Color Changes in Architectural Limestones from Pollution and Cleaning

Carlotta M. Grossi,[1]* Peter Brimblecombe,[1] Rosa M. Esbert,[2] Francisco Javier Alonso[2]

[1] School of Environmental Sciences, University of East Anglia, Norwich, nR4.7TJ United Kingdom

[2] Department of Geology, University of Oviedo, Oviedo, 33005, Spain

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Abstract: This article investigates the impact of sulfur dioxide attack, deposition of dark particles in urban environments and laser cleaning with Nd:YAG 1064 nm on color change in a range of ornamental limestones. We have used the CIELAB and CIELCH systems to compare the relative importance of the variation of each coordinate for the color change. Sulfur dioxide and dark particle deposition seems to increase the chroma, most particularly in the yellow component. Particle deposition also leads to an obvious darkening of stone surfaces. Laser irradiation at 1064 nm affects the red component of limestone, particularly if they already possess a reddish color. In general, the more intense the original color of the stone the greater are the chromatic changes, but the direction change of the color-parameter affected by a particular process remains the same. It has always been apparent in an atmosphere heavily polluted with soot that the main changes to light-colored stones are the exponential decrease in the parameter L* *(darkening–blackening). This has important aesthetic and social implications. However, in the near future it may be that in cleaner atmospheres, perhaps more dominated by organic pollutants, a yellowing process may be of greater concern.* © 2007 Wiley Periodicals, Inc. Col Res Appl, 32, 320–331, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/col.20322

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*Correspondence to: C.M. Grossi (e-mail: c.grossi-sampedro@uea.ac.uk).

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INTRODUCTION

Color is a characteristic of architectural stone that influences its use in a particular building. When exposed outdoors stone changes in color, which can be aesthetically beneficial, but is sometimes unpleasant. These changes are the consequence of either staining by foreign materials or discoloration by a change in the natural stone constituents.[1] The word discoloration normally refers to a permanent loss of color. The loss of color may or may not be permanent, so here we use the words *color change*, *blackening* or *yellowing* to avoid any suggestions about the reversibility of the changes.

A developing literature is available to describe the changes of material using colorimetric measurements.[2–8] Color differences are frequently measured using the CIELAB and CIELCH systems because they better represent human sensibility to color than other color encoding systems. It is well-known that the variable L^* represents lightness or luminosity, and a^* (red-green) and b^* (yellow-blue) are the chromatic coordinates. The attributes of chroma (C^*_{ab}: saturation or color purity) and hue (h_{ab}: referring to the color 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^* and h are more sensitive to changes on a^* or b^* depending on the original color of the material. For instance, creamy or yellowish building stones have b^* values much higher than a^*. When that is the case, C^* is strongly influenced by the coordinate b^*, whereas h is very sensitive to changes in a^*.

Color changes in building stones are produced by a wide range of environmental conditions, such as natural weathering, urban pollution, growth of organisms, bird droppings, fire damage, salt efflorescence, building defects, conservation treatments such as cleaning and ageing of coatings, and so forth. *Surface roughness*, surface

TABLE I. Stone characteristics and test methods.

Test	Stone characteristics	Method
Sulfur dioxide attack	Experiment 1: Yellowish ornamental low and medium porosity limestones with different surface finish, from Levante[14]: *Crema Cenia* honed (CCH) and flamed (CCF), *Crema Ambar* honed (CAH) and flamed (CAF) and *Crema Miel* honed (CM).	Exposure to SO_2 attack in a climatic chamber HERAEUS. Experiment 1: Concentration, 2 ppm; RH = 90%; $T = 25°C$; length of test: 8 days.
	Experiment 2: Porous monumental limestones[15]: reddish *Piedramuelle Roja* (PR) from Oviedo, white *Hontoria (H)* from Burgos yellowish and *Sta. Pudia* (SP) from Granada.	Experiment 2: Concentration, 3 ppm; RH = 90%; $T = 25°C$; length of test: 5 weeks.
Blackening	Experiment 3: Porous monumental stones[16]: white *Hontoria* (H-E3) limestone, *Hontoria* treated with a silane (HT) from Burgos and whitish Laspra (L-E3) dolostone from Oviedo.	Exposure at urban sites sheltered from rain-fall, horizontal surfaces. Experiment 3: Cathedral of Burgos (1 year: 1996–1997).
	Experiment 4: Porous monumental stones[16]: white *Hontoria* (H-E4) limestone from Burgos, yellowish *Piedramuelle Amarilla* (PA) limestone from Oviedo and whitish *Laspra* (L-E4) dolostone from Oviedo.	Experiment 4: Cathedral of Oviedo (7 months: 1997).
Laser irradiation on clean surface	Experiment 5: Porous monumental limestones[17]: reddish *Piedramuelle Roja* (PR) from Oviedo, white *Hontoria* (H) from Burgos and yellowish *Sta. Pudia* (SP) from Granada.	Q-switch ND:YAG 1604 nm laser irradiation on dry clean stone surfaces at 1.47 J cm^{-2}.
	Experiment 2: Low porosity ornamental limestones from Asturias[18]: pinkish *Griotte* (G), reddish *Rojo Cornellana* (RC) and the grayish *Gris Rañeces* (GR) and *Gris Vis* (GV).	Experiments 5 and 6: Same conditions.[17]

All stones are Spanish limestones.

finishes, or weathering can affect the color parameters, mainly lightness (L^*) and chroma (C^*) but not hue.[2] Different surface moisture loadings also give rise to color differences within the same stone. *Conservation treatments* represent an imposed alteration to the color of building stones, dependent on the treatment and original stone color.[3] Usually organic protective treatments on light colored *creamy* limestones result in a decrease in L^* and an increase in b^*,[4] although sometimes changes in a^* can also be detected.[5] *Biodecay* changes the color parameters depending on the bioreceptivity of the stone, climatic factors, and type and association of organisms.[6,7] *Heating* at high temperatures can alter the a^* parameter because of changes in Fe-rich components.[8] *Saline mist* exposure tests show the expected whitening during the salt exposure, which translates to changes in parameters, but still somewhat dependent on the original color of the stone (University of Oviedo report for Dragados OSHSA U.T.E).

This article investigates the impact of some weathering and conservation processes on the color of building limestone: sulfur dioxide (SO_2) attack, blackening or darkening in urban environments and laser irradiation for stone cleaning. These are all contemporary processes that alter the color of building stones. Sulfur dioxide can lead to alteration and changes on carbonate building stone surfaces even at extremely low atmospheric concentrations. Darkening of light-colored stones through the deposition of fine dark particles in urban and trafficked areas causes aesthetic damage and public discontent.[9,10]

The use of laser cleaning in conservation can induce changes on stone surfaces depending both on the laser and mineral characteristics.[11,12] The Q-switched Nd:YAG laser at the fundamental 1064 nm wavelength is the most common type of laser used for stone cleaning, and it is currently adopted to remove black crusts and other deposits. This pulsed laser does not make contact with the surface and the light pulses often have a self-limiting character, which allows elimination of dark deposits without damaging the underlying stone. However, this last characteristic is dependent on the chemical and mineralogical composition of the stone. Specifically, iron is a highly absorbent element at the 1064 nm wavelength. Chromatic modifications in laser-treated dry-stone surfaces are usually attributed to changes in the oxidation state of iron compounds.[11] Moreover, laser cleaning could also result in variations in surface roughness[13] that could alter stone color.[2] The damage thresholds for stone also depend on the physical state of the stone surface (e.g. wetness), pulse energy, duration, and frequency of the irradiation.

