

Green materials for heritage conservation

Prof. María Fernández Raga
Director of Nanoshield Research Group
Universidad de León, Spain

www.hieurecapro.eu | info@hieurecapro.eu

Contents

1

Introduction

3

Honors and Awards

2

Techniques

4

Ongoing research



Funded by
the European Union

1

Introduction

How to make heritage protection sustainably?

When we intervene to save a monument sustainably, we have to think of different dimensions of sustainability:

Temporally
sustainable

Economically
sustainable

Socially
sustainable



Where is my region?

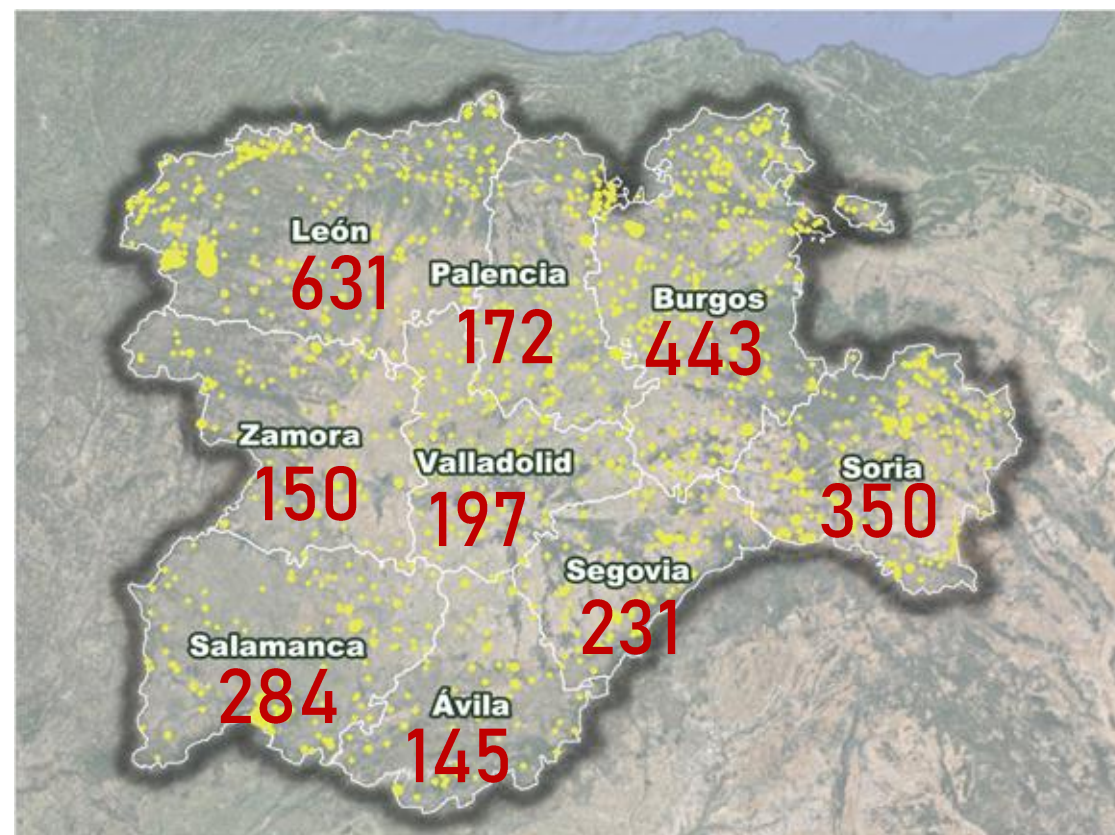


BIC

How many Assets of Cultural Interest
(BIC, Bienes de interés cultural) are
recognised in Castilla y León?

2596

90% of the BIC are
out in the open





Cathedral of Leon

Objective: **Deterioration of stone heritage**

- Natural process
- Loss of relief
- Accelerated by climate change
- Accelerated by pollution
- Cost to public authorities
- Inadequate solutions



