Garnet" (Nd:YAG) laser at the fundamental wavelength of 1064 nm is a widely type of laser used for cleaning building stone. This type of laser is generally considered very suitable for stone cleaning because of its ability for the selective removal of dirt [1]. The chemical and mineralogical composition of the stones affects the absorption to laser radiation and therefore possible chemical and physical transformations and their concomitant colour-related change.

Colour is one of the stone characteristics that influence its use as building material. Changes in stone colour can be publicly acceptable but also aesthetically unpleasant [2]. Therefore colour is a property that is often measured when undertaking research in conservation, especially when using laser cleaning [3-13].

Colour changes are frequently measured using the CIELAB and CIELCH systems because they better represent human sensibility to colour than other colour coding systems. The variable L* represents lightness or luminosity, and a* (red-green) and b* (yellow-blue) are the chromatic coordinates. Chroma ($C^*_{ab}$: saturation or colour purity) and hue ($h_{ab}$: colour wheel) in the polar system CIELCH are calculated by the equations: $C^*_{ab} = (a^{*2} + b^{*2})^{1/2}$ and $h_{ab} = \tan^{-1}(b^*/a^*)$. Consequently, changes in $C^*_{ab}$ and $h_{ab}$ are more sensitive to changes on a* or b* depending on the original colour of the material [8].

Colour in most building stones is strongly influenced by the content, oxidation state and types of iron compounds. In general, colour changes are usually attributed to changes in the state of oxidation of iron [14-16]. Iron compounds are highly absorbent to 1064 nm laser radiation and therefore strongly condition the response of stone to laser irradiation, especially regarding to colour changes. In our previous research [7,8] we found that the a* coordinate, or red–green component, is strongly affected. Pink granites and reddish limestones, with higher positive a* values experienced large colour changes, mainly a decrease in a*, leading also to changes in $h_{ab}$ (hue). Visually, red limestones stones turned into greener tones. We attributed changes in a* to thermal effects on the $Fe_2O_3$ likely contained in the rock minerals. However, we did not assess this experimentally.

Here we use X-ray photoelectron spectroscopy (XPS) as a novel method to investigate the causes of chemical variations leading to colour changes in a reddish limestone under laser irradiation at 1064 nm wavelength. The XPS technique has only been recently -and very rarely- used to analyse potential changes on stone surfaces by laser cleaning at different wavelengths [17,18]. One of the strengths of XPS is the identification of oxidation states [19] and it is widely used for quantitative analysis of surface chemical composition. The XPS detector quantifies the amount of photoelectrons emitted by the sample after being triggered with the X-ray source. Binding energy (BE) is related to the energy needed to extract the photoelectrons from the atom and is characteristic of each element and their oxidation state. Since core level electrons in solid-state atoms are quantized, the resulting energy spectra exhibits peaks characteristic of the electronic structure for atoms in the sample [20].

## 3. Materials and Methods

### *3.1. Material*

In this investigation, we have used the reddish building stone *Piedramuelle Roja,* which is extensively used in historic buildings of Oviedo (Asturias, Northern-Spain), including the Cathedral and the Pre-Romanesque monuments. *Piedramuelle Roja* is a limestone with calcite and Fe-rich dolomite (70-80%), quartz (15-25%), and iron oxides (5%), mainly as goethite and hematite, which confer the colour to the stone. Muscovite, chlorite, glauconite and illite are minor components of this stone. Open porosity ranges from 5 to 15% and the mean value of pore throat size is circa 0.1 µm [6, 21].

### *3.2. Methods*

#### *3.2.1. Laser irradiation*

Experiments were carried out using a Q-switching Nd:YAG laser system; $\lambda$= 1064 nm; spot diameter = 6 mm; pulse frequency rate = 20 Hz; pulse duration=6ns and maximum pulse energy varying around 353 – 415 mJ. Details of the method are described in Esbert et al., [6]. We irradiated clean stone samples as follows:

1. On dry surfaces (50 mm × 50 mm) at fluences ranging from 0.12 to 1.47 Jcm-2 along different strips. Each strip was irradiated five times.
2. On dry and wet surfaces (50 mm × 50 mm), applying a thin layer of water before laser irradiation, at two different fluences (0.5 and 1.47 J cm$^{-2}$).