The main purposes of this work are:

- To study the relevance of environmental conditions and conservation methods in changing the color of building limestone.
- To determine direction of the change L^*, a^*, and/or b^* as it is reflected in changes in lightness, chroma, and/or hue.
- To establish the influence of the original color of the natural stone and the consequence of its chemical nature and surface finish.

Here we focus both on the direction and relative magnitude of the changes. Relative changes are important because, for example, a change in half a unit on a white stone could represent less than 1% variation in L^* but more than 30% in a^*. In this way, even if the variation lies below the limit of perceptibility, it can be indicative of reactions in the stone.

MATERIALS AND METHODS

We compared the changes on the color coordinates of ornamental and monumental limestones from measurements

TABLE II. Color characteristics of the stones prior testing.

Stone	Experiment	L^*	a^*	b^*	C^*_{ab}	h_{ab}	Munsell approximation Hue	Munsell approximation Value	Munsell approximation Chroma	Lightness	Chroma	Hue	Visual
Sulfur dioxide attack													
Piedramuelle Roja (PR)	2	59	11	20	23	62	5YR	6	4	Medium	High	Red-yellow	Red
Crema Cenia F (CCF)	1	67	5.2	13	14	69	7.5YR	7	2–3	Medium	Medium	Red-yellow	Yellowish
Crema Cenia H (CCH)	1	61	6.5	17	19	69	7.5YR	6	3	Medium	High	Red-yellow	Yellowish
Crema Ambar F (CAF)	1	71	5.0	16	17	72	7.5YR	7	3	Medium	Medium	Red-yellow	Yellowish
Hontoria (H)	2	90	1.6	7.1	7.3	77	10YR	9	1	Light	Low	Yellow	White
Crema Ambar H (CAH)	1	65	3.7	21	22	80	10YR	7	4	Medium	High	Yellow	Yellowish
Crema Miel (CM)	1	74	2.2	16	16	82	10YR	7	3	Medium	High	Yellow	Yellowish
Sta. Pudia (SP)	2	81	1.0	13	13	86	2.5Y	8	2	Light	Medium	Yellow	Yellowish
Blackening													
Treated Hontoria (HT)	3	88	2.1	8.7	9.0	77	10YR	9	1	Light	Low	Yellow	Whitish
Hontoria (H-E3)	3	90	1.7	7.3	7.5	77	10YR	9	1	Light	Low	Yellow	White
Hontoria (H-E4)	4	90	1.7	8.2	8.4	78	10YR	9	1	Light	Low	Yellow	White
Piedramuelle Amarilla (PA)	4	81	3.3	18	18	80	10YR	8	3	Light	High	Yellow	Yellow
Laspra (L-E3)	3	86	1.1	9.5	9.6	83	2.5Y	9	1	Light	Low	Yellow	Whitish
Laspra (L-E4)	4	89	0.56	7.7	7.7	86	2.5Y	9	1	Light	Low	Yellow	Whitish
Laser irradiation on clean surfaces													
Griotte (G)	6	48	9.1	7.4	12	39	7.5R	5	2	Dark	Medium	Red	Dark Pink
Piedramuelle Roja (PR)	5	59	12	21	25	61	5YR	6	4	Medium	High	Red-Yellow	Red
Rojo Cornellana (RC)	6	53	5.6	14	15	68	7.5YR	5	2–3	Dark	Medium	Red-Yellow	Reddish
Gris Rañeces (GR)	6	44	0.58	2.2	2.3	75	10YR	4	1	Dark	Low	Yellow	Dark Gray
Gris Vis (GV)	6	55	1.7	6.8	7.1	77	10YR	5–6	1	Dark	Low	Yellow	Light Gray
Hontoria (H)	5	90	1.5	7.3	7.4	78	10YR	9	1	Light	Low	Yellow	White
Sta. Pudia (SP)	5	84	0.67	13	13	87	2.5Y	8	2	Light	Medium	Yellow	Yellowish

Stones are mainly monochromatic. We summarize mean values to two significant figures. No standard error is shown. In each test stones are ordered by hue. Munsell notation was approximated from L^*, a^*, b^*, C^*_{ab}, and h_{ab} values. The visual column summarized authors' visual approximation. Stones were classified in three relative groups of lightness, chroma and hue from cluster analysis of L^*, C^*_{ab}, and h_{ab}. Note that chroma values are low in any case.