Consolidated Research Unit 344,
I4 Institute



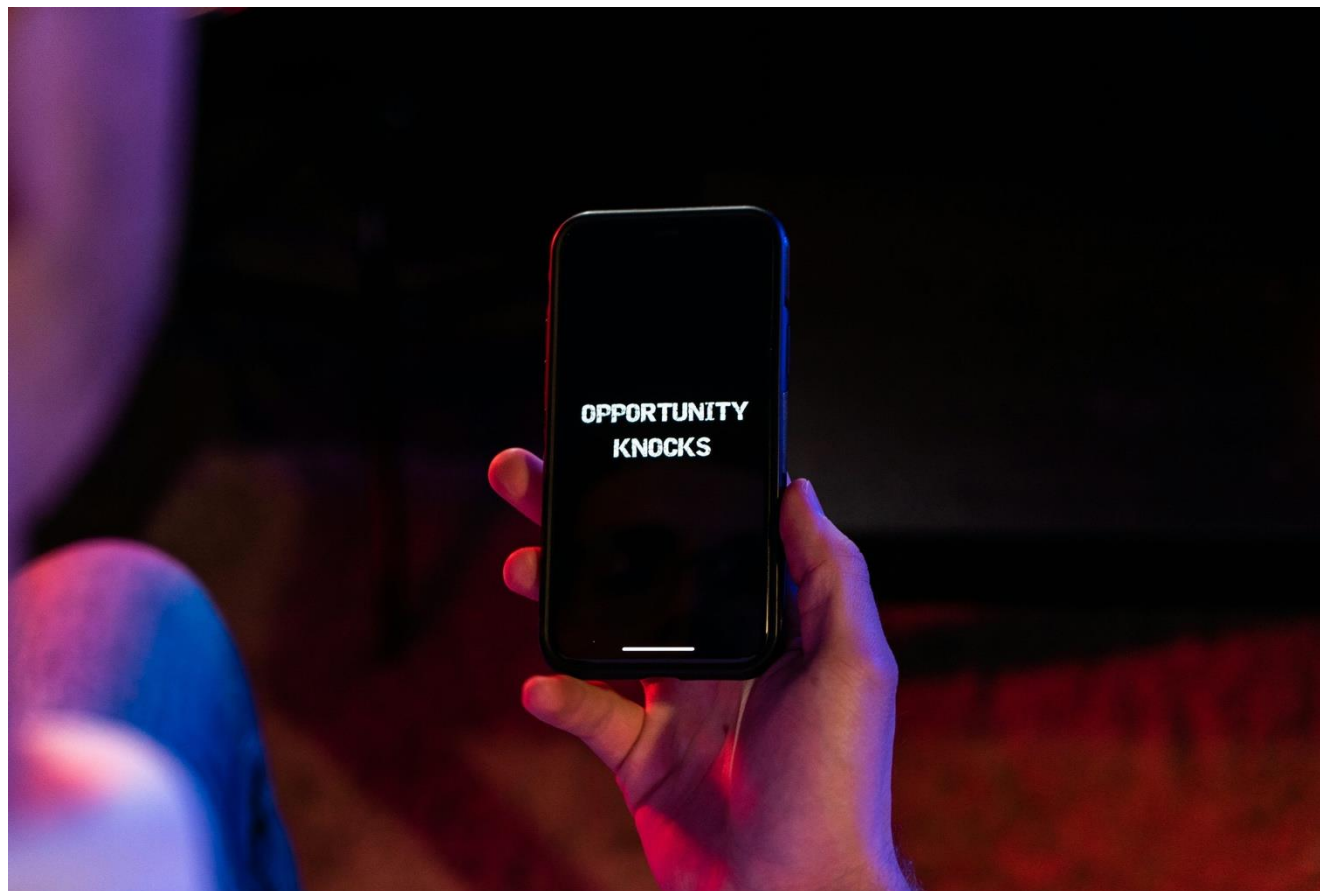
Funded by
the European Union

EXTREME WEATHER

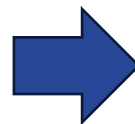
HEAVY RAINFALL



How did it all begin?



How did it all begin?



María Fernández Raga

Applied Physics.
Assistant doctor.
Study of splash
erosion in fires,
vulnerable areas.
Concern for
heritage



José Miguel González Domínguez

Chemistry.
Contracted by projects.
Resistance of aircraft
structures with
Graphene and its
derivatives.
Interest in heritage

We got to work on it!

María Fernández Raga



José Miguel González Domínguez



Nanoshield: A multidisciplinary research team

Physicists

Agricultural engineers

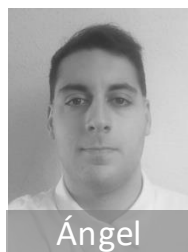
Environmental scientists

Chemists

Architects

Industrial engineers

Geologists

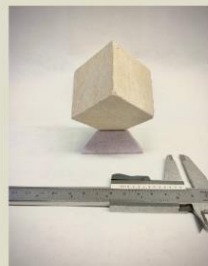


Experiments

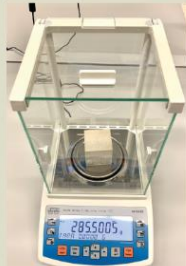
Application
of the
coating



Characterisation



Measures



Weight



Geometry

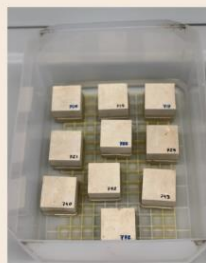


Scanner



Spectrometry

Testing



Absorption



Accelerated ageing



Extreme climate simulation

Objective: To prevent the deterioration of the stone heritage

Phases:

1. Select Nanotechnology to protect stone (undetectable, functional, cheap, available, accessible and sustainable)
2. Determine the optimal concentration.
3. Evaluate with official accredited laboratory tests.
4. Testing with non-destructive testing and interactions between products.

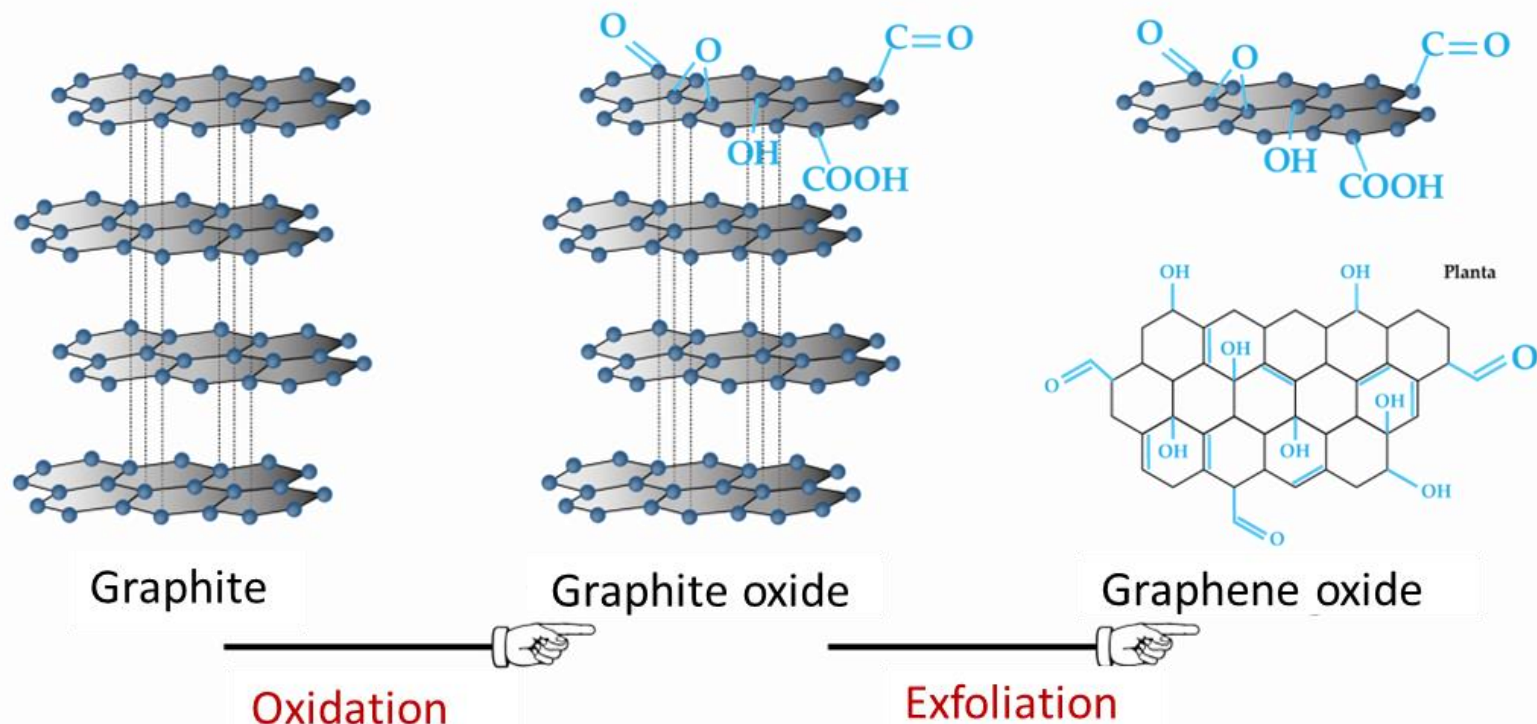
Products

José Miguel González Domínguez



DELEGACIÓN EN ARAGÓN
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Graphene oxide



