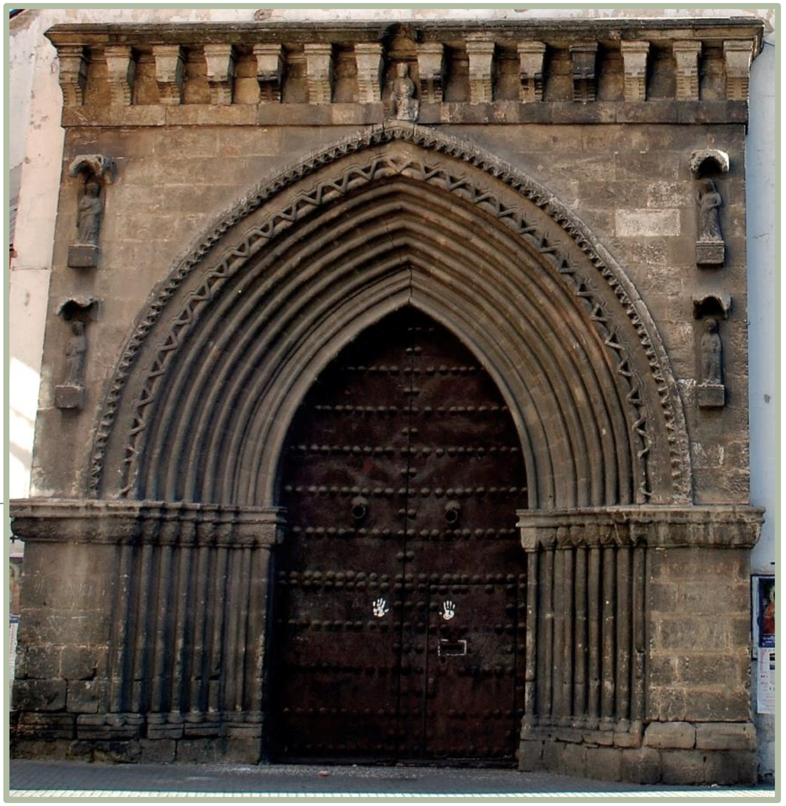
Nano 2019 Innovation
Rome, 11-14 June
Conference & Exhibition

NEW NANOMATERIALS FOR THE CONSERVATION OF HISTORIC LIMESTONE BUILDINGS



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UNIVERSIDAD PABLO DE OLAVIDE SEVILLA

ArtRisk

Proyect **INTELIGENCIA ARTIFICIAL APLICADA A LA CONSERVACION PREVENTIVA DE EDIFICIOS** (*ART-RISK*).

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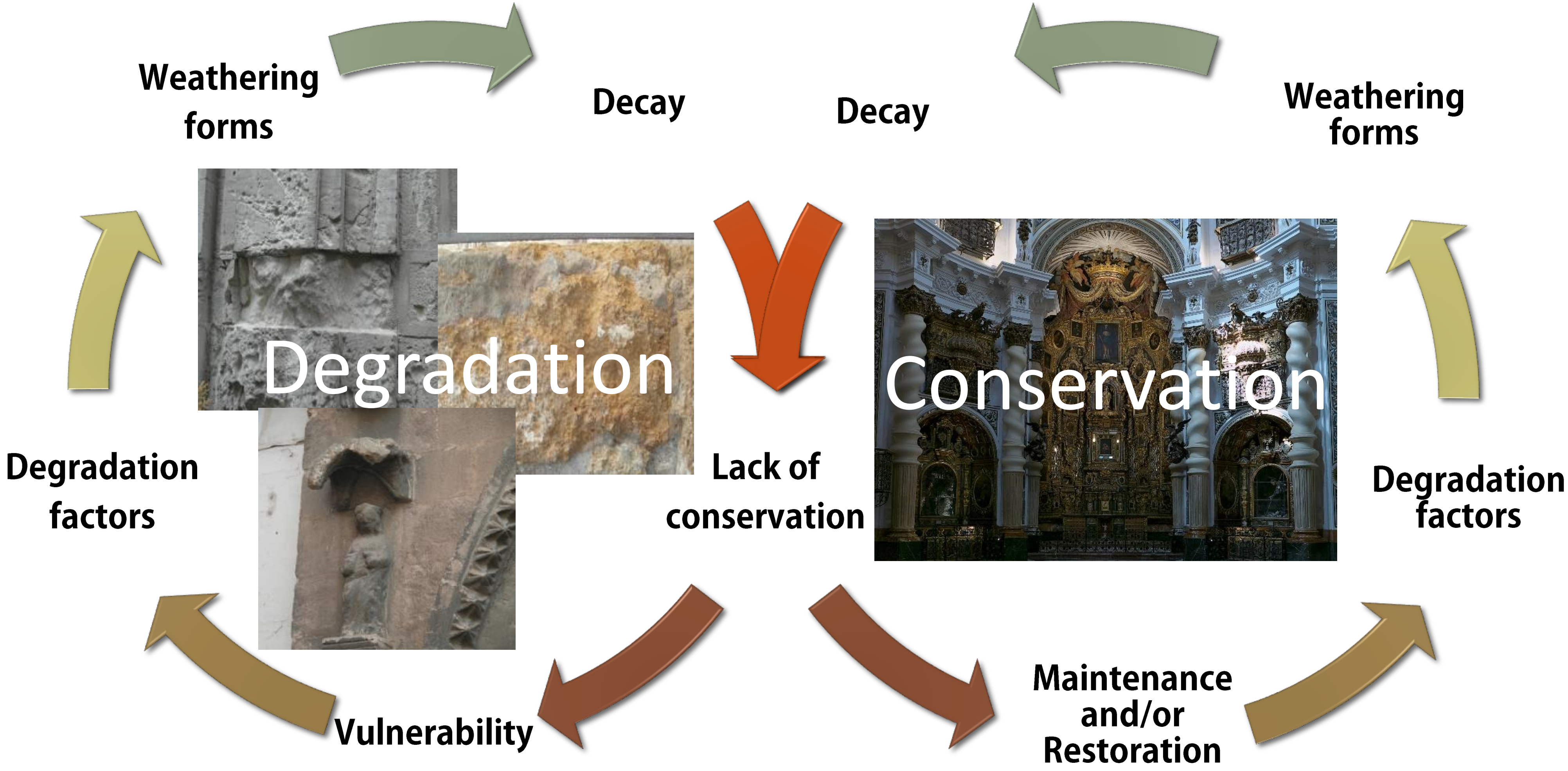
Art-Risk

@ProyectoArtRisk

Purpose: Generate a tool for the preventive conservation of Cultural Heritage based on models of artificial intelligent.

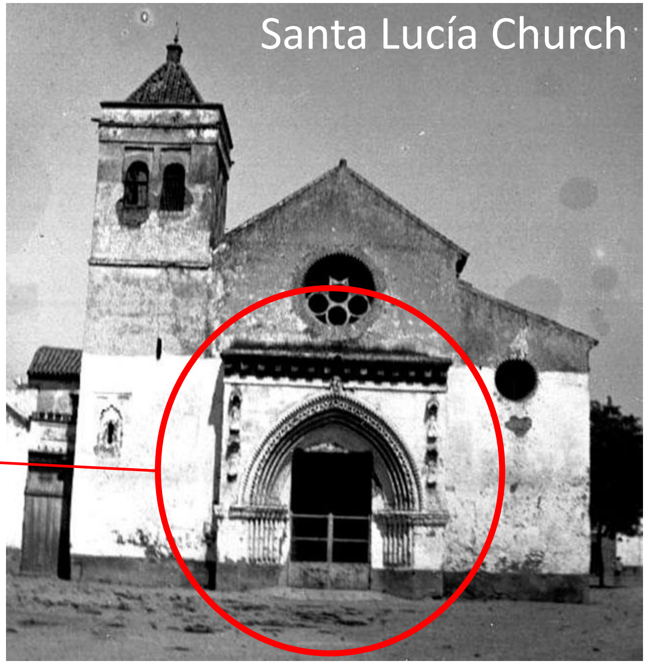
Stone damage



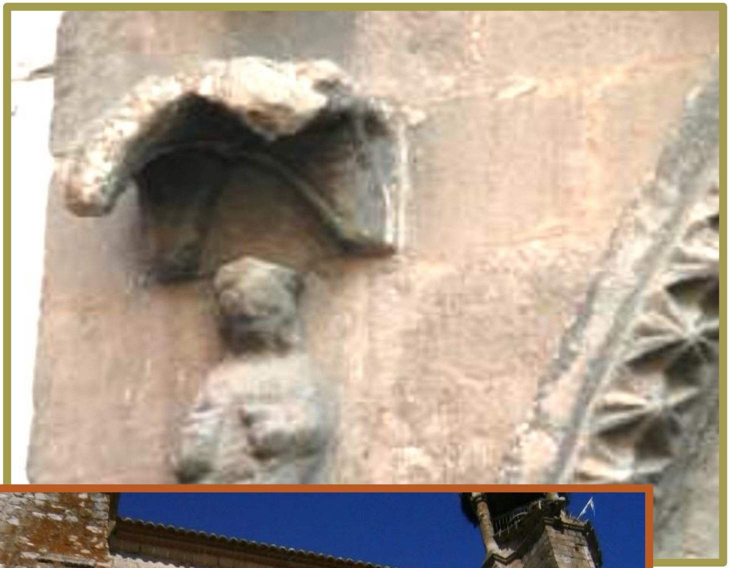
Façade of Santa Calatina Church (Seville)

Gothic-Mudejar church (1350-1399)
Monument (Gaceta 08/09/1912)

Main façade proceeded from Santa Lucía church (XIV century) and was placed in its current location in the XX century.