### *3.2.2. Colour measurements*

Colour was measured prior, and after irradiation with a MINOLTA CR-200 colorimeter using the illuminant C, beam of diffuse light of 8 mm diameter, 0º viewing angle geometry, specular component included and spectral response closely matching the CIE (1931) standard observer curves. A representative colour and reduced error because of colour variability was gained by using the differences between two successive cumulative averages of the parameters L*, a* and b*.

The CIELAB and CIELCH systems were used here to represent colour differences [EN ISO 105-J05, 22], and to compare the relative importance of each parameter in the colour change. We also refer to the total colour difference and an approximate corresponding grey scale rating (GSc) according to EN ISO 105-A05 [23]. Grey scale values indicate human visual discrimination to colour variation and vary from 5 (nonvisible changes) to 1 (very strong changes) and relate to intervals of $\Delta E^*_{94}$ from <0.40 to ≥11.60. Possible causes for colour changes were initially assessed by opaque minerals´ examination under reflected-light optical microscopy.

Descriptive statistics involved determination of means, standard errors and 95% confidence intervals. Statistical significance of the colour changes was evaluated by the Mann–Whitney (Wilcoxon rank) nonparametric test in STATA 14. Colour changes were plotted, for an easier visualisation, as polar and scatter plots.

### *3.2.3. XPS analysis*

X-ray Photoelectron (XPS) provides information about the oxidation state of the elements and their concentration at the sample surface. A K-ALPHA XPS system (Thermo Scientific) was used to analyse the state of the oxidation of iron in the samples before and after laser irradiation. All spectra were collected using K-alpha radiation (1486.6 eV), yielding a focused X-ray spot with a diameter of 300 µm, at 3 mA and 12 kV. Twenty eight cumulative scans were performed in order to obtain an adequate signal-to-noise ratio. Differences between pre and post laser application were analysed by calculating odds ratios of the spectra peak´s height and area for $Fe^{2+}$ vs $Fe^{3+}$ and their 95% confidence intervals using STATA 14.

## **4. Results and discussion**

### *4.1. Colour changes*

The main colour changes are summarised in Figs. 1-3 and in Table 1. *Piedramuelle Roja* limestone is strongly affected by laser radiation, mainly when irradiated on dry surfaces. Fig. 1 shows colour changes ($\Delta E^*_{94}$) and the equivalent grey scale rating (GSc) at different fluences on dry surfaces. Visual changes are detected from a fluence of 0.31 J $cm^{-2}$, with the stone showing a greening effect and very intense darkening. This changes are significant in L*, a* and b*. However, possible changes mainly in a* and perhaps b* could occur at lower fluences [see details in Esbert et al, 6].

Table 1 and Figures 2 and 3 show colour changes on tables irradiated at 1.47 J $cm^{-2}$. Colour change on wet surfaces is considerably lower but above the human visual detection threshold. *Piedramuelle Roja* limestone shows GSc values at 1.47 J $cm^{-2}$ that evidence visual colour variations. Wet surfaces of the stones experience smaller but significant changes in L*, a* and b*. On wet surfaces, there is an increase in the b* co-ordinate that results in a subsequent increase in chroma.

Hematite, limonite and goethite were identified under reflectance microscopy in the untreated surfaces. After laser irradiation on dry surfaces, the stone orange background disappears and no hematite is clearly observed [see details in Esbert et al., 6].

### *4.2. Variation of the oxidation state of iron*

The XPS analysis provided interesting information about oxidation sates of iron under different conditions. Table 2 and Figure 4 show the region of the spectrum corresponding to high-resolution iron $2p_{3/2}$ XPS transitions for the iron species in untreated and laser-irradiated *Piedramuelle Roja* dry surfaces. The spectra deconvolution is produced since they are clearly separated by about 1.2 eV and with ½ intensity ratios between them [24]. Each deconvoluted peak is a 30% mixed Lorentzian/Gaussian function. The obtained deconvolution of the iron $2p_{3/2}$ spectra shows three main peaks.