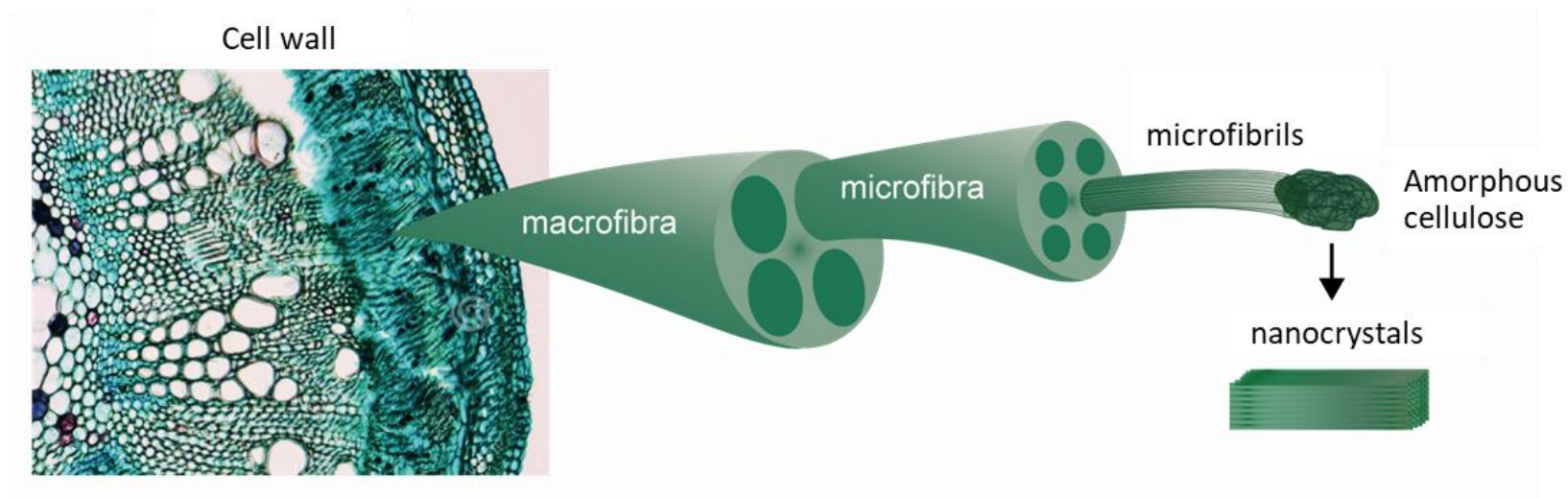
Products

José Miguel González Domínguez



DELEGACIÓN EN ARAGÓN
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Cellulose nanocrystals



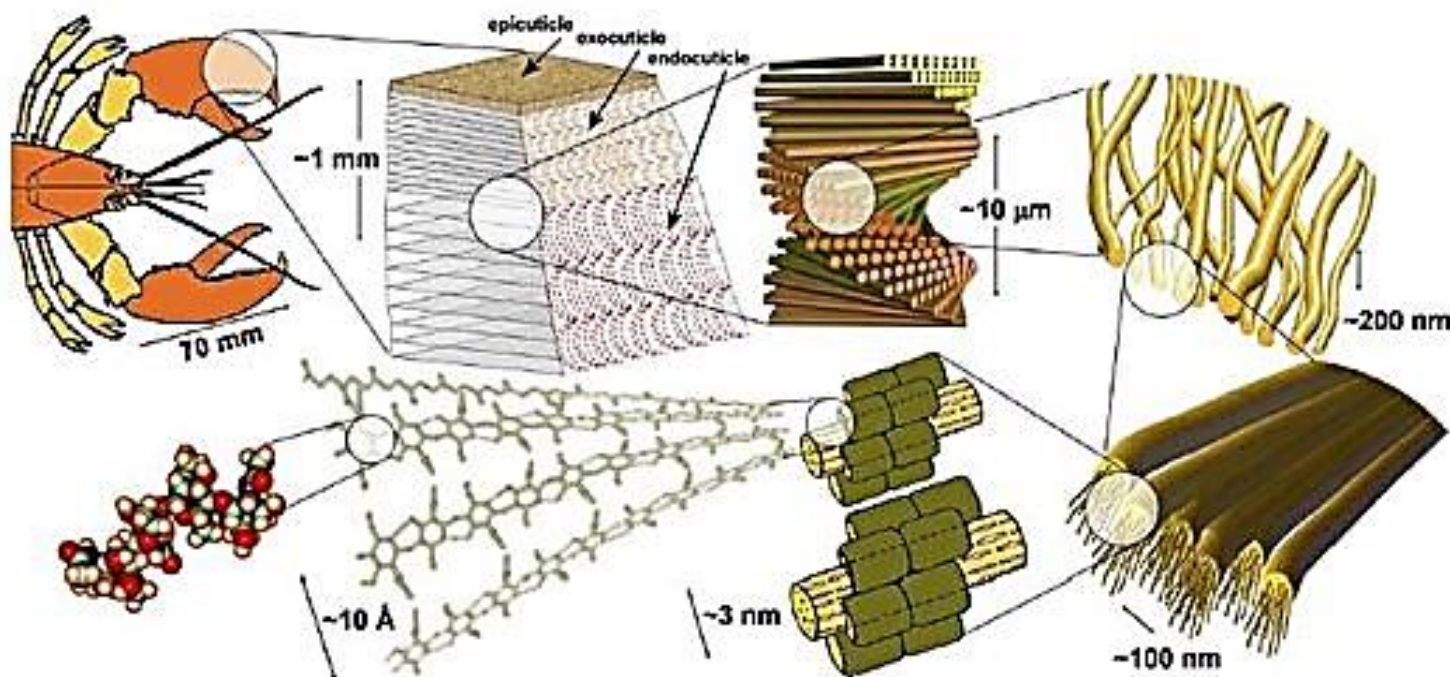
Products

José Miguel González Domínguez



DELEGACIÓN EN ARAGÓN
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Chitin nanocrystals