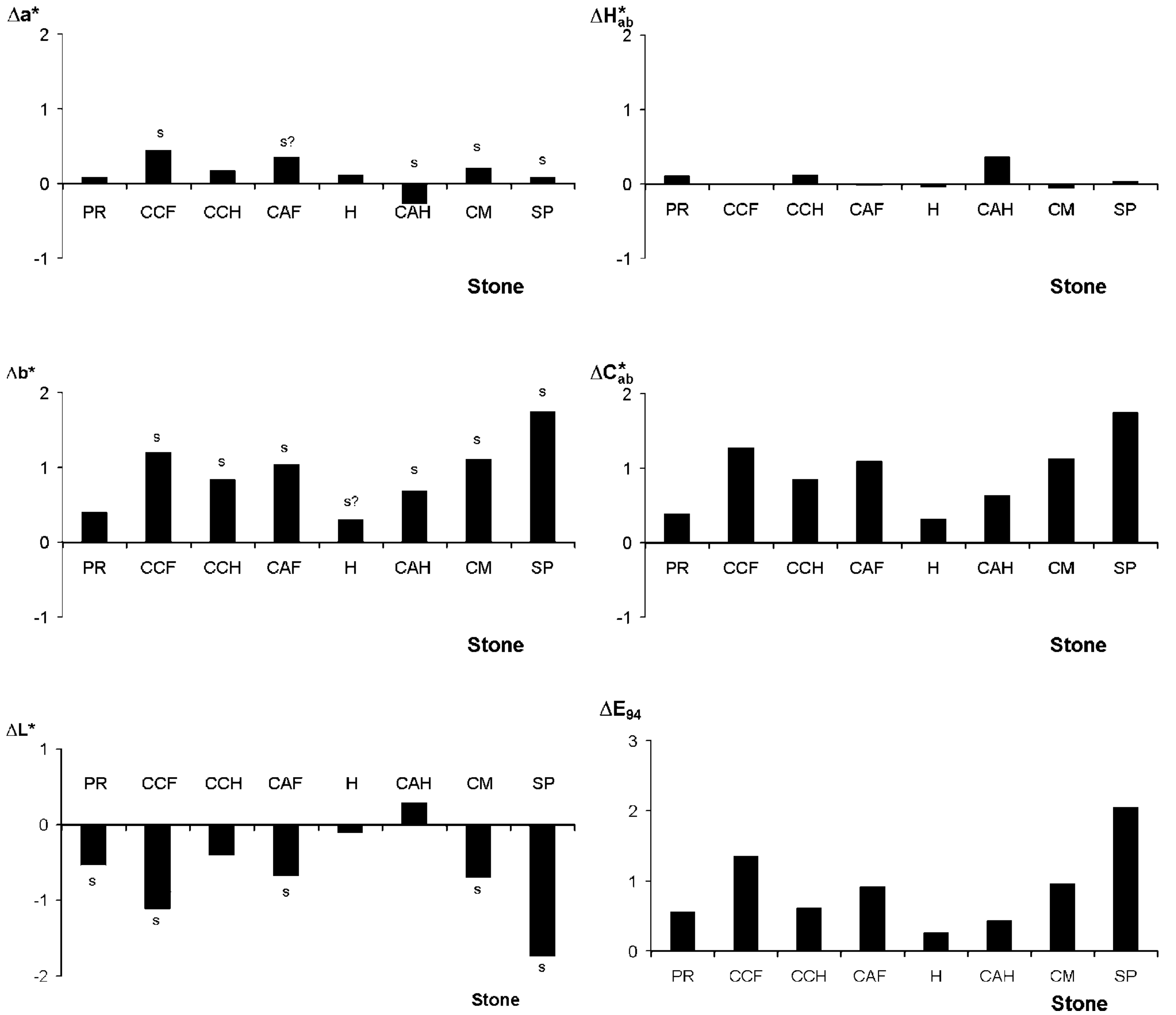

FIG. 1. Color changes under sulfur dioxide attack (Experiments 1 and 2). Stones are ordered by hue values (lower to the left and higher to the right of the plot).

made within different research projects on weathering and conservation. The experiments reported here focused on SO_2 attack, blackening in urban environments and laser irradiation for stone cleaning.[14–17] Color has been quantitatively measured with a MINOLTA CR-200 colorimeter prior, during and after laboratory and onsite trials on different-colored carbonate stones: whitish, grayish, yellowish, pinkish, and reddish. The selected limestones were mostly monochromatic, uniform in color, and did not exhibit notable surface color variation. Some of the limestones are used as ornamental material in modern construction, and others were used in historic buildings. The colorimetric measurements were objective, accurate, and able to detect small variations imperceptible to the unaided eye. Laboratory tests made possible the investigation of color changes induced by a specific process without further external interference, whereas onsite experiments were useful for measuring real color changes in ambient environments. Tables I and II summarize the experimental method and the color characteristics of the stones under investigation. Stones were grouped in the tables according to the experimental method. They were also classified by lightness (light, intermediate, dark), hue (red, red-yellow, yellow), and chroma (low, medium, high). Because of different project requirements, not all or the same stones were subjected to the three experiments. Therefore, care must be taken when analyzing the results. However, in most cases we have used stones of similar color characteristics and mineralogical nature, hence they are reasonably comparable.

Color was measured prior, during and after testing on nominal $50 \times 50 \times 10$ mm^3 stone specimens, with the MINOLTA CR-200 colorimeter using the Illuminant C, beam of diffuse light of 8-mm diameter, 0° viewing angle geometry, specular component included and spectral response closely matching the CIE (1931) standard observer curves. A representative color and reduced error because of color variability was gained by using the dif-

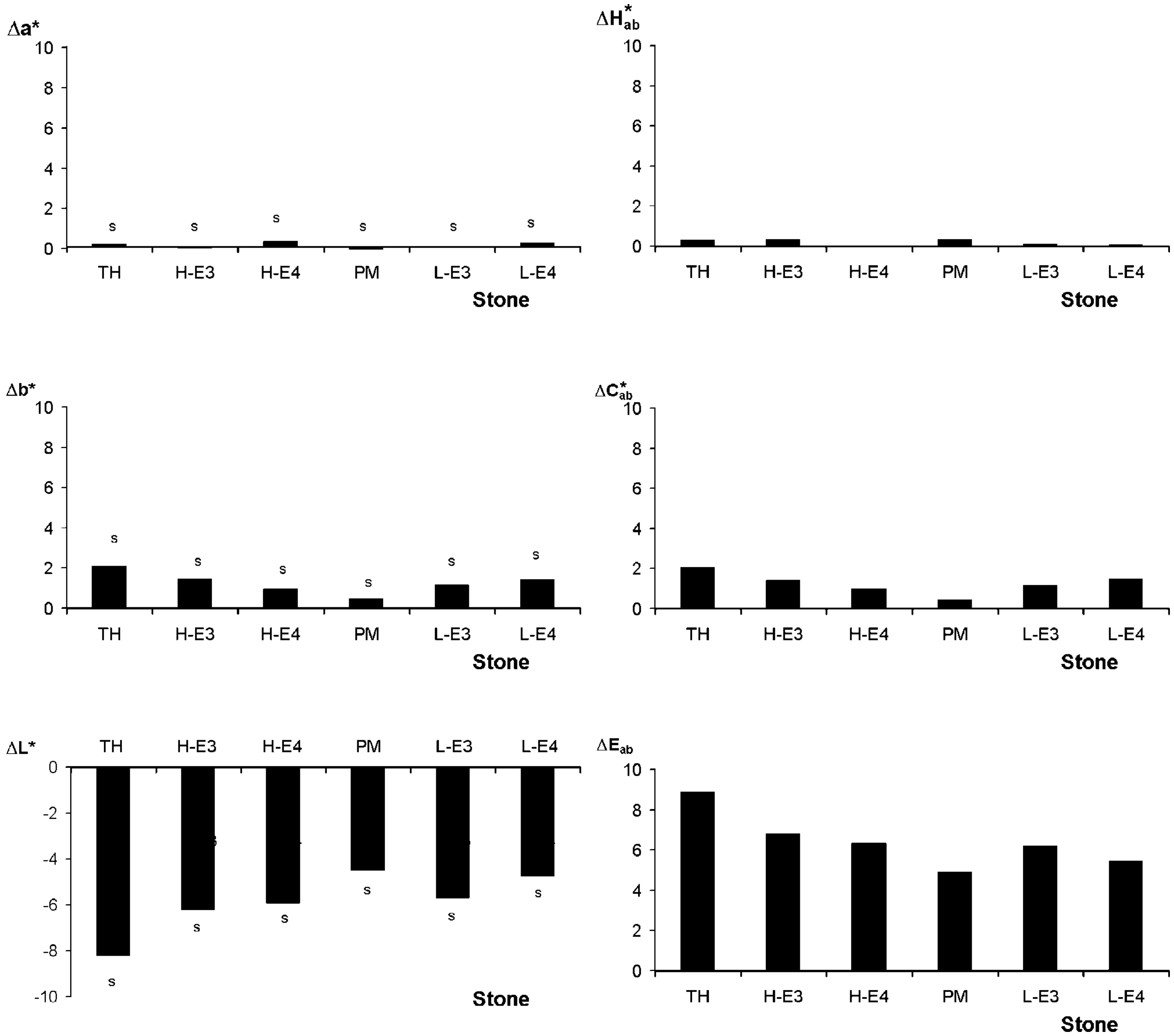

FIG. 2. Color changes after four months for sheltered exposure in urban background environments: Burgos (Experiment 3) and Oviedo (Experiment 4). Stones are ordered by hue values (lower to the left and higher to the right of the plot). The letter s indicates statistically significant changes at a 0.05 level.