Peak A occurs at a binding energy (BE) about 709 eV, peak B at 711 eV and peak C at 714 eV. The low-BE (peak A) corresponds to ferrous ($Fe^{2+}$) compounds and the main peak in the centre of spectra (peak B) includes the ferric ($Fe^{3+}$) compounds. The high-BE peak (peak C) is assigned to a surface or satellite peak, which has been ascribed to shake-up or charge transfer processes [20,25-28]. Consequently, the evolution of oxidation state of iron compounds is studied through the peaks A and B.

We used the binding energy of the deconvoluted peaks to analyse the evolution of oxidation state of iron compounds. The binding energy values of these peaks significantly changed by laser irradiation, although their values slightly decrease to the reduce form (Table 2).

The intensity has been defined as both height and area ratios of the peaks A and B (A/B). This means that laser irradiation produces a reduction of the oxidised iron, which is presented in *Piedramuelle Roja* minerals mainly as hematite. Thus, the A/B height and area ratios ($Fe^{2+}/Fe^{3+}$ compounds) tend to increase after laser irradiation, which seems to be significant as there is not overlapping between the 95% CI pre and post laser (Table 2). Odds ratios $Fe^{2+}$ vs $Fe^{3+}$ for height and area post vs pre laser are significant higher than 1, with 95% CI both lower and upper bounds higher than 1. Height and area odds ratios are very similar, around 1.4 (95%CI 1.3-1.5) suggesting an increase in the odds of $Fe^{2+}$ of around 40% after laser irradiation at this experimental conditions.

## 5. Conclusions

The analysis carried out by XPS proved that iron reduction is the main responsible of colour changes on dry surfaces of *Piedramuelle Roja* limestone irradiated with laser at 1064 nm, i.e. at absorbing near-red wavelengths. As iron is the element that has the strongest influence on the colour of limestone, this is translated in strong visible colour changes (hue and chroma), statistically significant in all colour coordinates, with the a*coordinate (red-green) being especially sensitive.

Visible colour changes and potential aesthetic damage occurred on dry surfaces from a fluence of 0.31 J $cm^{-2}$, with the stone showing a greening effect and very intense darkening. The colour change on dry surfaces is considerably higher than on wet surfaces, which at the highest fluence (1.47 J $cm^{-2}$) is also above the human visual detection threshold.

XPS could be routinary used to analyse causes of colour changes during laser cleaning in other type of coloured building stones.

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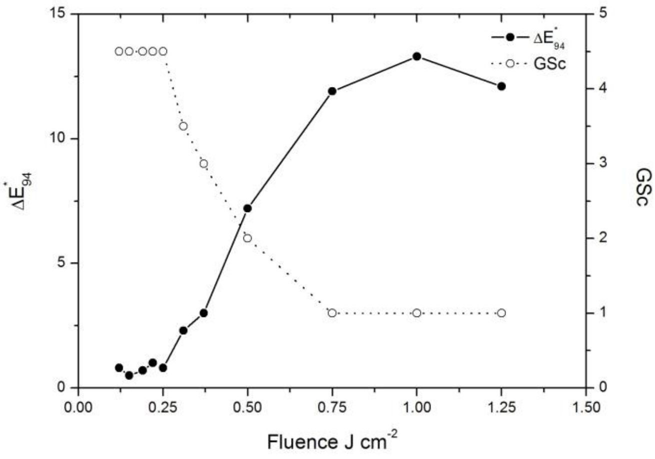
| | $L^*$ | $a^*$ | $b^*$ | $C^*_{ab}$ | $h_{ab}$ | $\Delta E^*_{94}$ | GSc |
|---|---|---|---|---|---|---|---|
| PRE DRY | 59.1 (58.7-59.6) | 11.9 (11.6-12.2) | 21.5 (20.9-22.1) | 24.6 (23.9-25.2) | 60.9 (60.4-61-4 ) | | |
| POST DRY | 54.0 (53.6-54.4) | 4.4 (4.2-4.6) | 15.0 (14.7-15.4) | 15.6 (15.3-16.0) | 73.7 (73.2-74.3) | 11.2(10.9-11.4) | 1.5 |
| p-value* | <0.001 | <0.001 | <0.001 | | | | |
| PRE WET | 59.2 (58.8-59.5) | 12.2 (11.9-12.4) | 20.1 (19.8-20.5) | 23.5 (23.2-23.9) | 58.9 (58.5-59.3) | | |
| POST WET | 57.2 (57.0-57.5) | 11.2 (11.0-11.3) | 21.5 (21.4-21.7) | 24.3 (24.1-24.4) | 62.6 (62.2-63.0) | 2.6 (2.6-2.6) | 3.5 |
| p-value* | <0.001 | <0.001 | <0.001 | | | | |