Neith Aracely Pacheco Lopez. Extracción biotecnológica de quitina para la producción de quitosanos : caracterización y aplicación. Domain sdv.aen. Université Claude Bernard - Lyon, 2010. España

Laboratory

María Fernández Raga



Laboratory

María Fernández Raga



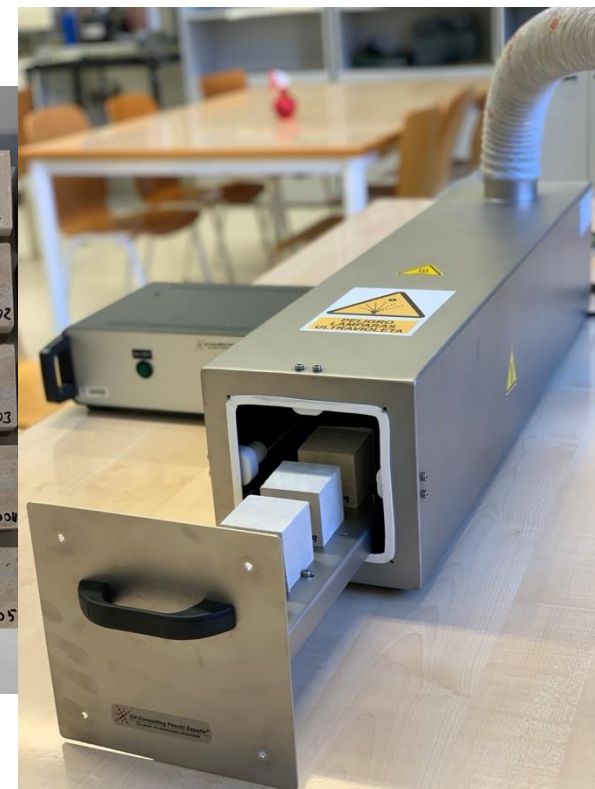
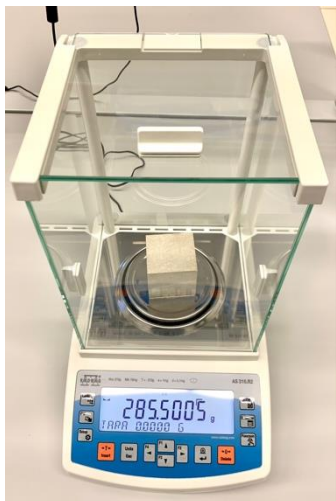


universidad
de León

Laboratory Universidad de León



HI • EURECA • PRO
HERITAGE INNOVATION



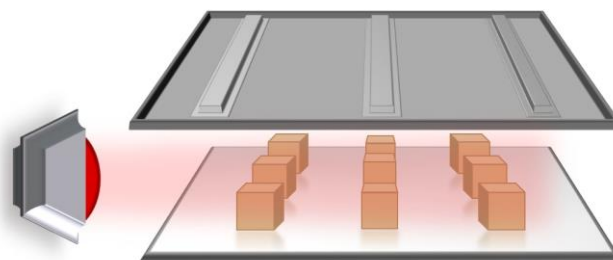
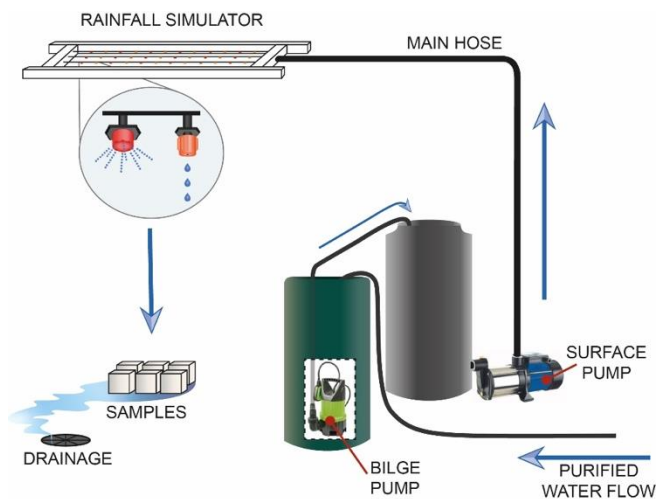


universidad
de león

Laboratory



HI • EURECA • PRO
HERITAGE INNOVATION



Funded by
the European Union

2

Techniques

Erosion tests

Rain simulation



Thermal changes

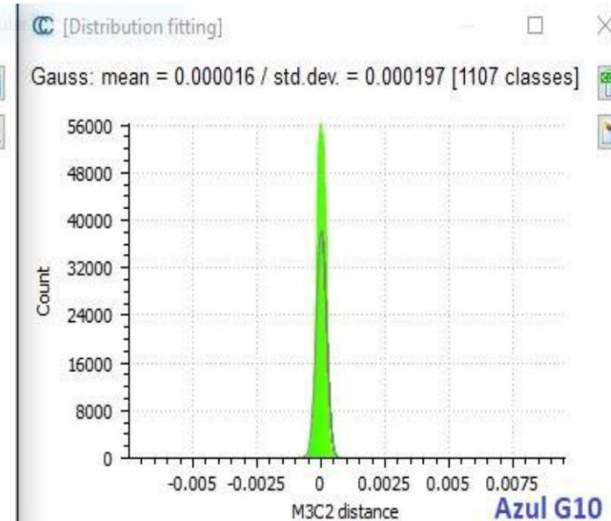
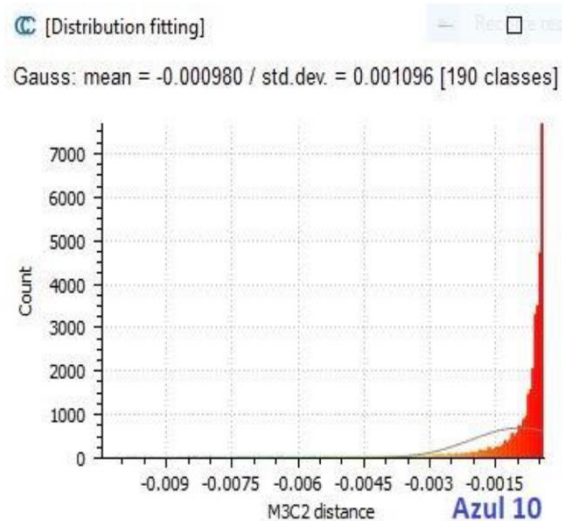