Main processes carried out in a restoration of historic and contemporary stone buildings:



Lack of cohesion → **CONSOLIDATION**

Biodeterioration → **PROTECTION**

Requirements for consolidation and biocide treatments

- Effectiveness
- Durability
- Penetration, without generating interfaces between the treated and untreated areas
- Maintain the porosity of the stone to allow its breathing and water circulation
- Chemical compatibility, avoiding chemical reactions or the formation of layers on the substrate
- Avoid altering the aesthetic aspect, both in its color and its brightness. Besides, the treatment must maintain its properties over time, without deteriorating due to the effect of external agents

CONSOLIDANT

NPs $Ca(OH)_2$ (50-600 nm)

- Chemical compatibility with carbonated materials
- Durability
- Effectiveness
- Application with different solvents

+

QDs ZnO (8 nm)

- Fluorescence

→

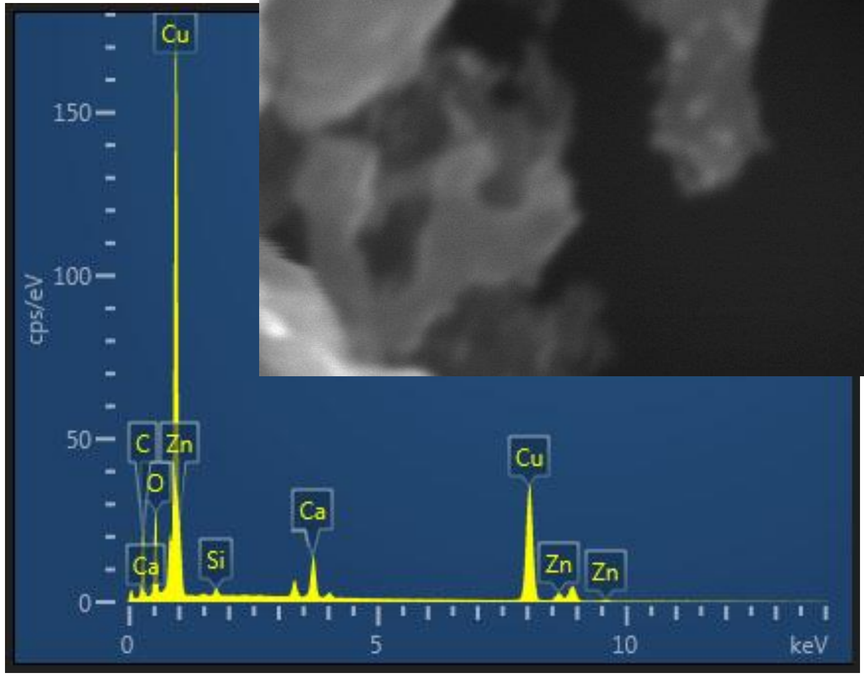
New nanocomposites based on NPs $Ca(OH)_2$ doped with QDs ZnO