* From Mann–Whitney (Wilcoxon rank) test

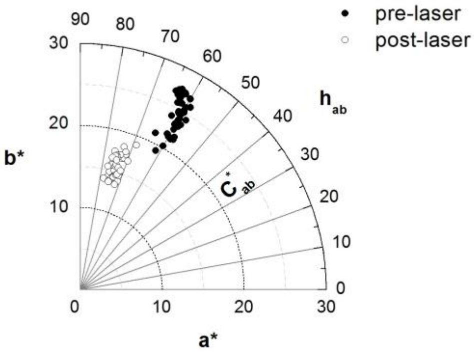
Table 1.- Mean and 95% confidence intervals of colour variables pre and post laser irradiation at 1.47 J $cm^{-2}$ on dry and wet *Piedramuelle Roja* surfaces and colour changes ($\Delta E^*_{94}$ and GSc) measured following EN ISO recommendations [22, 23].

| | Pre-laser | Post-laser |
|---|---|---|
| Energy (eV) | | |
| Peak A ($Fe^{+2}$) | 709.9 | 709.83 |
| Peak B ($Fe^{+3}$) | 711.89 | 711.53 |
| Peak C (Satellite) | 714.25 | 713.31 |
| A/B height ratio | 0.81 (0.79-0.83) | 1.14 (1.12-1.15) |
| A/B area ratio | 0.68 (0.67-0.69) | 0.93 (0.92-0.94) |
| | **Odds Ratio Post-laser vs Pre-laser** | |
| Height $Fe^{+2}$ vs $Fe^{3+}$ | 1.41 (1.29-1.54) | |
| Area $Fe^{+2}$ vs $Fe^{3+}$ | 1.37 (1.30-1.45) | |

Table 2.- Change in the Energy of $2p_{3/2}$ XPS Fe-peaks on *Piedramuelle Roja* surface pre and post Nd:YAG laser irradiation at 1064 nm wavelength on dry surfaces. In brackets 95% confidence intervals. Odds ratios and confidence intervals were calculated on 28 cumulative scan counts.