ferences between two successive cumulative averages of the parameters L*, a* and b*.[14,19] Three or four stone specimens were used for each test and the number of shots for specimen varied from 9 to 16.[14–17]

The CIELAB and CIELCH systems were used here to represent color differences (EN ISO 105-J03: 1997 recommendations[20]), and to compare the relative importance of each parameter in the color change. We also refer occasionally to the *total* color difference CIE 1994[21] $\Delta E_{94} = \sqrt{\left(\frac{\Delta L^*}{k_L S_L}\right)^2 + \left(\frac{\Delta C^*_{ab}}{k_C S_C}\right)^2 + \left(\frac{\Delta H^*_{ab}}{k_H S_H}\right)^2}$ and an approximate corresponding gray scale rating (GSc) according to EN ISO 105-A05: 1997.[22] Gray scale values indicate human visual discrimination to color variation and vary from 5 (nonvisible changes) to 1 (very strong changes) and relate to intervals of ΔE from <0.40 to ≥ 11.60.

Experimental Method

Sulfur Dioxide Attack

The tests were undertaken to study the effects of the dry deposition of SO_2 on ornamental and monumental carbonate stones of different color (whitish, yellowish, and reddish) and surface finish. The specimens were subjected to controlled SO_2 atmospheres in a climate chamber. Color measurements were taken before and after exposure. Sulfur dioxide concentration was 2–3 ppm and the temperature and relative humidity were 25°C and 90%, respectively (Experiments 1 and 2, Tables I and II). Time of exposure varied from 1 to 5 weeks, depending on the purpose of the experiment.[14,15] We didn't use the more aggressive alternative experiments such as immersion in H_2SO_4 to avoid the effect wet deposition (acid rain) as well as material loss

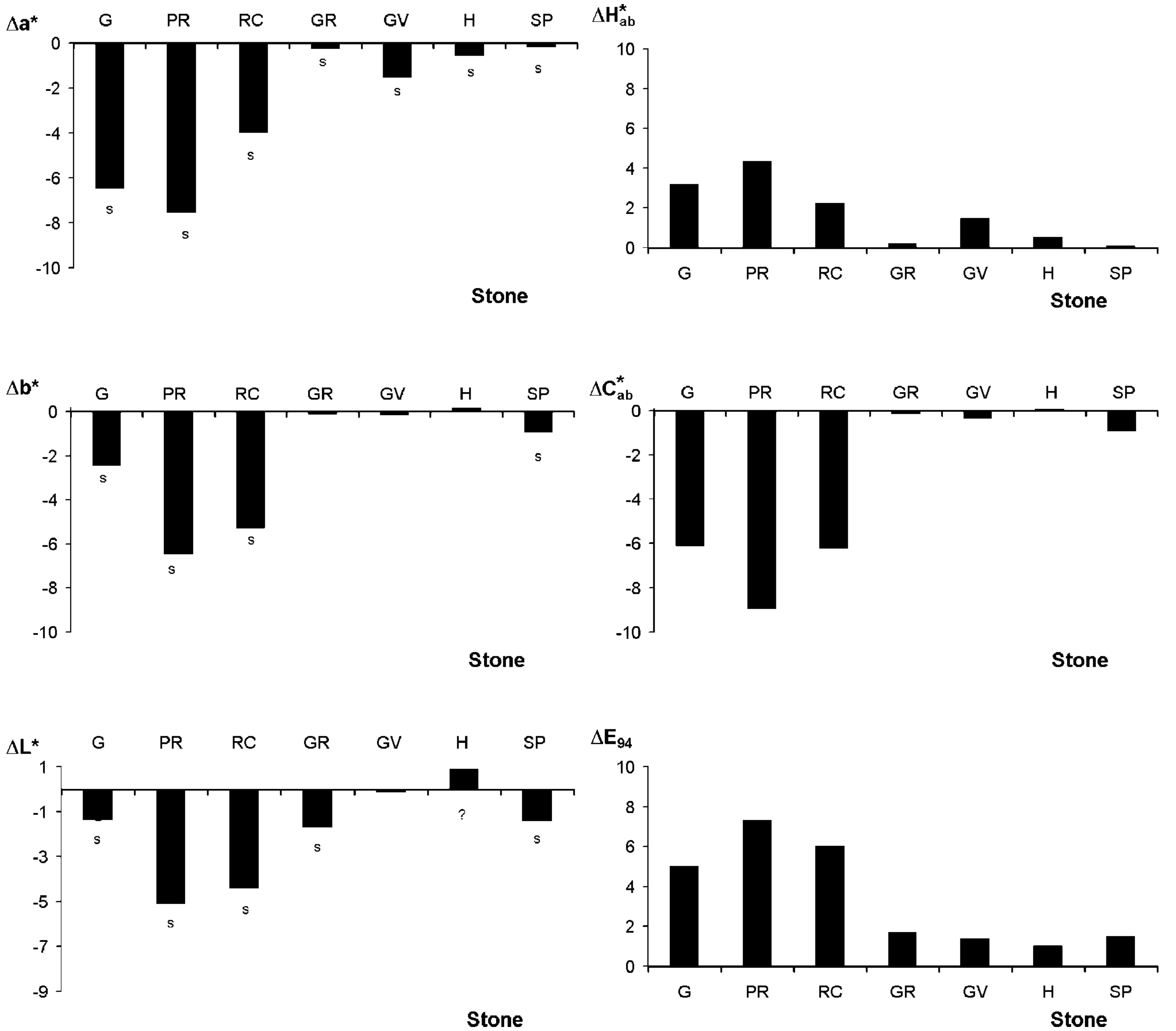

FIG. 3. Color changes of stones subjected to the1064 nm laser irradiation test (Experiments 5 and 6). Stones are ordered by hue values (lower to the left and higher to the right of the plot). The letter s indicates statistically significant changes at a 0.05 level. Changes in *b**, *C**, and *L** are perhaps inconsistent for *Hontoria* due to anomalous low values in one of the pretested samples (Fig. 5).

because of an intense dissolution[2] and the experimental SO_2 concentrations adopted are quite high.

Blackening-Darkening

Onsite experiments studied both gas and particulate deposition in urban environments. Samples of whitish and yellowish limestone were exposed in urban background areas, sheltered from the direct action of rainfall.[16] The sites were located at the Cathedrals of Burgos (1 year-exposure) and Oviedo (7 months), both in Spain (Experiments 3 and 4, Tables I and II). Color was monitored once and occasionally twice at month during the exposure period.