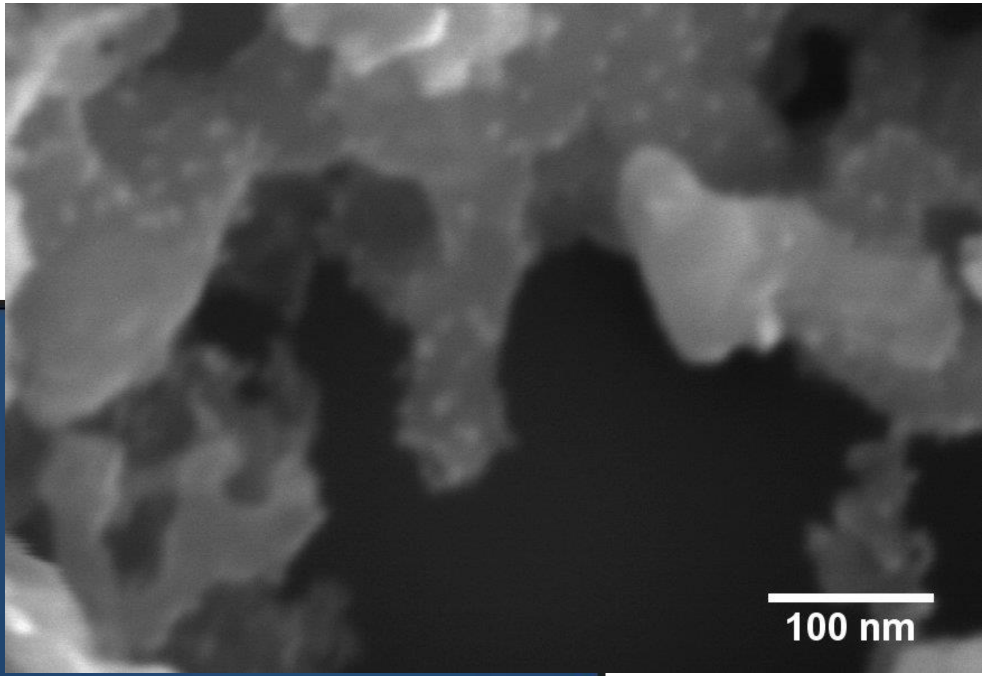
NPs $Ca(OH)_2$/ZnO

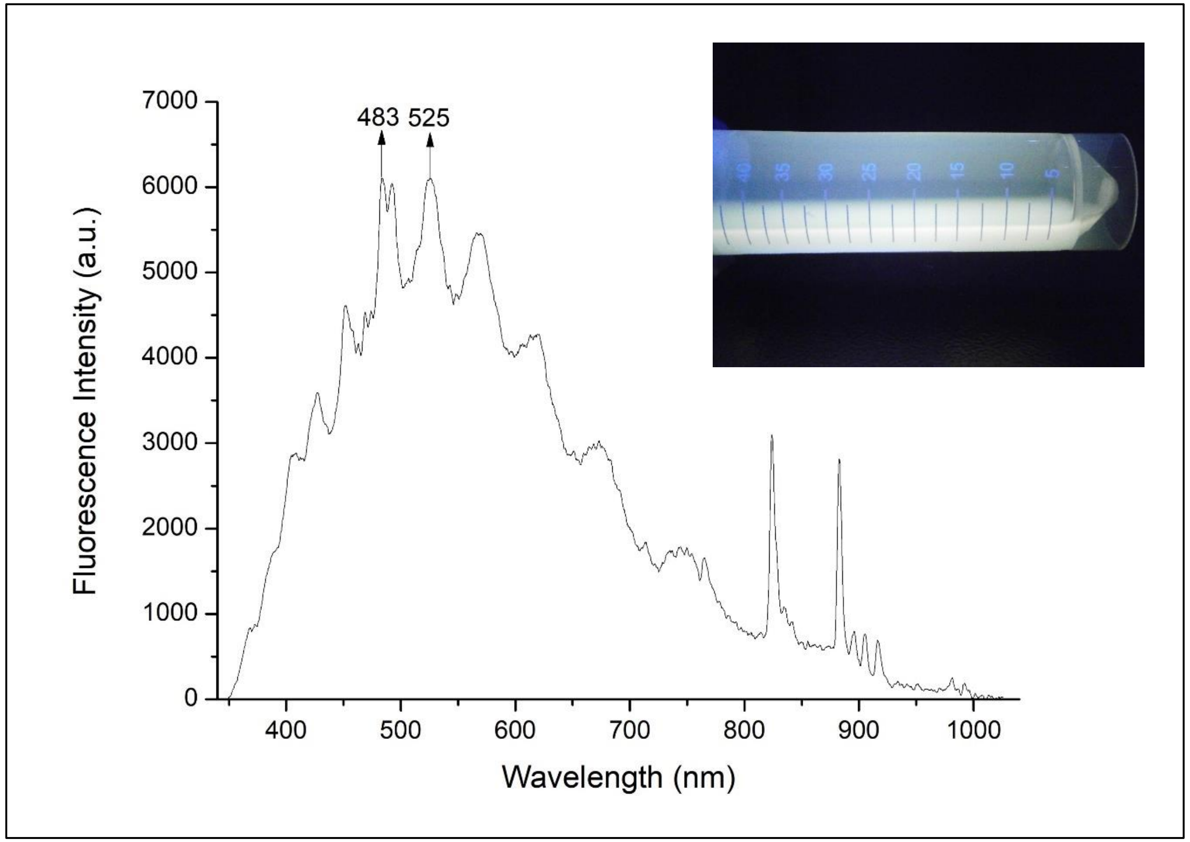
↓

PATENT P201831200

Characterization of Nanodots



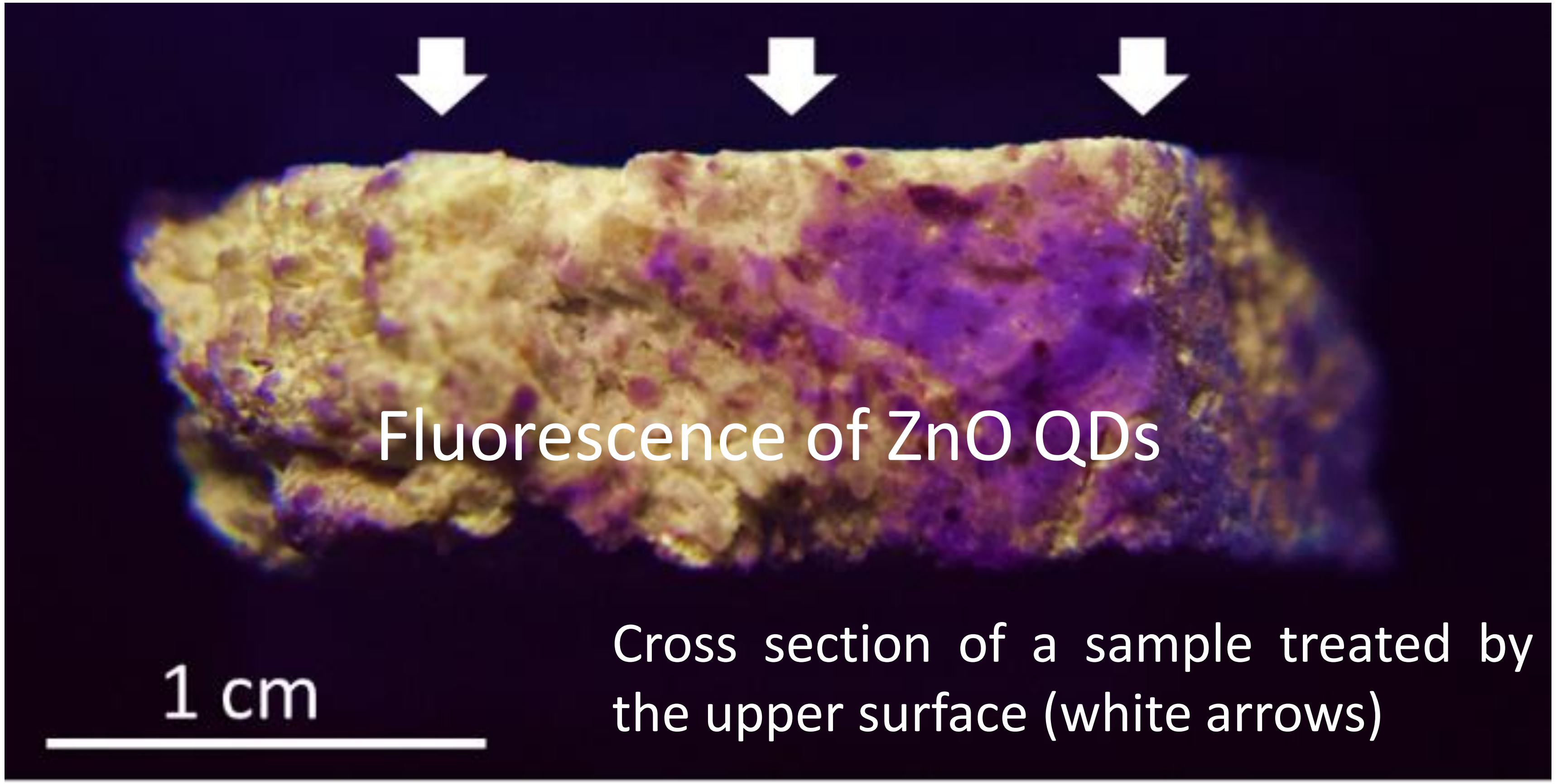




J. Becerra, P. Ortiz, J.M. Martín, A.P. Zaderenko, Nanolimes doped with quantum dots for stone consolidation assessment, Constr. Build. Mater. 199 (2019) 581–593. doi:10.1016/j.conbuildmat.2018.12.077.

PATENT
NPs $Ca(OH)_2/ZnO$

UV light (254 nm)



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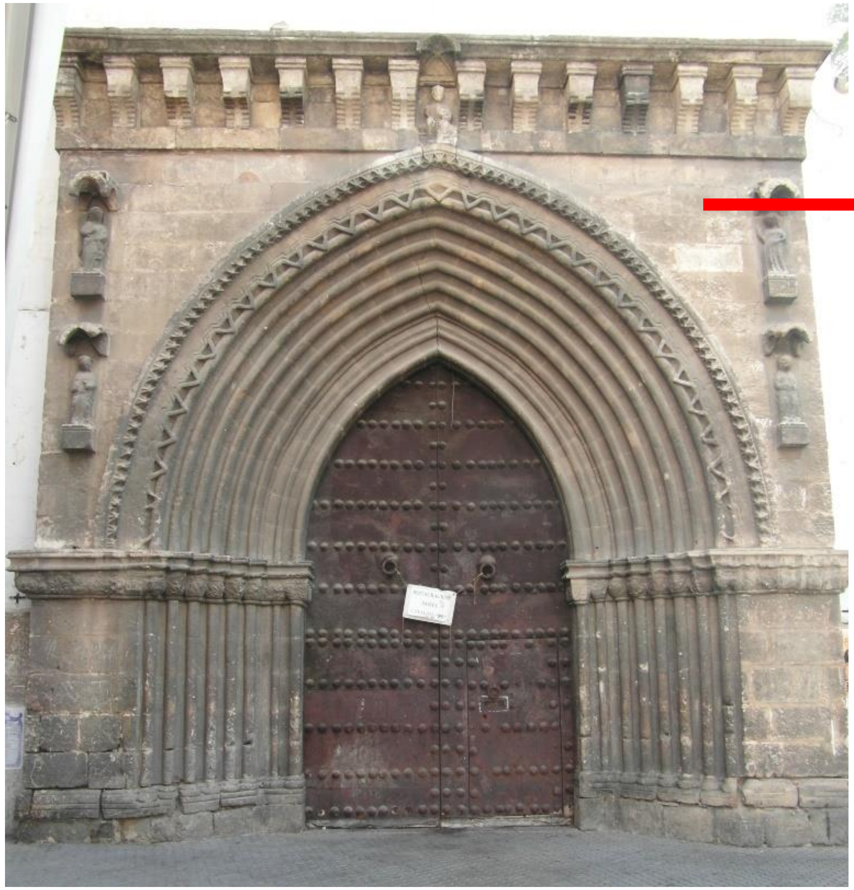
Stone samples: properties



Limestone from Puerto de Santa María quarry (Cádiz)

Sample	Pore diameter (µm)	Open porosity (%)
calcarenite	10-100	38

Applications

Untreated

Treated with Nanodots

Nanodots were applied over the stone samples in **ethanol** suspension at concentration of **2.5 g/L.**

Four doses of 0.15 mL/cm^2 were applied on stone surfaces.

The samples were **dried during 20 days** after last application at room temperature (24±2^{o}C) to guarantee the end of the carbonatation process.

J. Becerra, P. Ortiz, J.M. Martín, A.P. Zaderenko, Nanolimes doped with quantum dots for stone consolidation assessment, Constr. Build. Mater. 199 (2019) 581–593. doi:10.1016/j.conbuildmat.2018.12.077.

Not colour changes

Colour change = ΔE*

$$\Delta E^*=(\Delta L^2+\Delta a^{*2}+\Delta b^{*2})^{1/2}$$

where ΔL, Δa* and Δb* characterize the variations between initial and final colour slabs defined by the CIELAB colour-system

ΔE*<5 for Cultural Heritage

Untreated

Treated with Nanodots

$\Delta E^*=2.04 \pm 1.3$

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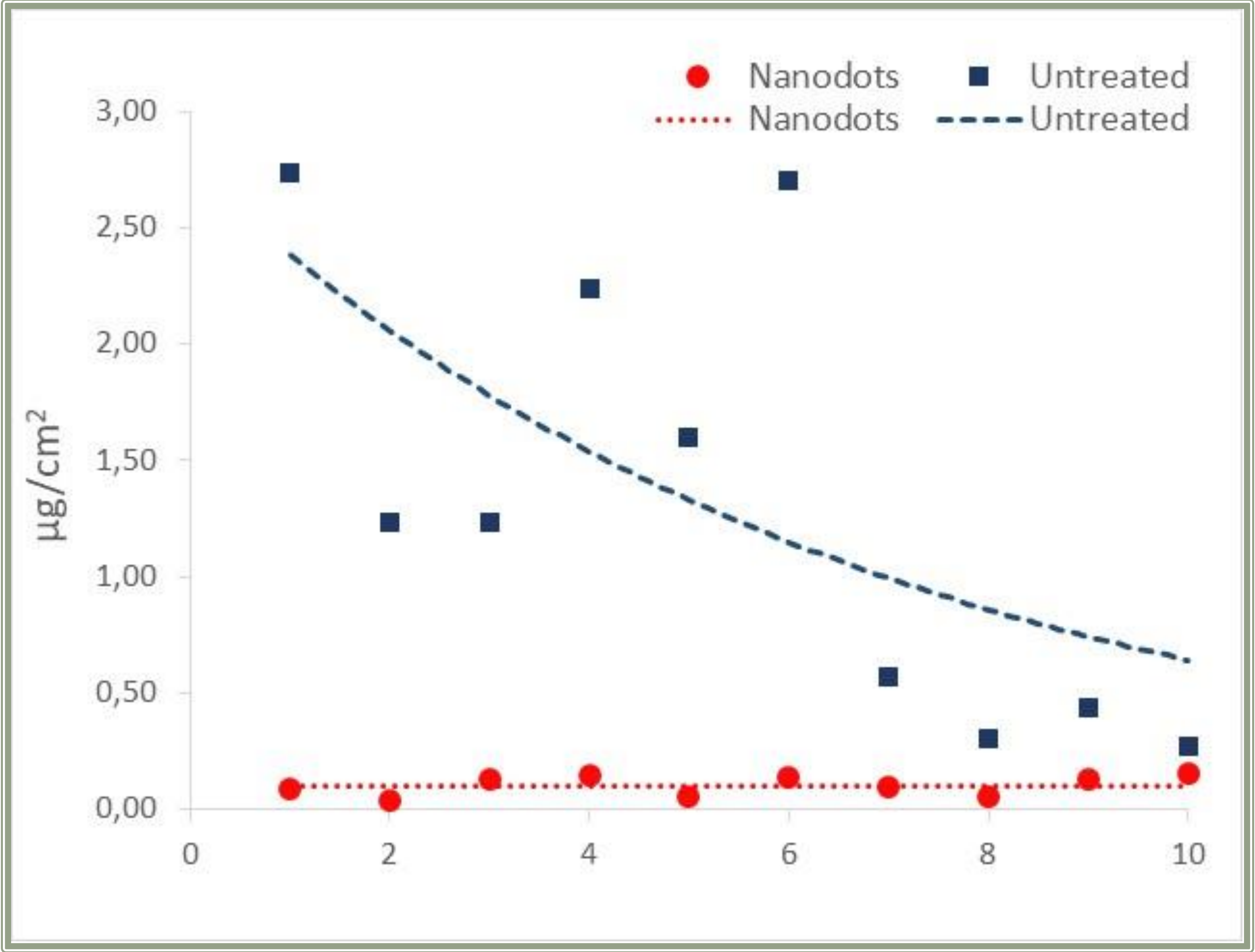
Consolidation: peeling test

The consolidation of treated limestones was studied by the peeling test. This assay was carried out using Scotch Cristal tape (3M) with 10 repetitions over the same location.