Techniques



Large

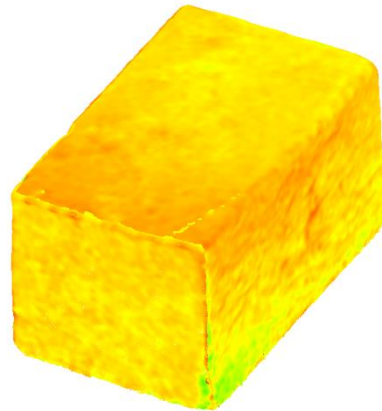
Photogrammetry - Structured Light Scanner



Interpretation: GeoEnvironmental Research Group (GIGA). Area of Physical Geography. University of Extremadura.

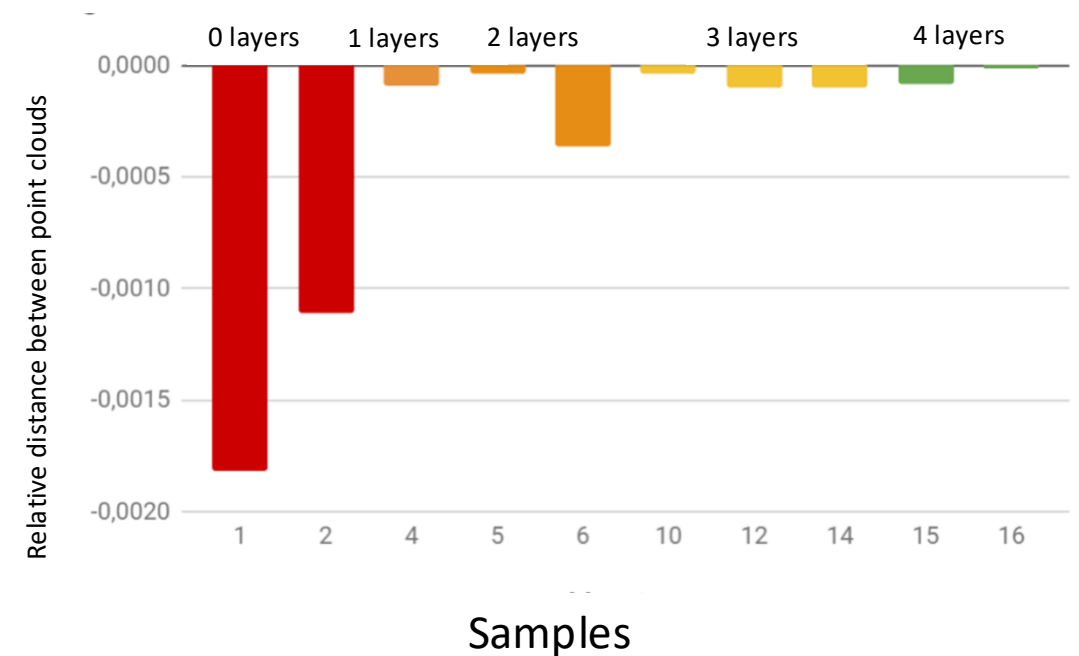
Analyses carried out

Photogrammetry



Medium

Wear and tear on the samples



Collaboration: GeoEnvironmental Research Group (GIGA). Area of Physical Geography. University of Extremadura.

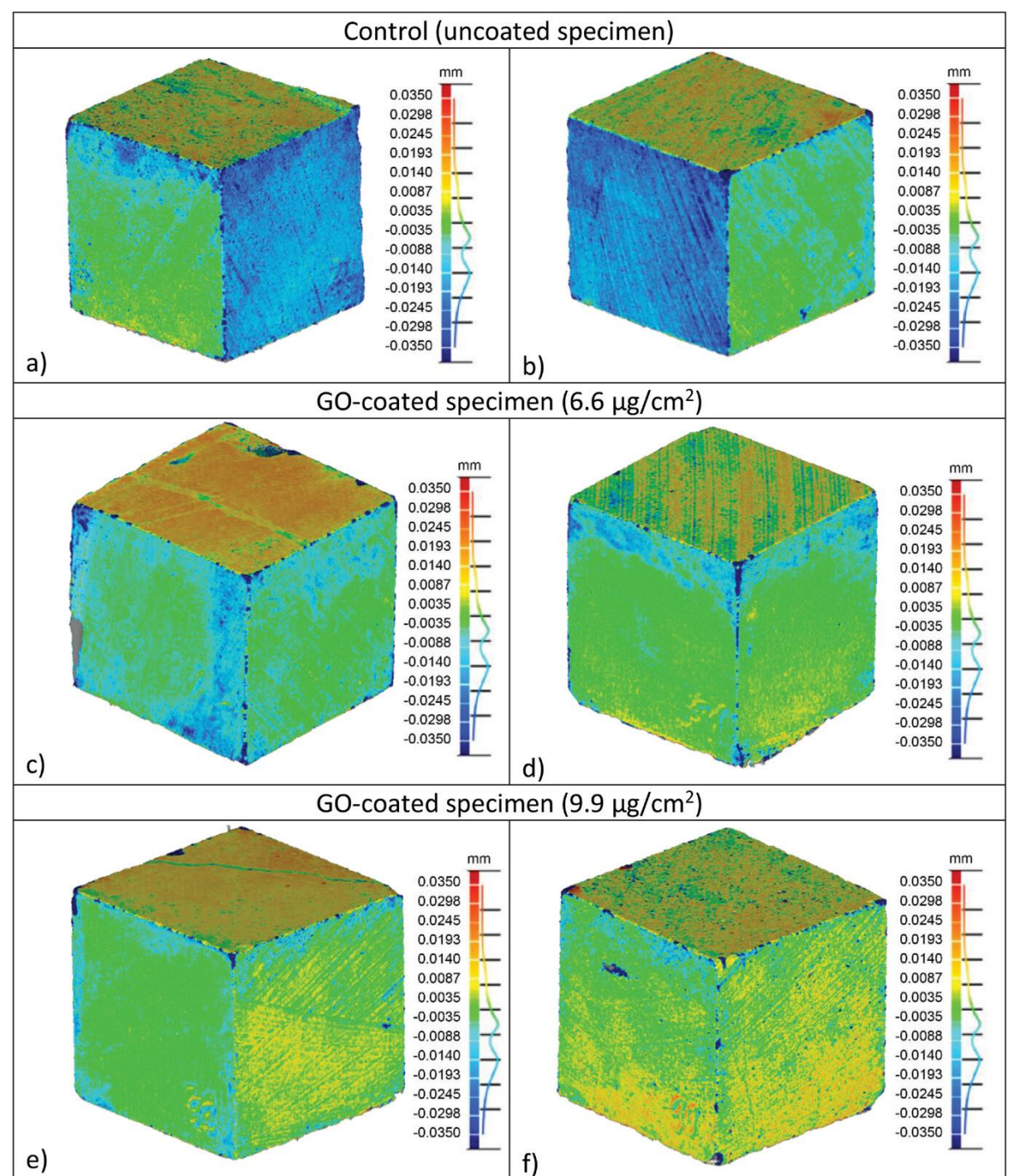
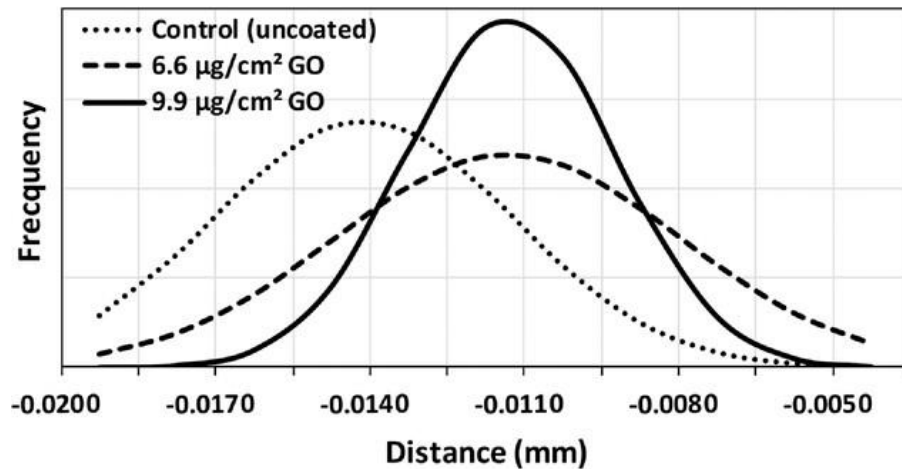