Laser Cleaning

The effect of laser radiation on the color of limestone of different shades—whitish, grayish, yellowish and reddish—was examined in laboratory experiments through the irradiation on clean-dry stone surfaces with a Q-switched Nd:YAG laser at the fundamental 1064 nm wavelength.[17] The stone color was measured prior and after irradiation at the maximum fluence or energy density provided by the device (1.47 J cm^{-1})—Experiments 5 and 6, Tables I and II.

In all cases, the statistical significance of the color changes was evaluated by the Mann–Whitney nonparametric test. Color changes were plotted, for an easier visualization, as increments and also as *real* values as scatter

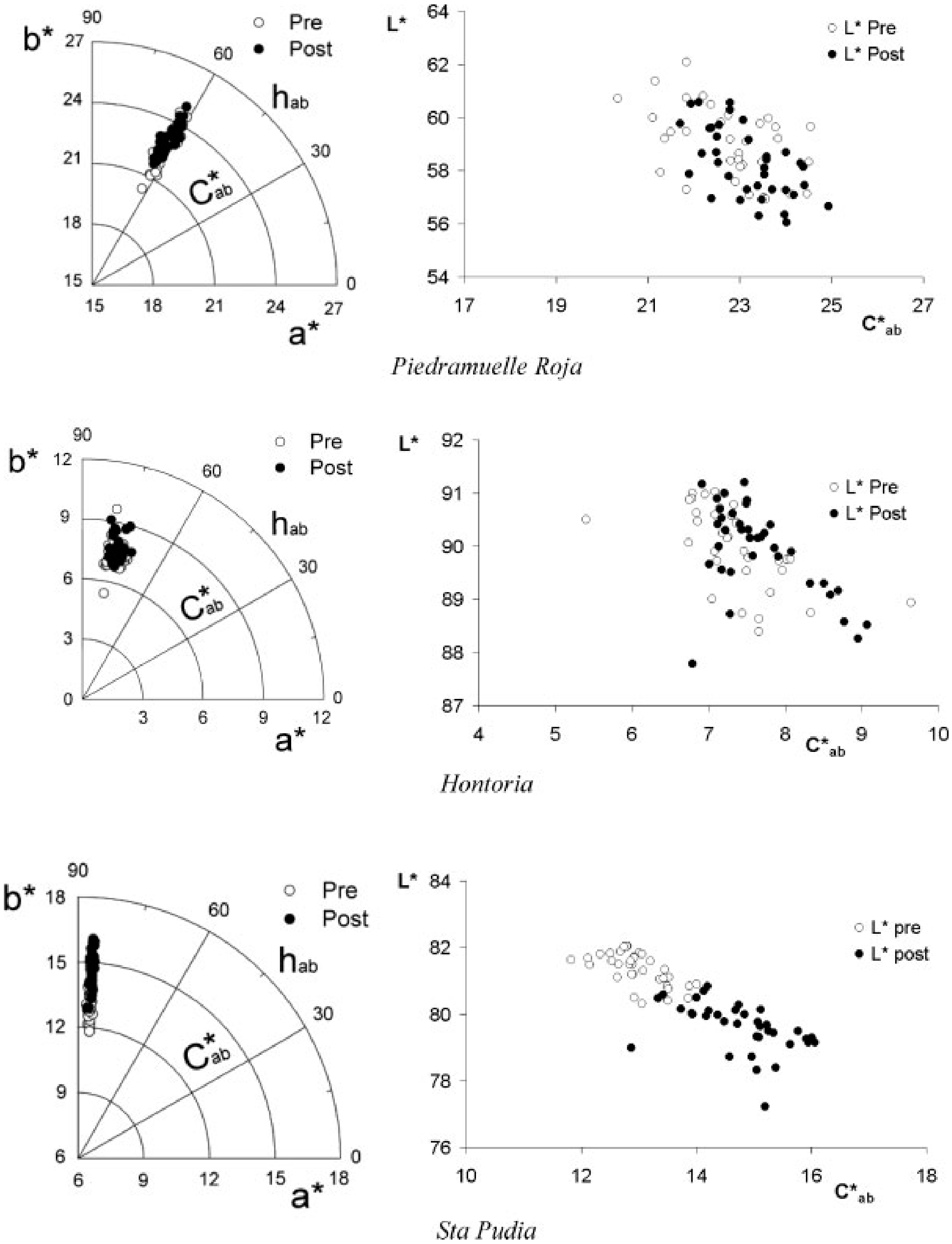

FIG. 4. Polar and Cartesian scattergrams for *Hontoria* (white), *Sta. Pudia* (yellowish), and *Piedramuelle Roja* (reddish) stones subjected to sulfur dioxide exposures (Experiment 2).

diagrams in both polar and Cartesian coordinates (Figs. 1–6).

RESULTS

The main color changes for each test are summarized in Table III and Figs. 1–6. We have used bar-graphs to plot the mean changes of the L^*, a^*, and b^* parameters for all the stones (statistically significant differences at a 0.05 level are indicated with an *s*). In Figs. 1–3, ΔL^*, Δa^*, and Δb^* were plotted to show the location of the color changes and ΔL^*, ΔC^*_{ab}, Δh_{ab}, and ΔE_{94} to investigate any possible aesthetic implication.

As an example and for further comparison, Figs. 4–6 show scattergrams for three stones: *Piedramuelle Roja* (reddish), *Hontoria* (white), and *Sta. Pudia* (yellowish) subjected to SO_2 exposure (Experiment 2) and laser irradiation (Experiment 5) and *Hontoria* (white), *Piedramuelle Amarilla* (yellowish) and *Laspra* (whitish) after the four first months of exposure to Oviedo urban-background (Experiment 4).

Finally, in Table IV and Fig. 7 we summarize the most distinctive changes in each experiment.

Sulfur Dioxide Attack

The deposition of SO_2 during the laboratory tests yielded, in most cases, a statistically significant increase in the b^* coordinate and consequently in the chroma on light-yellowish limestone surfaces. The parameter L^* usually shows a decrease, whereas a^* exhibited only significant changes in some cases, generally an increase[14,15]