The percentage of consolidation (% Consolidation) relative to that of untreated samples was calculated according to Eq.:

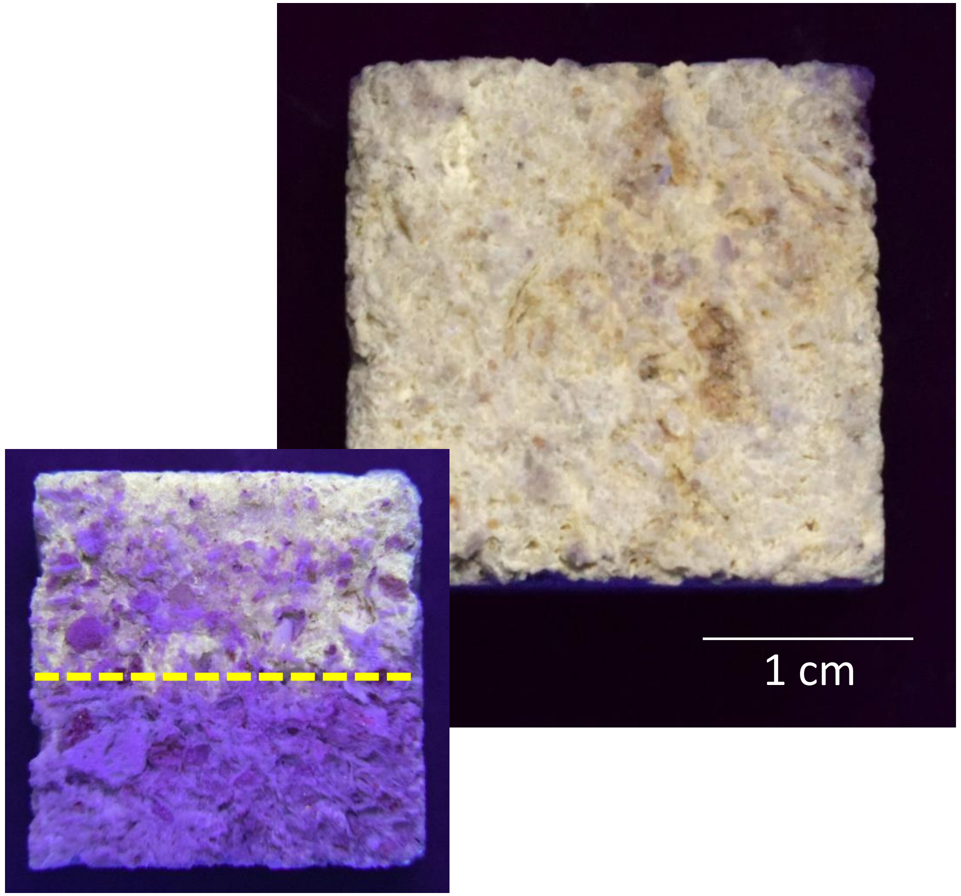
$$\%\text{Consolidation} = \frac{\text{TRM}_{\text{untreated}} - \text{TRM}_{\text{treated}}}{\text{TRM}_{\text{untreated}}} * 100$$

% Consolidation = 92%

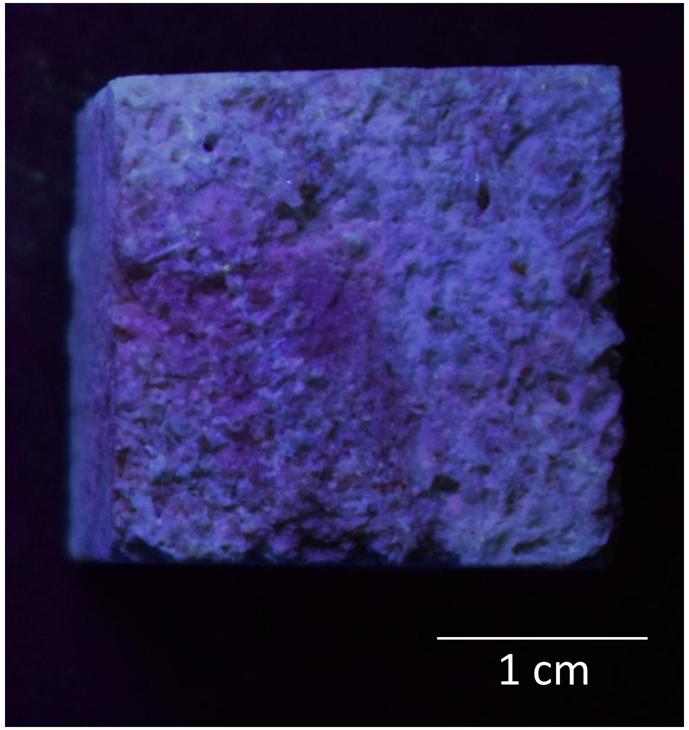


Discernibility and penetration depth

Treated with Nanodots



Untreated



Under UV light
λ=254 nm

J. Becerra, P. Ortiz, J.M. Martín, A.P. Zaderenko, Nanolimes doped with quantum dots for stone consolidation assessment, Constr. Build. Mater. 199 (2019) 581–593. doi:10.1016/j.conbuildmat.2018.12.077.

PROTECTION AGAINT BIODETERIORATION

Ag NPs

- Biocide

TiO_2 NPs

- Photocatalytic property under UV light

Nanocomposite of

Ag/TiO_2

Ag NPs improve the photocatalytic properties of TiO_2 NPs, increasing their reactivity through the visible spectrum

Stabilizing agent

- Trisodium citrate
- Tetraethyl orthosilicate (TEOS)

Nanocomposites of

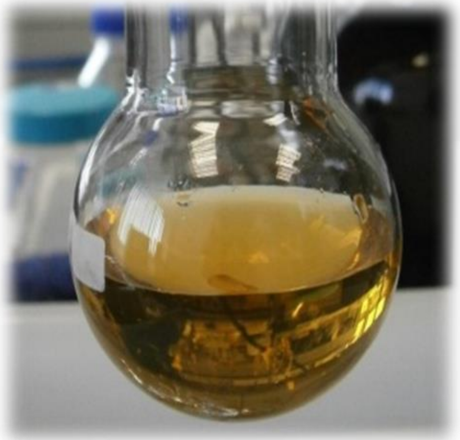
$Ag@CIT/TiO_2$

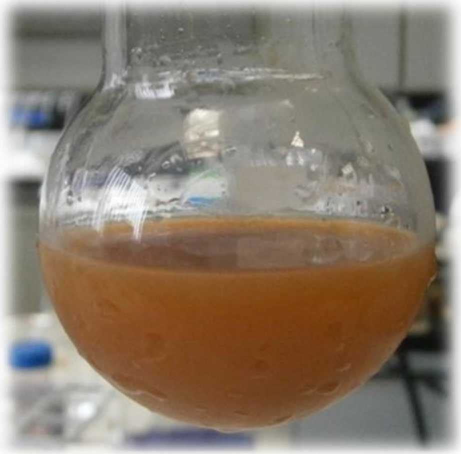
or

$Ag@TEOS/TiO_2$

Treatments	HD	ζ (>|30|)
TiO_2	184±49	-17±2
Ag/TiO_2	94±33	-17±3
Ag@CIT	36±8	-63±3
$Ag@CIT/TiO_2$	52±11	-27±1
Ag@TEOS	5±1	-125±19
$Ag@TEOS/TiO_2$	120±16	-37±4

HD: Hydrodynamic diameter= NP size + solvation layer
ζ: Zeta potential = surface charge of NP in the dispersion