universidad
de león

3D scanner using structured light.
Breuckmann smart SCAN3D-HE scanner.



Martínez-García, R., et al.
<https://doi.org/10.1002/admt.202300486>

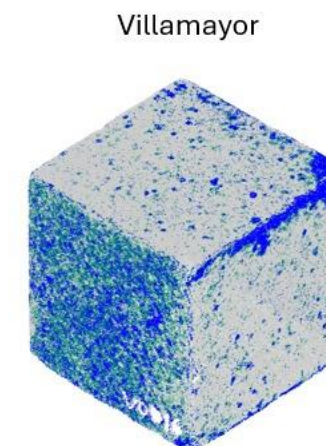
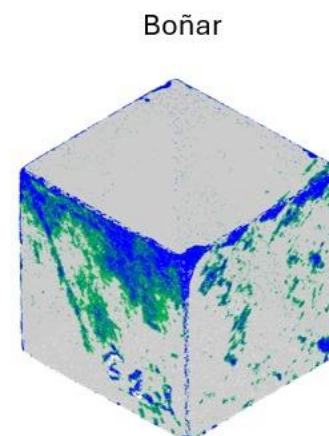


3D scanner using structured light.
Breuckmann smartSCAN^{3D}-HE scanner.

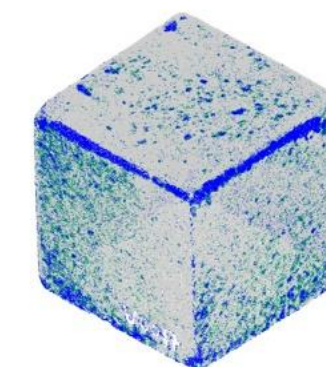
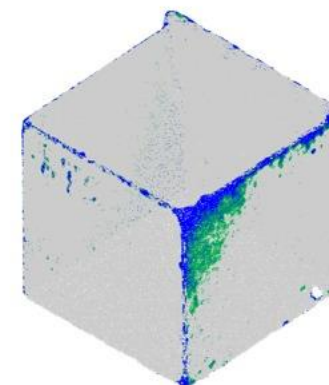


Chitin and crystalline cellulose.