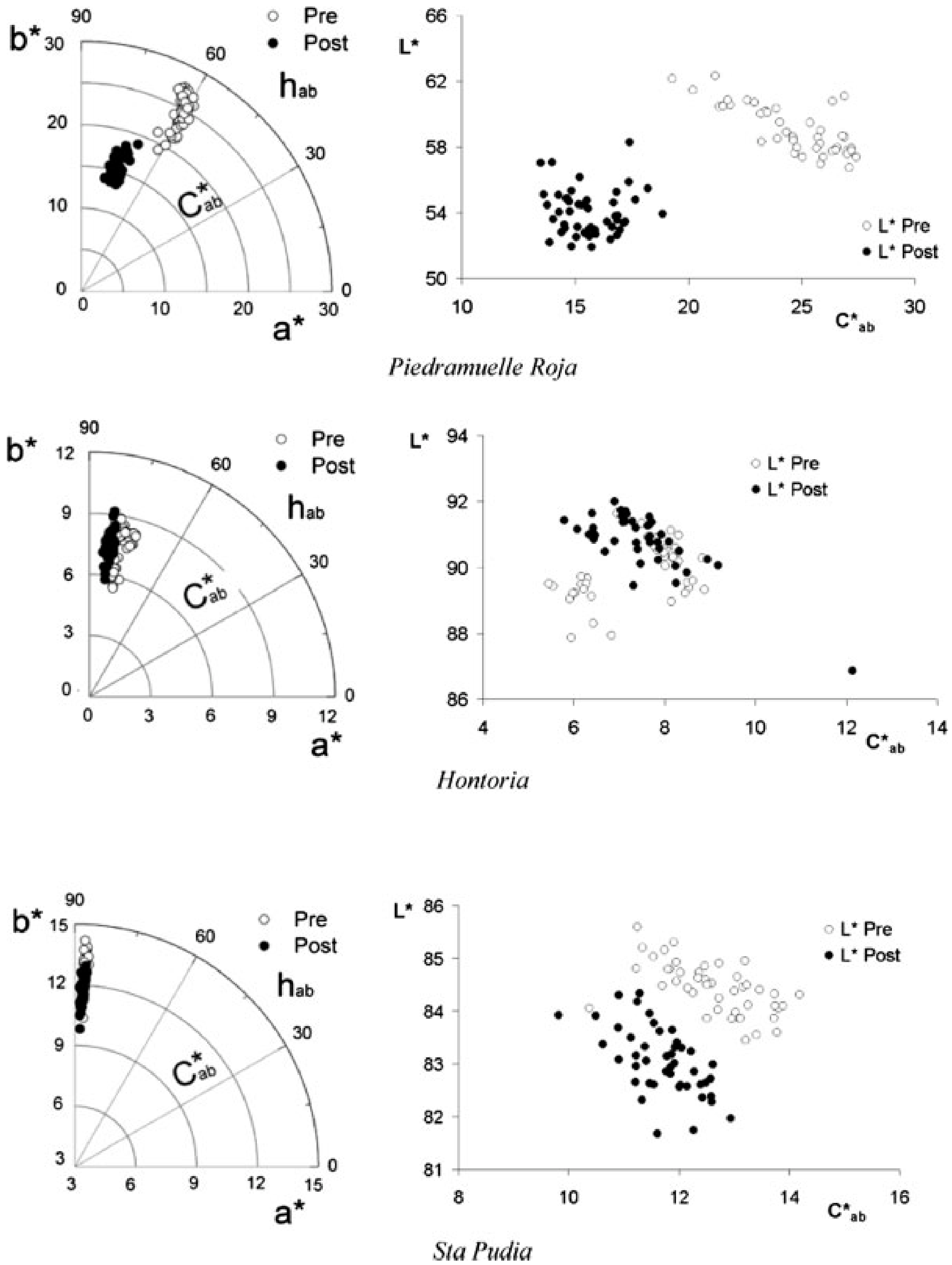

FIG. 5. Polar and Cartesian scattergrams for *Hontoria* (white), *Sta. Pudia* (yellowish), and *Piedramuelle Roja* (reddish) stones subjected to a 1064 nm laser irradiation test (Experiment 5). Note the different L^* and C^*_{ab} values of several points (from one of the specimens) of pretested *Hontoria*.

(Fig. 1). However, the color change could not be detected visually as, under these test conditions, it was below the perceptibility threshold[2] (i.e. $\Delta E_{94} < 3$). Benavente *et al.*,[2] referring to Berns[23] and Völz,[24] mention three units as the perceptibility limit generally taken in the CIELAB space. Other stones, such as dark green gneiss and serpentinites, were reported not to exhibit any measurable change under same test conditions.[14]

Changes in b^* units are sometimes only slightly higher than changes in L^*. However, original values of L^* are much higher implying that the sulfation process is potentially more relevant to shifts in b^*. Increases in b^* and chroma seem to be clearer in yellowish stones; note that white *Hontoria* and reddish *Piedramuelle Roja* exhibited lower measurable changes than the ornamental limestones (Fig. 1), even though they were subjected to a more aggressive and longer test (Experiments 1 and 2, Table I). However, the surface roughness and porosity can condition SO_2 uptake.[14] For example, *Sta. Pudia* stone used in Experiment 2, has a much higher porosity than *Piedramuelle roja*, and the specific surface is an order of magnitude higher than *Hontoria*.[15] As shown in Fig. 1 and Table III, changes do not seem to be large enough to be aesthetically relevant, although that might not be true in more aggressive environments.

Blackening

The deposition of atmospheric urban pollutants on light colored carbonate stones during onsite experiments led mainly to changes in L^* (a decrease) and b^* (an increase) as shown in Figs. 2 and 6. Stone darkening or blackening