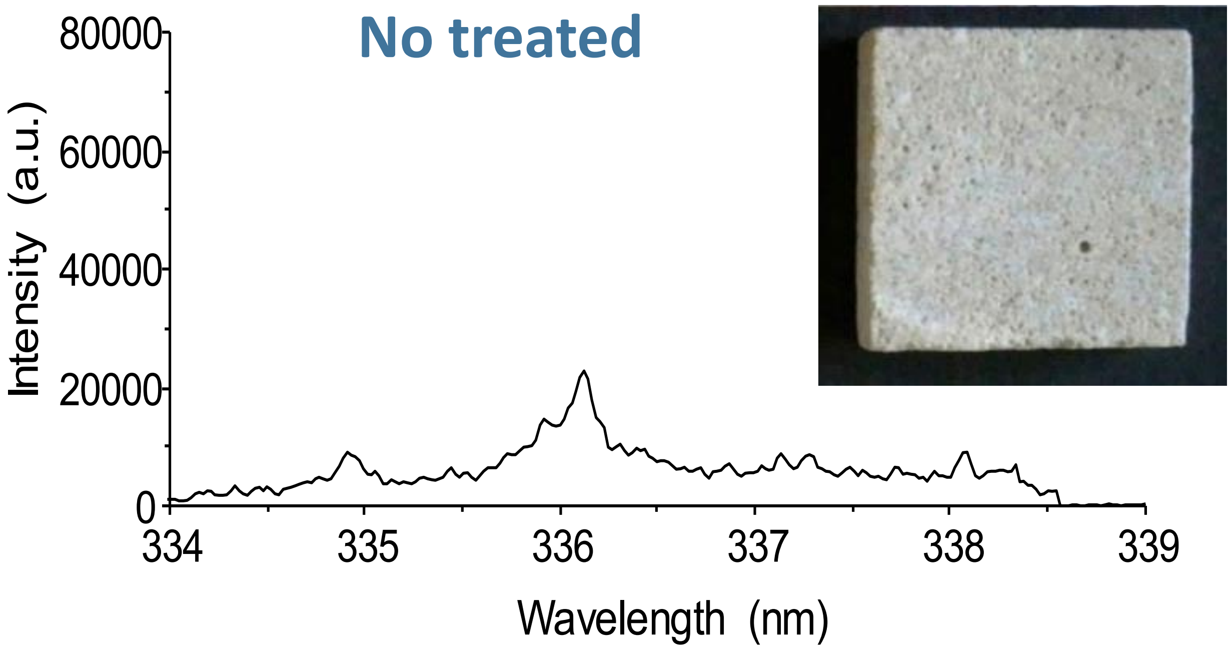




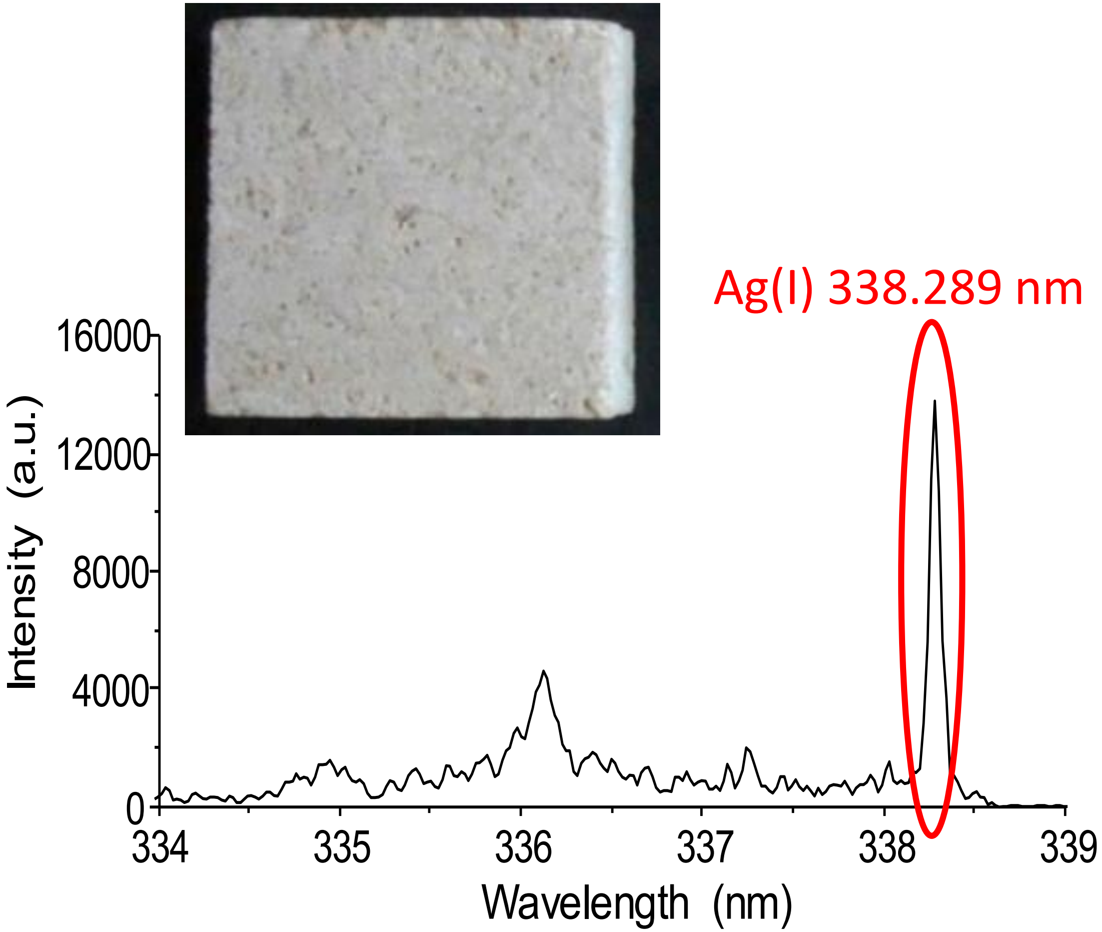
- J. Becerra, A.P. Zaderenko, P. Ortiz, Silver/dioxide titanium nanocomposites as biocidal treatments on limestones, Ge-Conservación. 11 (2017) 141–148.
- J. Becerra, A.P. Zaderenko, M.J. Sayagués, R. Ortiz, P. Ortiz, Synergy achieved in silver-TiO2 nanocomposites for the inhibition of biofouling on limestone, Build. Environ. 141 (2018) 80–90. doi:10.1016/j.buildenv.2018.05.020.
- J. Becerra, M. Mateo, P. Ortiz, G. Nicolás, A.P. Zaderenko, Evaluation of the applicability of nano-biocide treatments on limestones used in cultural heritage, J. Cult. Herit. 38 (2019) 126–135. doi:10.1016/j.culher.2019.02.010.
- J. Becerra, P. Ortiz, A.P. Zaderenko, I. Karapanagiotis, Assessment of nanoparticles/nanocomposites to inhibit micro-algal fouling on limestone façades, Build. Res. Inf. (2019) 1–11. doi:10.1080/09613218.2019.1609233.

LIBS instrumentation set-up :

- Pulsed Nd:YAG laser 532 nm, energy: 27 mJ/pulse , pulse duration = 5 ns
- Focusing optics - planoconvex quartz lens, focal length 100 mm
- Collecting optics - quartz optical fibre
- Spectrograph – Echelle, spectral region of 200–850 nm
- Detector - ICCD camera, delay time (2.5 µs) and integration time (10 µs)
- All experiments performed in air under atmospheric pressure



Treated with Ag@Cit NPs



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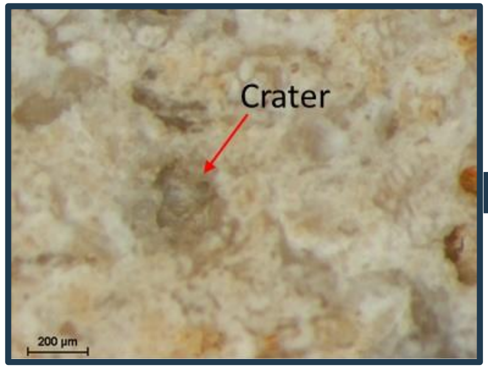
PENETRATION DEPTH OF TREATMENT=

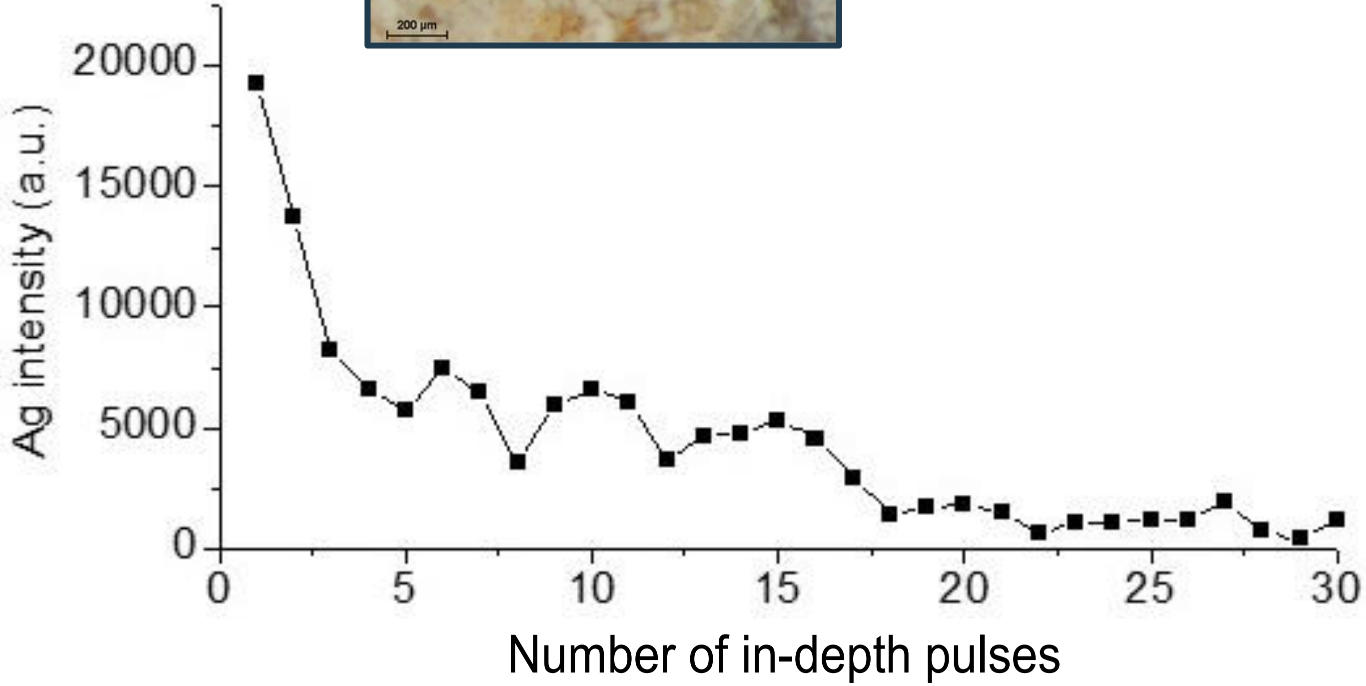
Last pulse-laser with Ag X Average depth of a crater generated by a pulse-laser