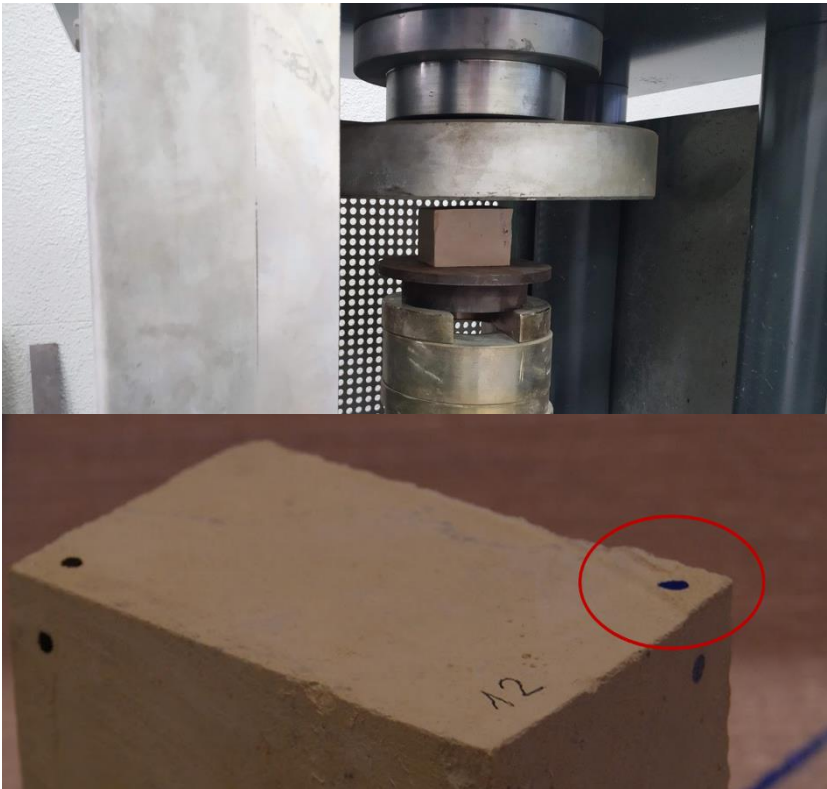
Uncoated



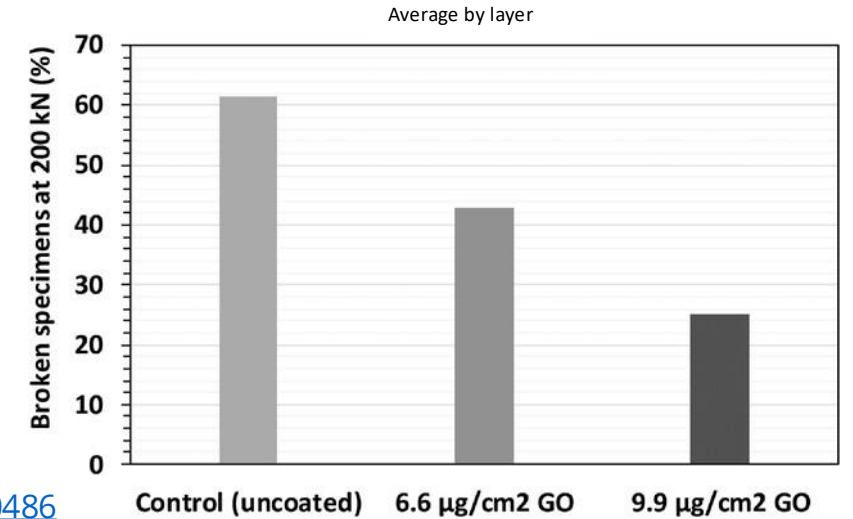
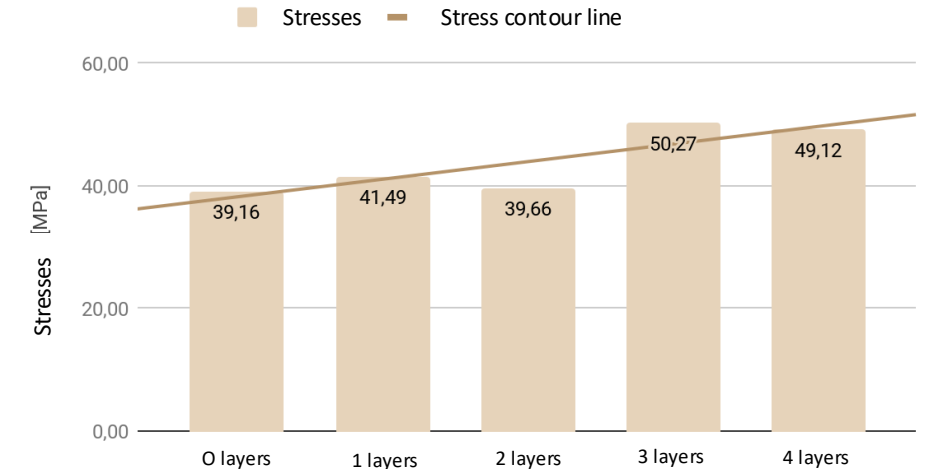
CNC I



Hydraulic Press



Stresses – average per layer



Martínez-García, R., et al.
<https://doi.org/10.1002/admt.202300486>

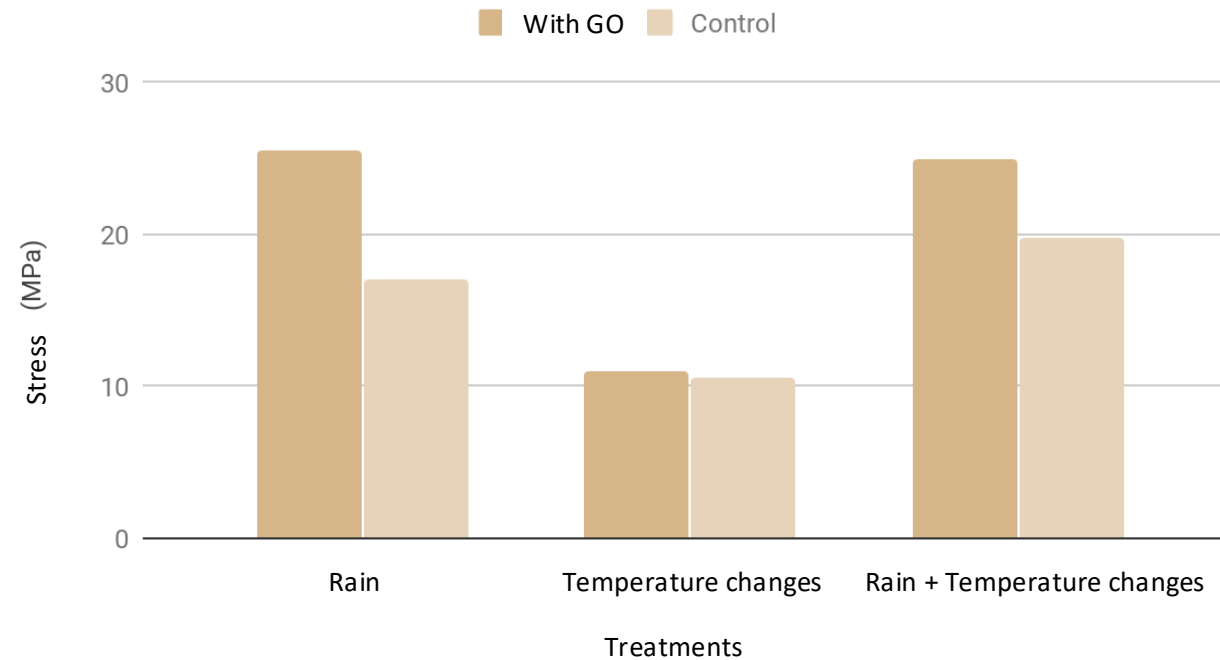
Collaboration: Dr. Manuel Ignacio Guerra Romero, professor at the School of Agricultural and Forestry Engineering of the University of León.

Hydraulic Press



Large

Strength tests on a hydraulic press



Collaboration: Dr. Manuel Ignacio Guerra Romero, professor at the School of Agricultural and Forestry Engineering of the University of León.