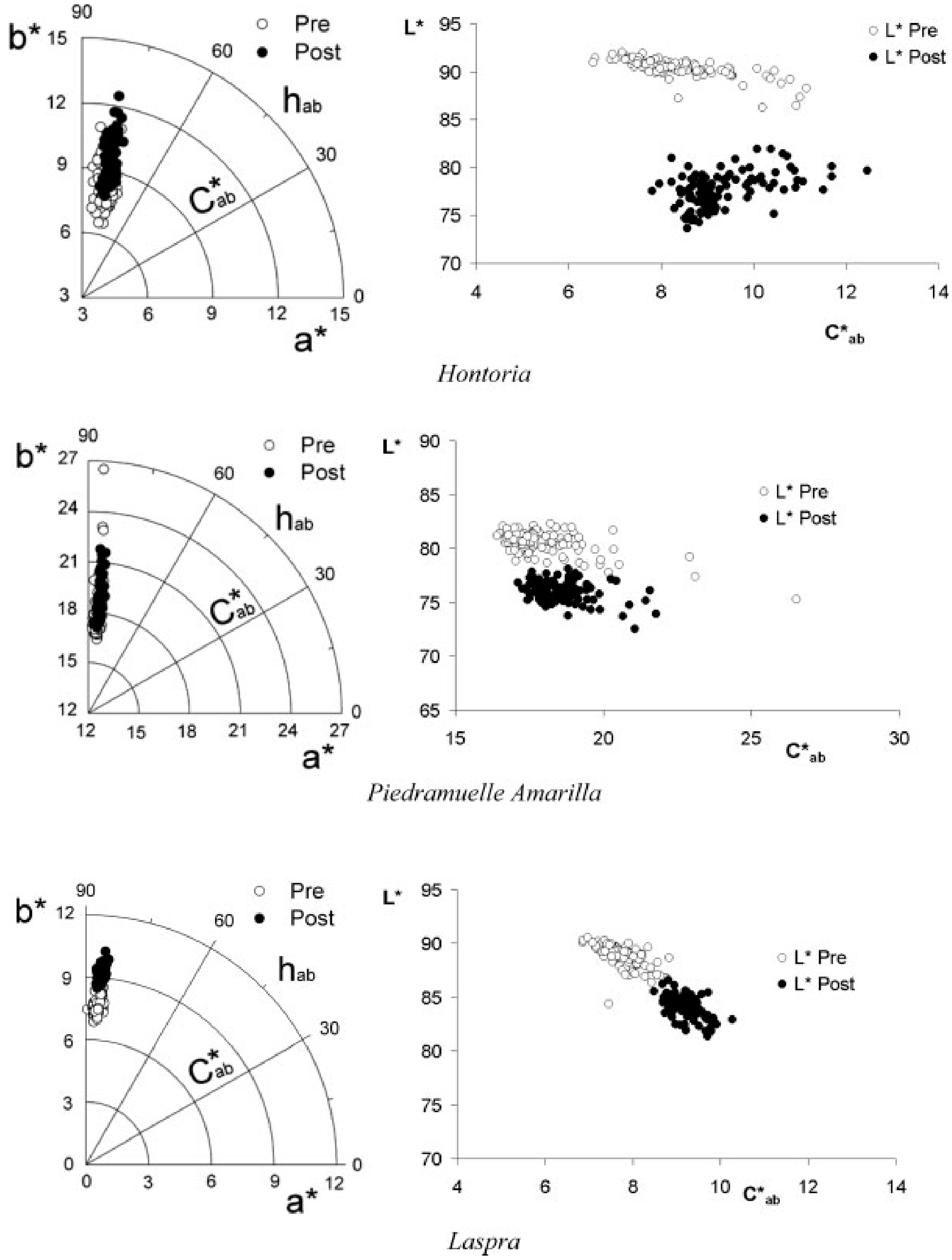

FIG. 6. Polar and Cartesian scattergrams for *Hontoria* (white), *Laspra* (withish), and *Piedramuelle Amarilla* (yellowish) after four months of exposure to Oviedo urban-background (Experiment 4).

was visually noticeable during the exposure. The contribution to the chromatic coordinates (especially a^*) is small compared with the decrease in lightness, which is in this case the main driver for aesthetic implications.[10] In Fig. 8 we have plotted the evolution of L^*, a^*, and b^* in *Hontoria* stone during a one-year sheltered exposure in the Burgos urban background environment (Experiment 3). Decreases in L^* (blackening) and increases in b^* (yellowing) follow exponential expressions such as $L^*_t = L^*_o - (L^*_o - L_\infty) \cdot [1 - \exp(-kt)]$ or $b^*_t = b^*_o + (b^*_o - b_\infty) \cdot [1 - \exp(-kt)]$; where L^*_t or b^*_t are L^* or b^* at time t; L^*_o or b^*_o the initial color of the stone and $(L^*_o - L^*_\infty)$ or $(b^*_o - b^*_\infty)$ the total change. The value k, time constant, indicates the rate of the process. The reciprocal $1/k$ might be regarded as a kind of folding time or more familiarly $\ln(2)/k$, would be the half life for the process.[25] Figure 8 shows a shorter folding time for the b^* coordinate hinting a faster rate for the yellowing (probably sulfation) process.

Laser Cleaning

The experiments show that the a^* coordinate (red-green) is sensitive to laser radiation. Reddish limestones with higher a^*-values exhibit larger color changes, always involving a decrease in a^*. This variation in a^* also lead to changes in h (hue or color) that shifts to the values nearer to 90 (yellow). Coordinates L^* and b^* can also show changes, always a decrease, mainly in more chromatic stones, which translates into a general darkening and decrease in chroma (Figs. 3 and 5). The moderately chromatic, but low-a^* *Sta. Pudia* stone shows a slight vis-

TABLE III. Color characteristics of the stones after testing.

Stone	Experiment	L^*	a^*	b^*	C^*_{ab}	h_{ab}	ΔE^*_{94}	GSc[22]	Munsell approximation Hue	Value	Chroma	Potential aesthetic implications[a]
Sulfur dioxide attack												
Piedramuelle Roja (PR)	2	59	11	20	23	62	0.56	4.5	5YR	6	4	Very low
Crema Cenia F (CCF)	1	66	5.6	15	16	69	1.4	4	7.5YR	7	3	Low
Crema Cenia H (CCH)	1	60	6.7	18	19	70	0.61	4.5	7.5YR	6	3	Very low
Crema Ambar F (CAF)	1	70	5.3	17	18	72	0.92	4.5	7.5YR	7	3	Very low
Hontoria (H)	2	90	1.7	7.5	7.6	77	0.26	5	10YR	9	1	None
Crema Ambar H (CA-H)	1	66	3.4	22	22	81	0.44	4.5	10YR	7	4	Very low
Crema Miel (CM)	1	74	2.4	17	17	82	0.96	4.5	10YR	7	3	Very low
Sta. Pudia (SP)	2	80	1.1	15	15	86	2.1	4	2.5Y	8	2	Low
Blackening												
Treated Hontoria (H-T)	3	80	2.2	11	11	78	8.9	1.5	10YR	8	2	(Very) high
Hontoria (H-E3)	3	84	1.6	8.7	8.9	80	6.8	2	10YR	8	1	High
Hontoria (H-E4)	4	84	2.0	9.1	9.3	78	6.4	2	10YR	8	1	High
Piedramuelle Amarilla (PA)	4	76	3.0	18	19	81	4.9	2.5	10YR	8	3	High
Laspra (L-E3)	3	80	1.1	11	11	84	6.2	2	2.5Y	8	2	High
Laspra (L-E4)	4	84	0.75	9.2	9.2	85	5.5	2.5	2.5Y	8	1	High
Laser irradiation on clean surfaces												
Griotte (G)	6	46	2.6	5.0	5.6	62	5.0	2.5	5YR	5	1	High
Piedramuelle Roja (PR)	5	54	4.4	21	16	74	7.4	2	7.5YR	5	3	High
Rojo Cornellana (RC)	6	49	1.6	8.5	8.6	79	6.0	2	10YR	5	1	High
Gris Rañeces (GR)	6	42	0.35	2.1	2.2	81	1.7	4	10YR	4	1	Low
Gris Vis (GV)	6	54	0.17	6.7	6.7	89	1.4	4	2.5Y	5	1	Low
Hontoria (H)	5	91	0.98	7.4	7.5	82	1.0	4.5	10YR	9	1	Very low
Sta. Pudia (SP)	5	83	0.52	12	12	87	1.5	4	2.5Y	8	2	Low

[a] Authors' opinion. See notes in Table II.

ual darkening, evidence of higher absolute changes in L^* and b^*. Other types of crystalline carbonate materials such as veined marbles, for instance, are reported to darken and suffer some chromatic shifts to the yellow.[26]

DISCUSSION AND CONCLUSIONS

Subtle color changes in light colored limestones are driven by a range of environmental and conservation factors. Deposition of urban air pollutants leads to an increase in the *yellowness* (i.e. an increase in chroma or saturation of the yellow color; Figs. 1 and 4). This and previous research indicates that this chroma may later be lost as the surface becomes covered by dark particles.[27,28] Changes in b^* are faster (although of smaller magnitude), which may mean that sulfation occurs more rapidly than the darkening process[28] (Fig. 8). Changes in chroma are also caused by other processes, such as the oxidation of trace iron in the stone, mineralogical changes, or polymerization of organic compounds[29] or even weathering and increases in surface roughness.[2] Today urban atmospheric deposits are richer in oily organics relative to elemental carbon, so particularly under oxidation, they are liable to produce brownish-yellowish coatings on urban building limestones.[30,31,32]

Pollution driven processes seem to increase chroma. The changes may be subtle, but they are important because they alter the light color of the original stone. However, to what extent is this viewed as a patination raise subtle questions that are worth further research both from the point of views of aesthetics and chemistry.