Sample treated with Ag@Cit NPs



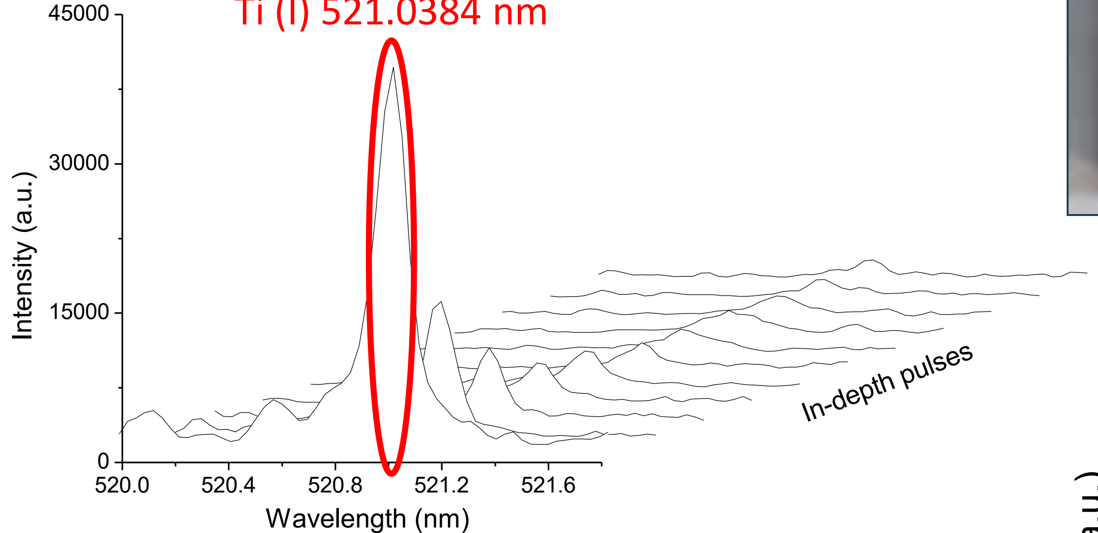
Limestone from Utrera

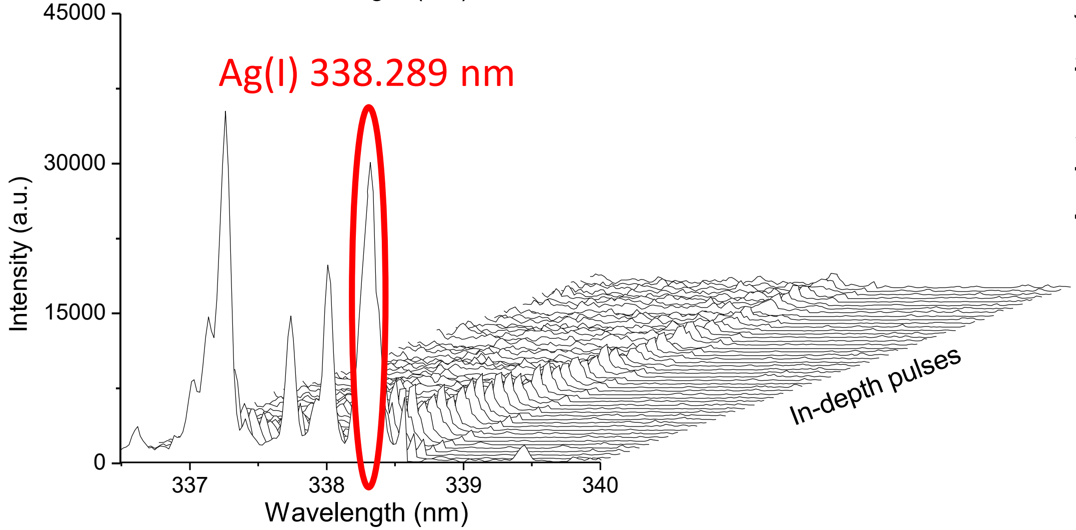
1 pulse-laser = 10 µm

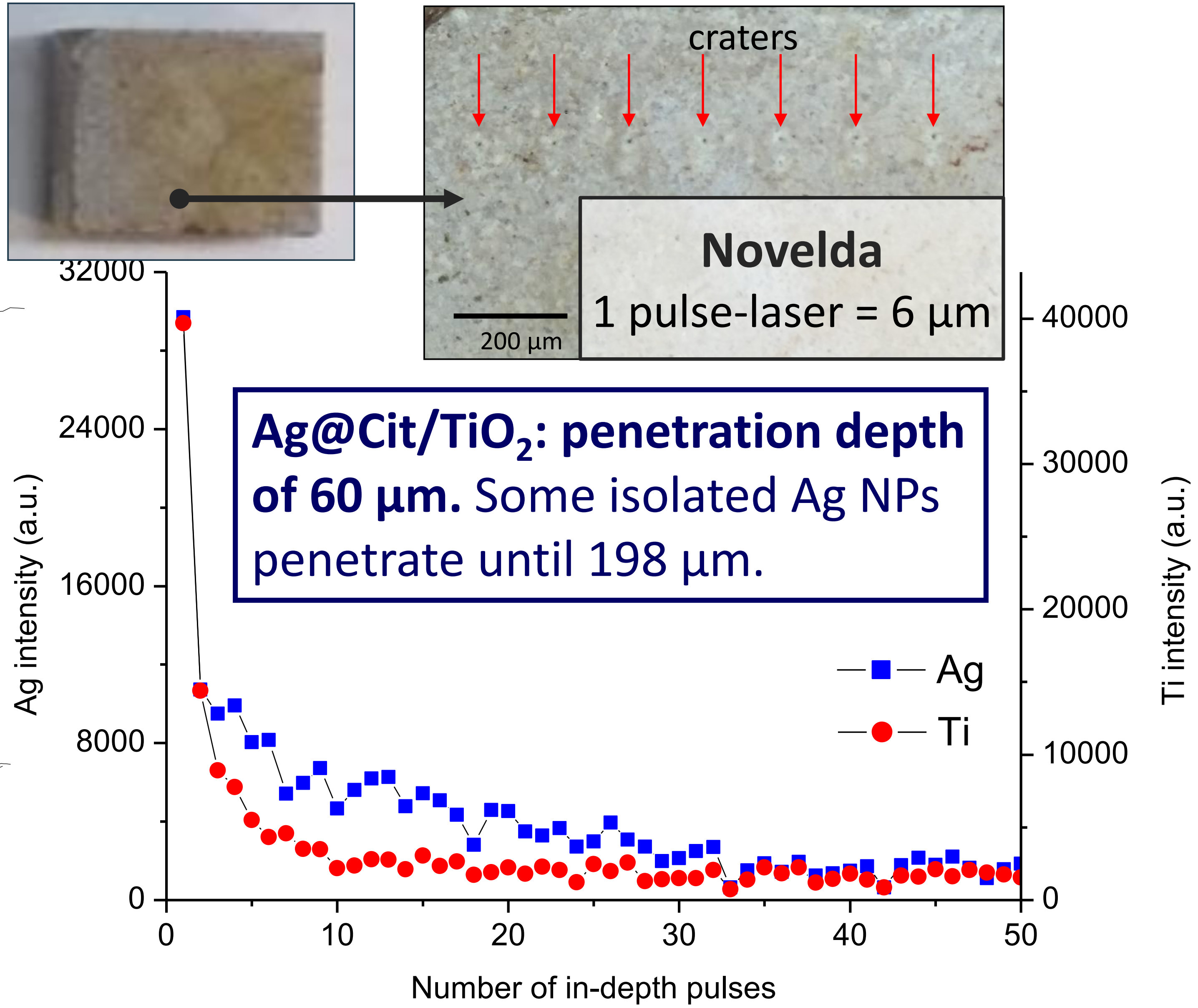


Point	Nº pulse- laser	Penetration (µm)
1	18	180
2	20	200
3	16	160
4	19	190
5	13	130
6	13	130
7	23	230
8	14	140
Average penetration depth		**170**