15
10
5
0
0.00
0.25
0.50
0.75
1.00
1.25
1.50
5
4
3
2
1
0
$\Delta E^*_{94}$
GSc
Fluence J cm$^{-2}$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b*
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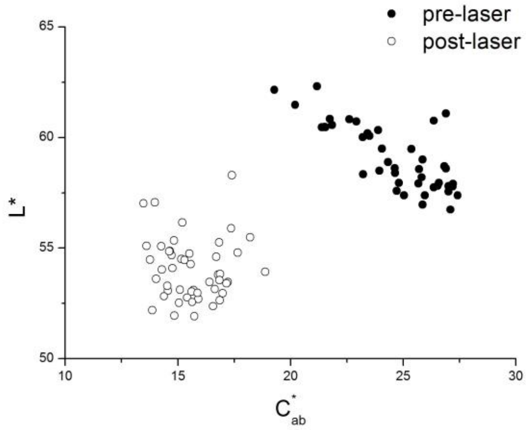
C*_ab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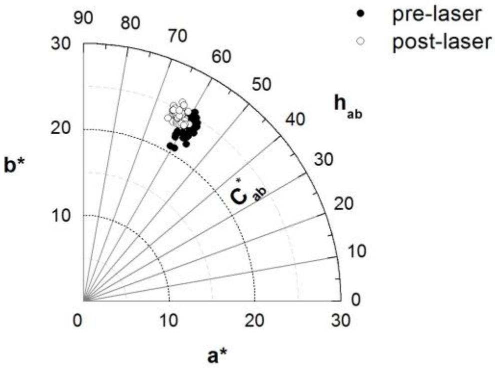
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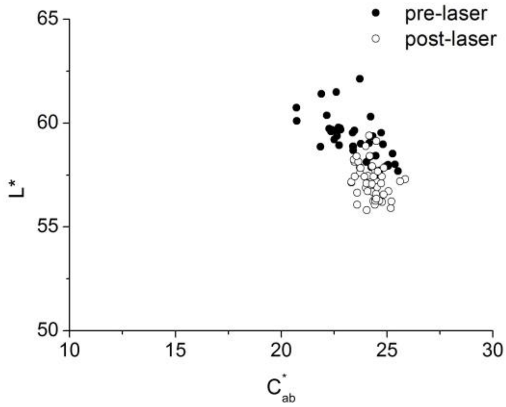
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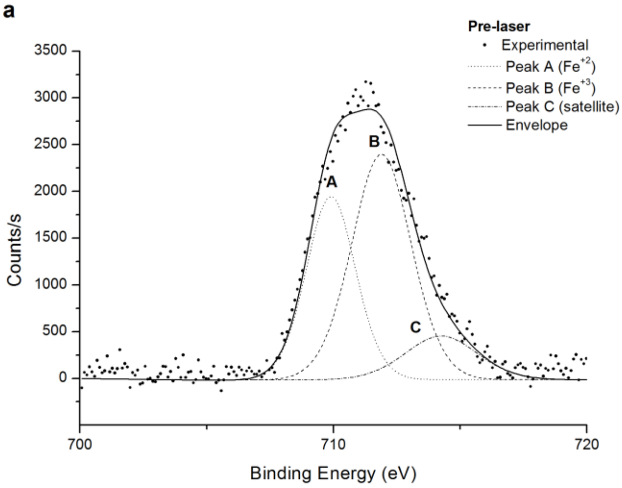
**a**


Pre-laser
Experimental
Peak A (Fe+2)
Peak B (Fe+3)
Peak C (satellite)
Envelope
A
B
C
Counts/s
Binding Energy (eV)
3500
3000
2500
2000
1500
1000
500
0
700
710
720

**b**

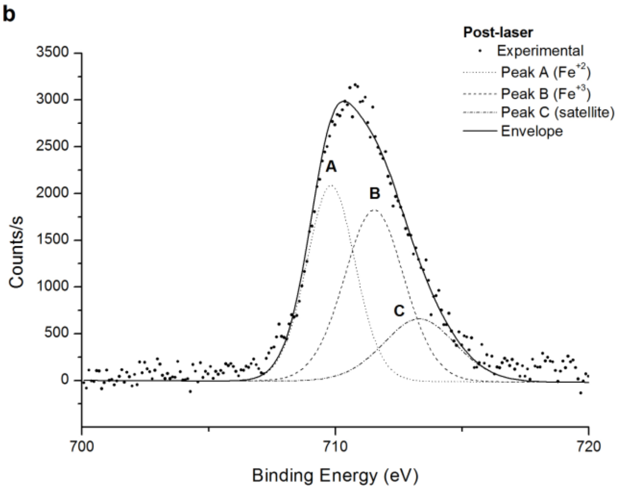

Post-laser
Experimental
Peak A (Fe+2)
Peak B (Fe+3)
Peak C (satellite)
Envelope
A
B
C
Counts/s
Binding Energy (eV)
3500
3000
2500
2000
1500
1000
500
0
700
710
720

Fig. 1. Colour changes ($\Delta E^*_{94}$) and grey scale rating (GSc) at different fluences on dry surfaces of *Piedramuelle Roja* [EN ISO 105-A05, 24].

Fig. 2. Polar and Cartesian scattergrams for *Piedramuelle Roja* limestone irradiated with Q-switched Nd:YAG 1064nm laser at 1.47 J $cm^{-2}$ on dry surfaces [8].

Fig. 3. Polar and Cartesian scattergrams for *Piedramuelle Roja* limestone irradiated with Q-switched Nd:YAG 1064nm laser at 1.47 J $cm^{-2}$ on wet surfaces.

Fig. 4: Evolution of Fe $2p_{3/2}$ XPS spectrums for *Piedramuelle Roja* limestone pre (a) and post (b) irradiation with Q-switched Nd:YAG 1064nm laser on dry surfaces.