Laser irradiation at 1064 nm affects the red component (a^*) of limestones, very noticeably if they already possess a reddish color (Figs. 3 and 5). The coordinate b^* is also affected. This radiation is strongly absorbed by iron, the

TABLE IV. Relative colour changes on architectural limestones.

Process	Most distinctive change Rectangular	Polar	Possible cause	Colour change process	Main affected stones	Aesthetics implications
Sulfur dioxide attack	b^*	Chroma	SO_2 reaction and deposition	Deposition and reaction	Yellowish limestones	Usually negligible
Blackening	L^*	Lightness	Mainly particle deposition	Deposition	Whitish limestones	High
Laser[a] irradiation on clean surfaces	a^*, b^*	Hue, chroma	Chromophorous elements change; mainly Fe-compounds	Reaction	Reddish limestones	Scarce to high

[a] The "yellowing" effect related to laser cleaning of black crust of whitish stones could be mainly a staining effect rather than a permanent colour change because of the mineral response mentioned earlier. No change in surface roughness considered here.

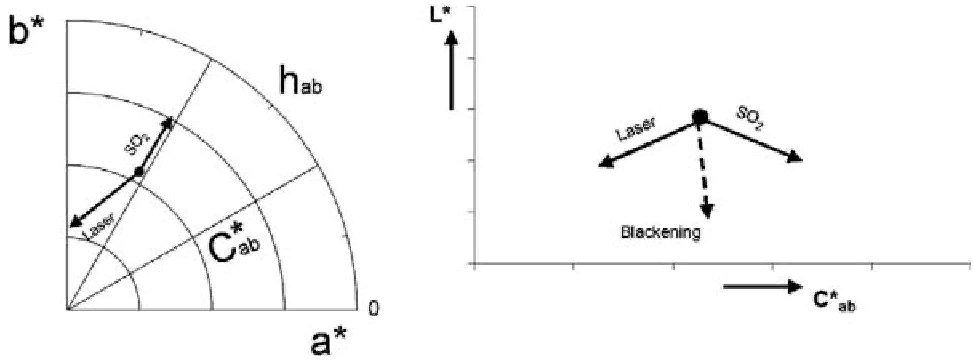

FIG. 7. Polar and Cartesian scattergrams summarizing most distinctive changes in each experiment.

element that has the strongest influence on the color of limestone. It probably arises from thermal reactions in iron-rich minerals that give this dramatic change in color. Other authors[13] have found mechanical damage and roughening of marble surfaces at irradiative fluences lower than that used in this research. Laser clean can also increase surface roughness, but the expected changes would be towards lighter and more saturated tones.[2] The color changes because of the chromophorous minerals seem to be, in this case, so strong that could conceal any possible small changes because of increases in surface roughness.

The reported yellowing displayed by some light colored carbonate substrates after the laser cleaning may have an additional cause.[12,33,34] The chromatic effect can appear when the black crust is removed and not merely through exposure of clean substrates to laser light. Such yellowing might originate from water-soluble organic compounds from soot that have migrated into the underlying porous stone. These could be immobilized by the formation of calcium complexes, which are not effectively removed by Nd: YAG 1064 nm radiation and remain as a yellow patina near the stone surface.[33] Portgieter-Vermaak *et al.*[34] also suggested that the darker-yellowish color of limestones cleaned at that wavelength was due to higher concentrations of gypsum, as well as iron oxide and calcium oxalate. Such cleaning could also uncover a surface previously made yellow by reactions with atmospheric sulfur dioxide or organic deposition.

Differences in the original color of the stone affect the way color changes. The more intense the natural color, the greater the chromatic changes are when pollutants are deposited or laser radiation interacts with the stone. However, the direction of change in the color-parameter affected by the particular process is the same (Figs. 1–6).

It always been apparent that in an atmosphere heavily polluted with soot, the main changes to light-colored stones are a decrease in the parameter L^* (darkening or blackening). This has important aesthetic and social implications.[9,10] However, in the near future it may be that in cleaner urban atmospheres, perhaps more dominated by organic pollutants, a yellowing process could become of greater concern.[32]

Aesthetic implications depend on the direction and the magnitude of color change. Earlier work[10] suggests that when visitors (not trained in color vision) are asked to describe the color of a limestone building, quite naturally they do not see it in terms of bright colors, but use words such as *cream*, *gray*, and so forth. When offered a Munsell chart to aid identification of the color of a building they are likely to choose *chips* that reflect large changes in darkness or lightness rather than hue or chroma. Thus the visitor is more likely to express an opinion that a building is too dark (or occasionally too light in terms of

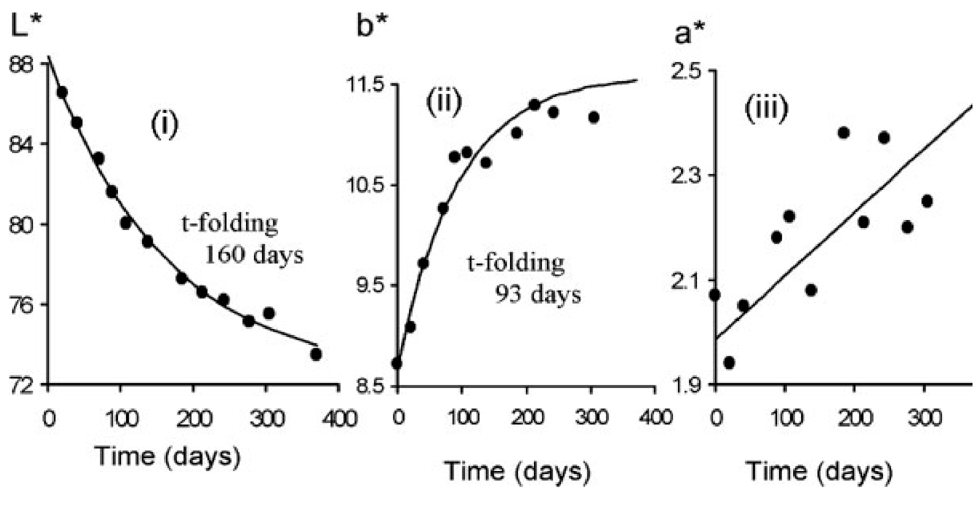

FIG. 8. Changes in L^* (i); b^* (ii); and a^* (iii) of a white limestone (*Hontoria*) during a one-year sheltered exposure in an urban environment (Burgos). The graphs give a hint of different processes may have different rates: (i) blackening reflects soot deposition; (ii) yellow, faster sulfation; and (iii) red signal, very weak and noisy.

recently cleaned buildings), rather than to say it is too yellow or too red. This may in part be due to the subtlety of color changes of building stones, but also reflect the wide public concern over blackened buildings.

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