Sample treated with Ag@Cit/TiO_2 NPs



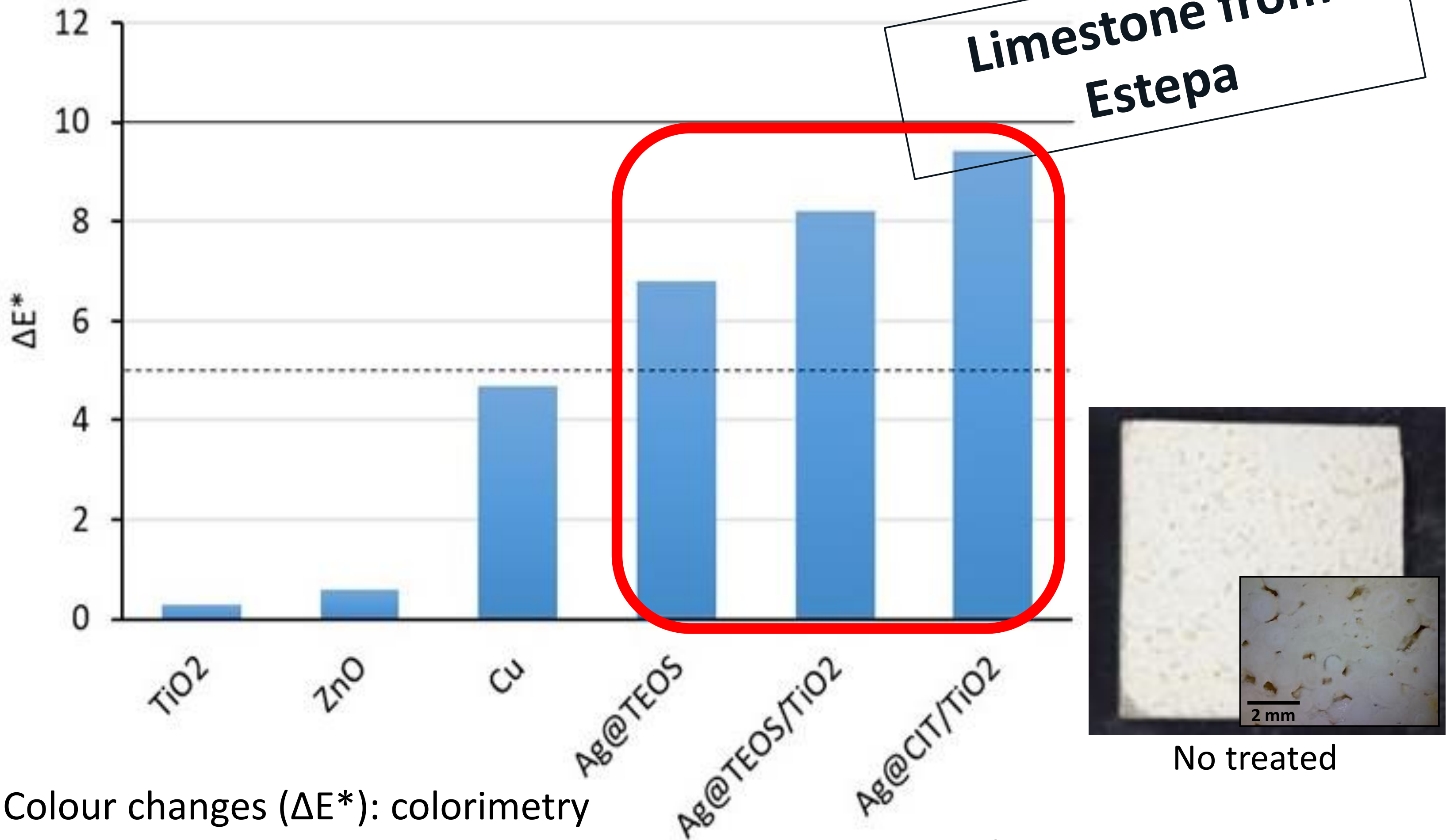


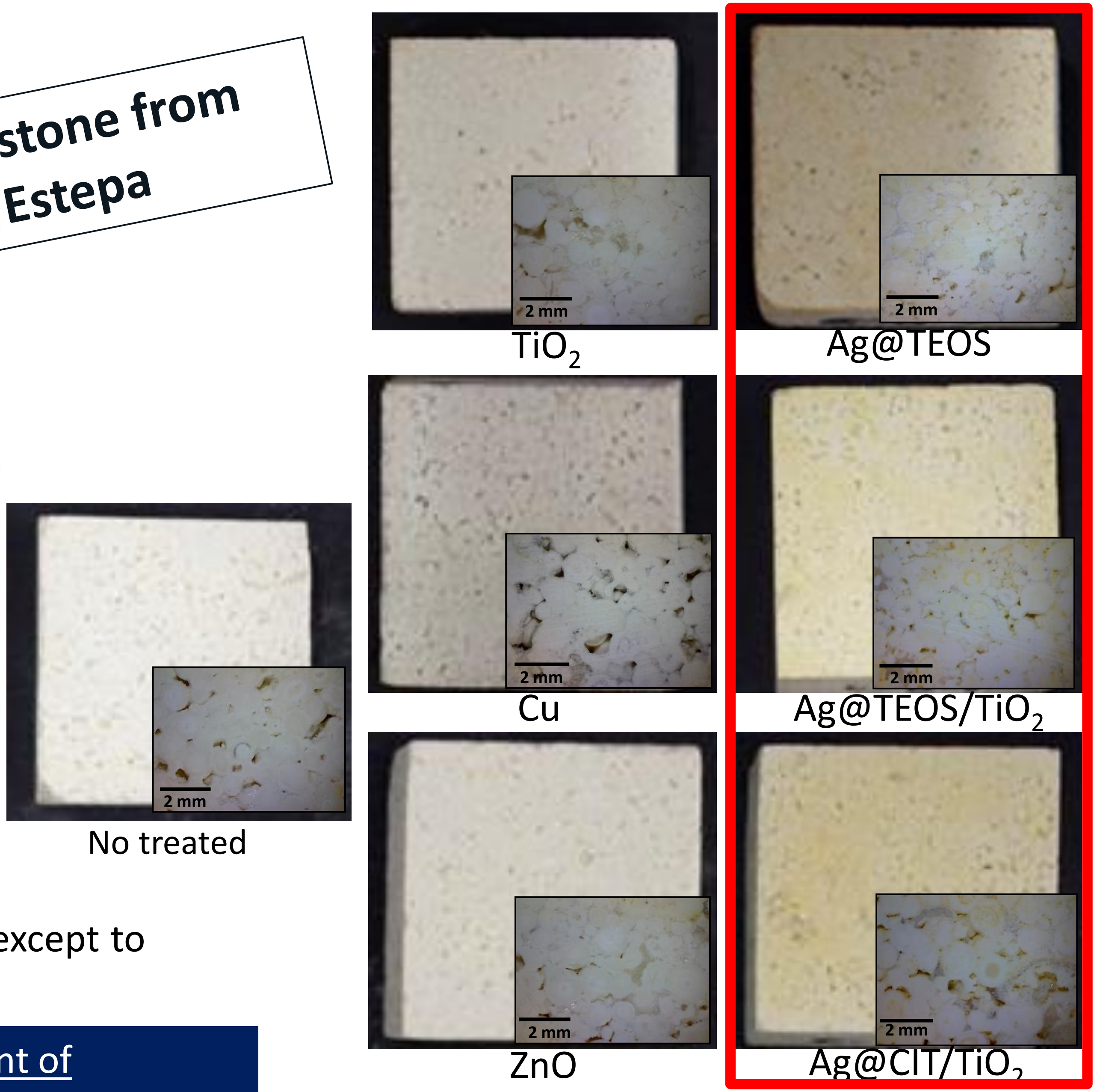


Ag@Cit/TiO_2: penetration depth of 60 µm. Some isolated Ag NPs penetrate until 198 µm.

M. Mateo, J. Becerra, A.P. Zaderenko, P. Ortiz, G. Nicolás, Laser-induced breakdown spectroscopy applied to the evaluation of penetration depth of bactericidal treatments based on silver nanoparticles in limestones, Spectrochim. Acta Part B At. Spectrosc. 152 (2019) 44–51. doi:10.1016/j.sab.2018.11.010.

Applicability on limestone



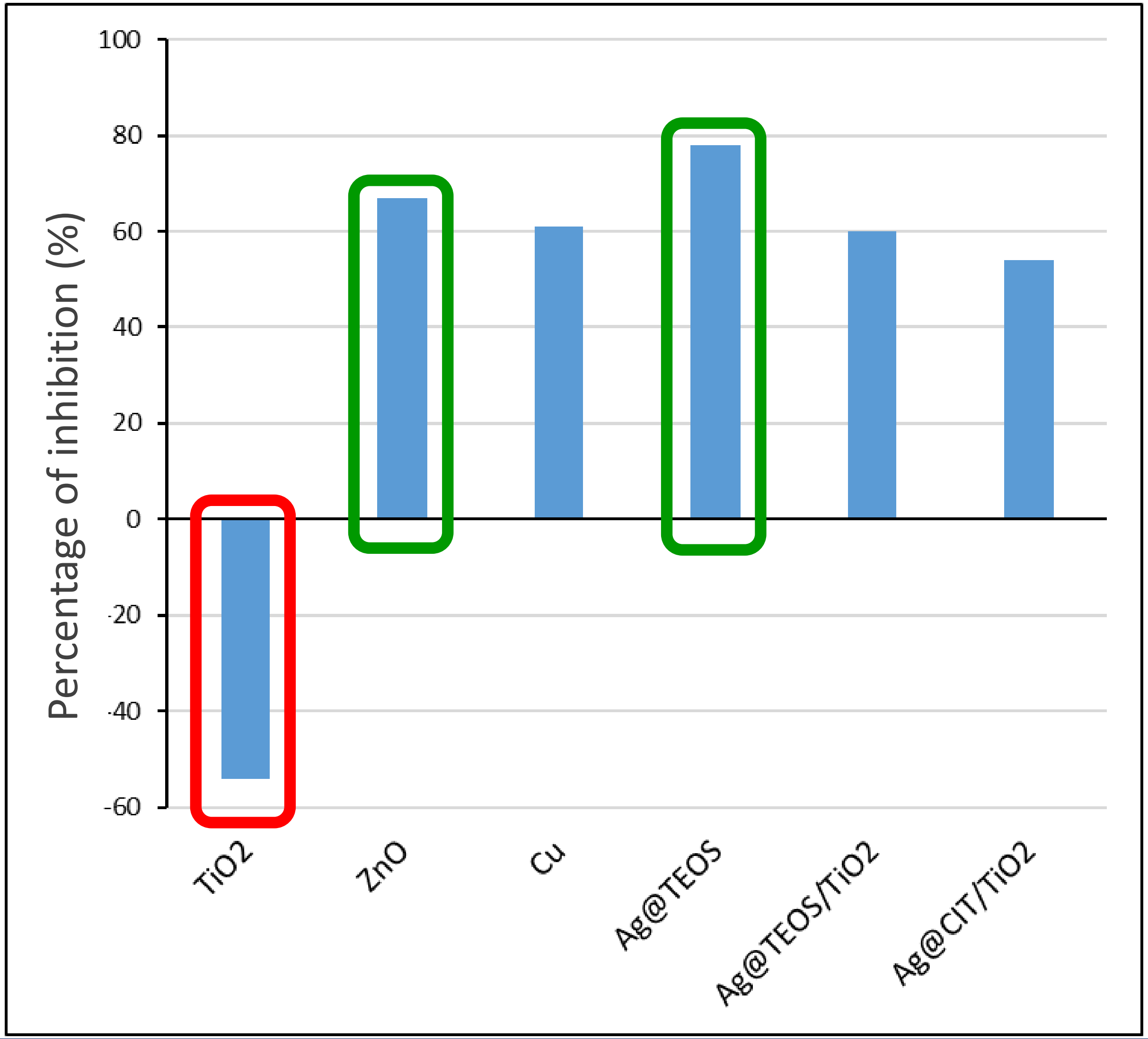


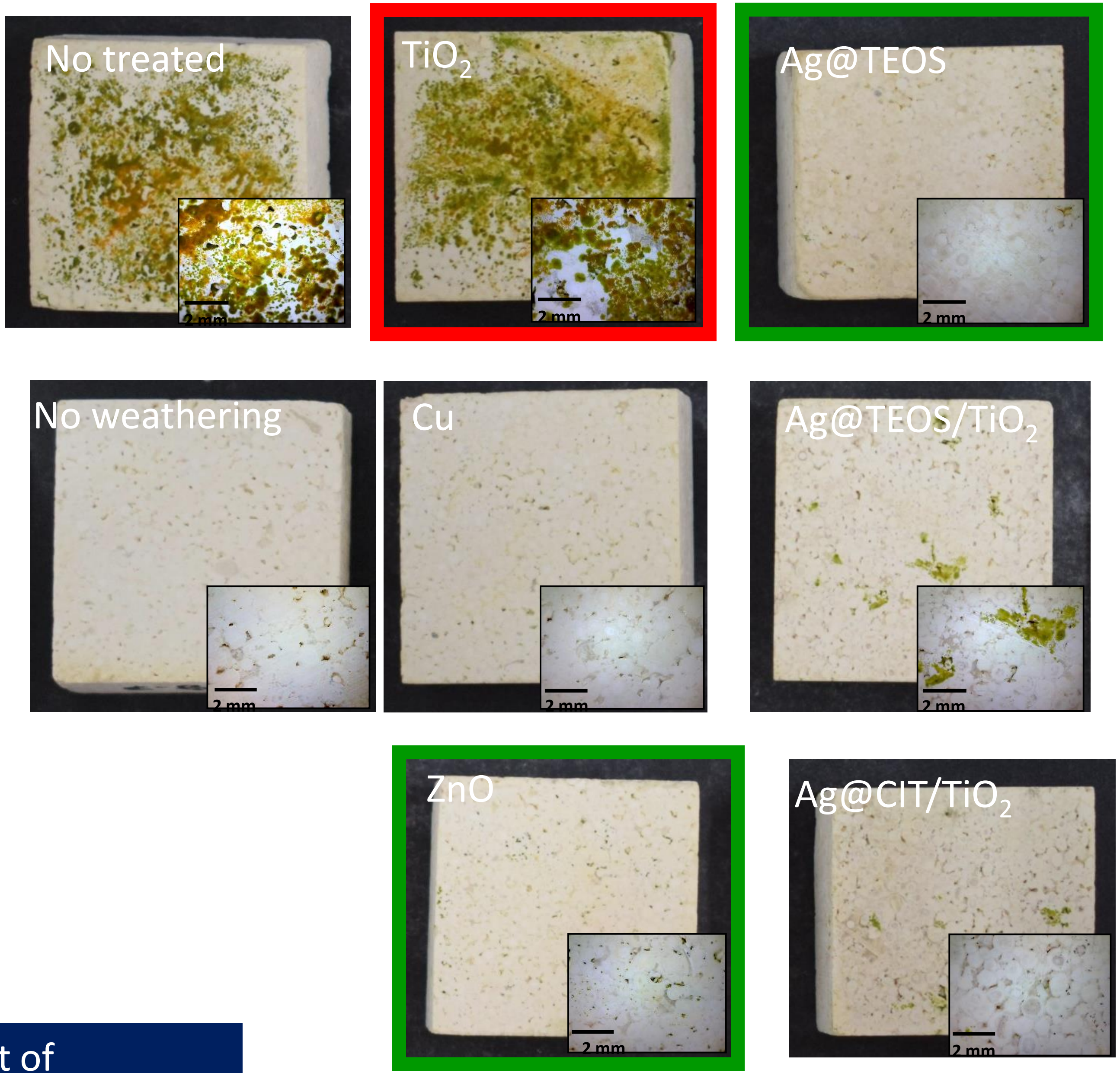
Colour changes (ΔE*): colorimetry

The treatments were applied at concentration of 0.3 mg/mL, except to Ag NPs : 0,03 mg/mL

J. Becerra, P. Ortiz, A.P. Zaderenko, I. Karapanagiotis, Assessment of nanoparticles/nanocomposites to inhibit micro-algal fouling on limestone façades, Build. Res. Inf. (2019) 1–11. doi:10.1080/09613218.2019.1609233.

EFECTIVENESS: colorimetry





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EFECTIVENESS: biofilm extension

Biofilm extension(%)			
	wavelength(nm)		
Product	420	520	620
TiO_2	**28.3±15.7**	**26.8±15.3**	**19.2±12.6**
Cu	0.3±0.1$^+$	0.8±0.4$^+$	0.2±0.1$^+$
ZnO	1.3±0.3$^+$	2.2±0.2$^+$	0.84±0.2$^+$
Ag@TEOS	3.6±0.8$^+$	0.8±0.7$^+$	0.5±0.3$^+$
Ag@TEOS/TiO_2	2.5±1.2$^+$	5.6±1.2$^+$	3.9±1.4$^+$
Ag@CIT/TiO_2	4.6±1.3$^+$	4.0±1.0$^+$	1.9±0.6$^+$
No treated	**20.5±11.5**	**24.9±11.9**	**19.1±10.8**

$^+$P-value<0.05

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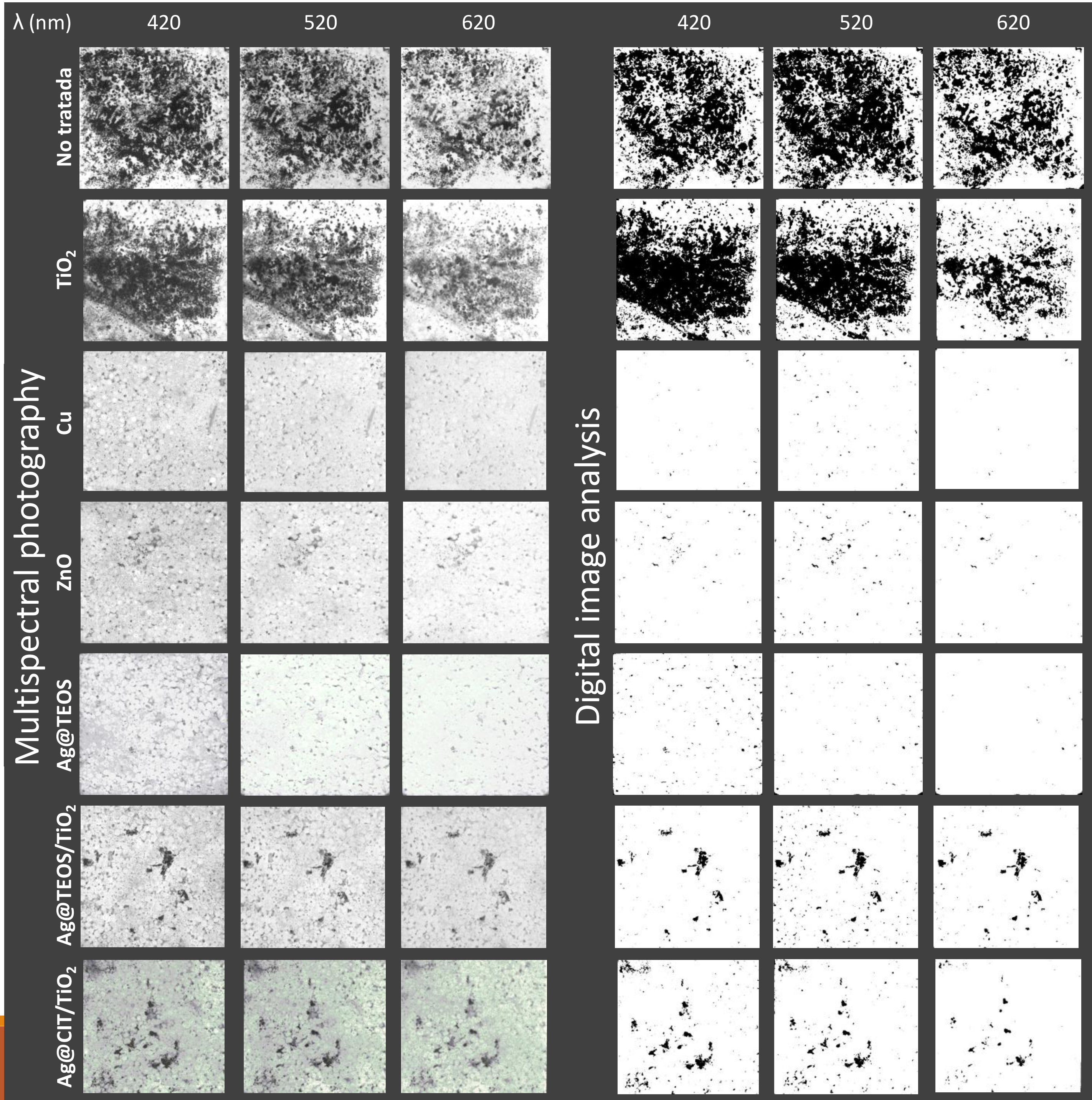
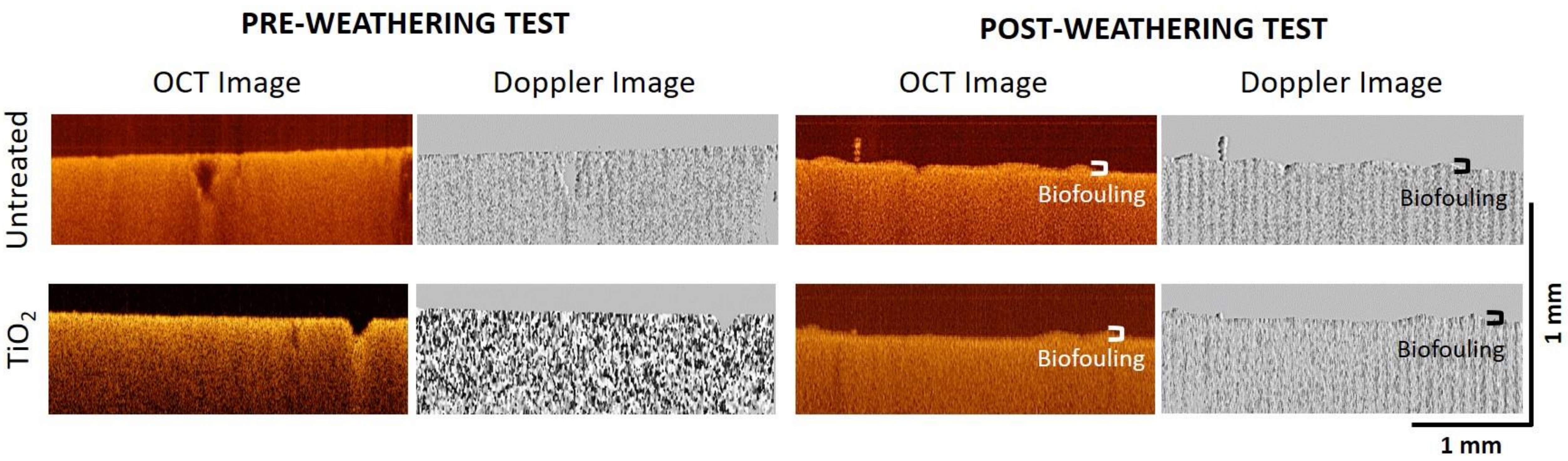


BIOFILM THICKNESS: Optical coherence tomography (OCT)



Maximum thickness of 0,03 mm

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Conclusions

- Preliminary studies on the causes of the decay in monuments of Seville (Spain) conclude that biodeterioration, together with other weathering elements, is major risk factor that leads to the deterioration of our Cultural Heritage constructions.

- Regarding consolidant treatments, we have developed a new nanocomposite based on calcium hydroxide and zinc oxide nanoparticles with fluorescence properties that allow us to check the surface intervened and measure easily the penetration depth of the treatment under ultraviolet light. Additionally, this product has good consolidation properties.

- In the case of biocide, silver and silver/titanium dioxide nanoparticles have shown a high capability to inhibit algal biofilms. The use of correct concentration allowed to avoid undesirable aesthetical changes while, in other cases, it is possible to use other nanoparticles with similar results, i.e., zinc oxide nanoparticles.

- LIBS has shown good results for measuring the penetration depth of metals nanoparticles and nanocomposites inside substrate stone.

- Optical coherence tomography (OCT) and multispectral images have been useful to analyze the thickness layer and extension caused by biofilms over the surface stone.

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Art-Risk

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"thank you for your ATTENTION :)"

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