Lichens



Large



Verrucaria sp



Lecidea sp



Aspicilia sp

Interpretation: Dr. Arsenio Terrón Alfonso from the Department of Biodiversity and Environmental Management and Botany of the Faculty of CC. Biological and Environmental Sciences, from the University of León

Loss Observation Analysis



Medium

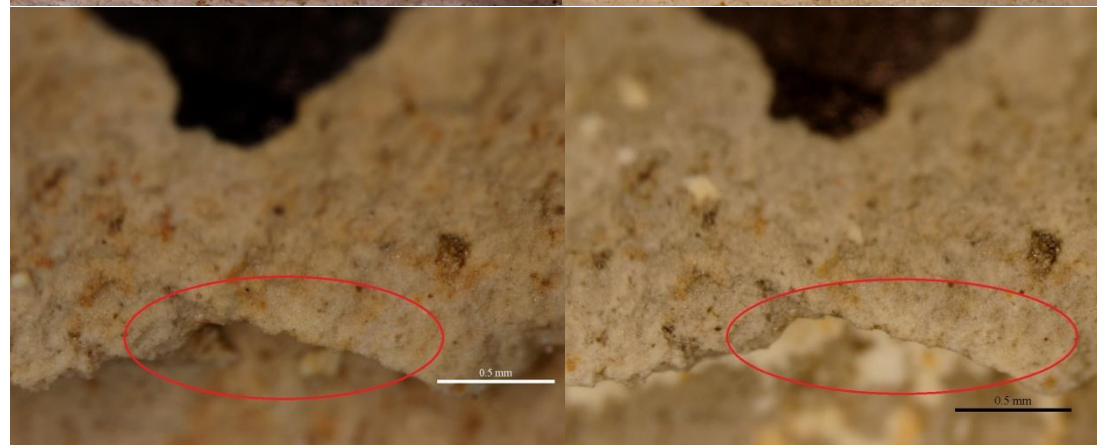
Glass



With GO



Without GO

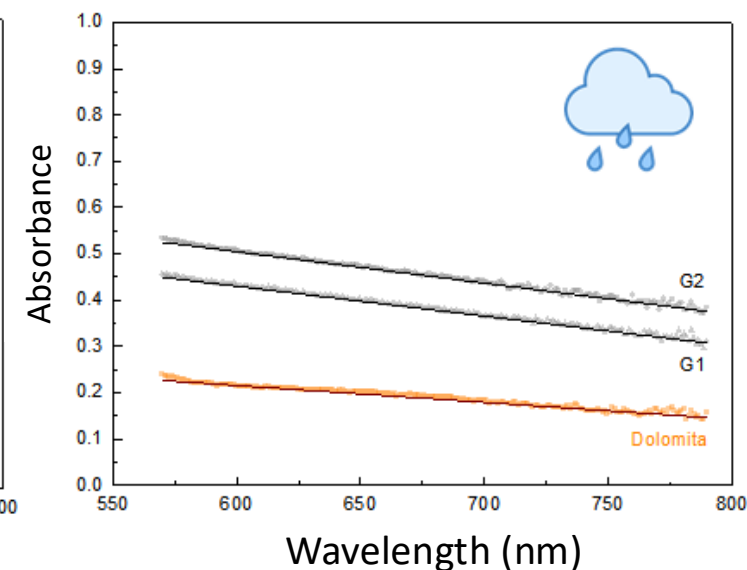
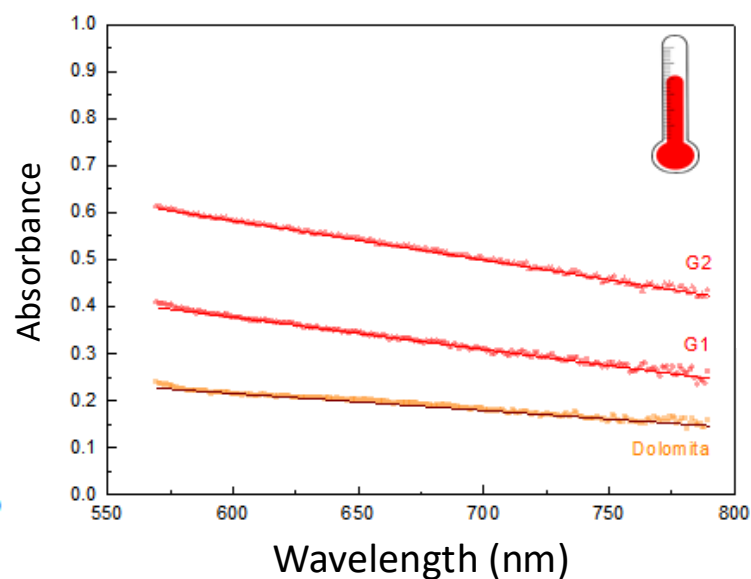
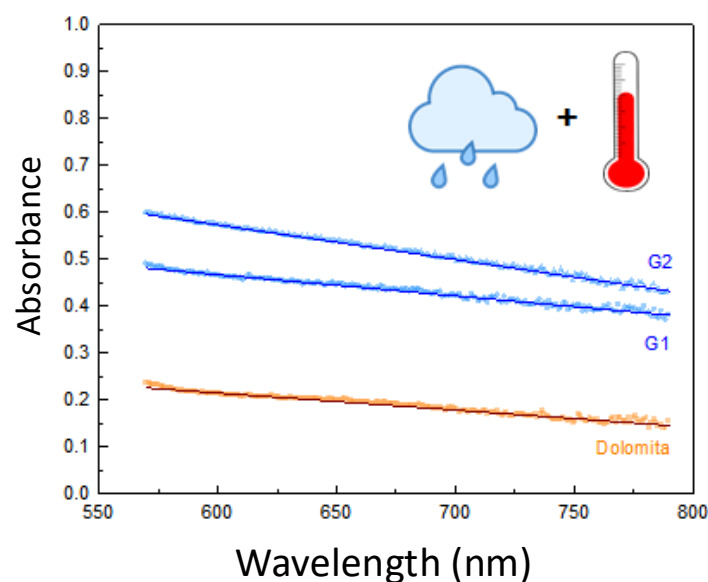


Collaboration: Dr. Benjamín Rabanal García: Laboratory of Instrumental Techniques, University of León.

Diffuse Reflectance UV-Vis Spectroscopy

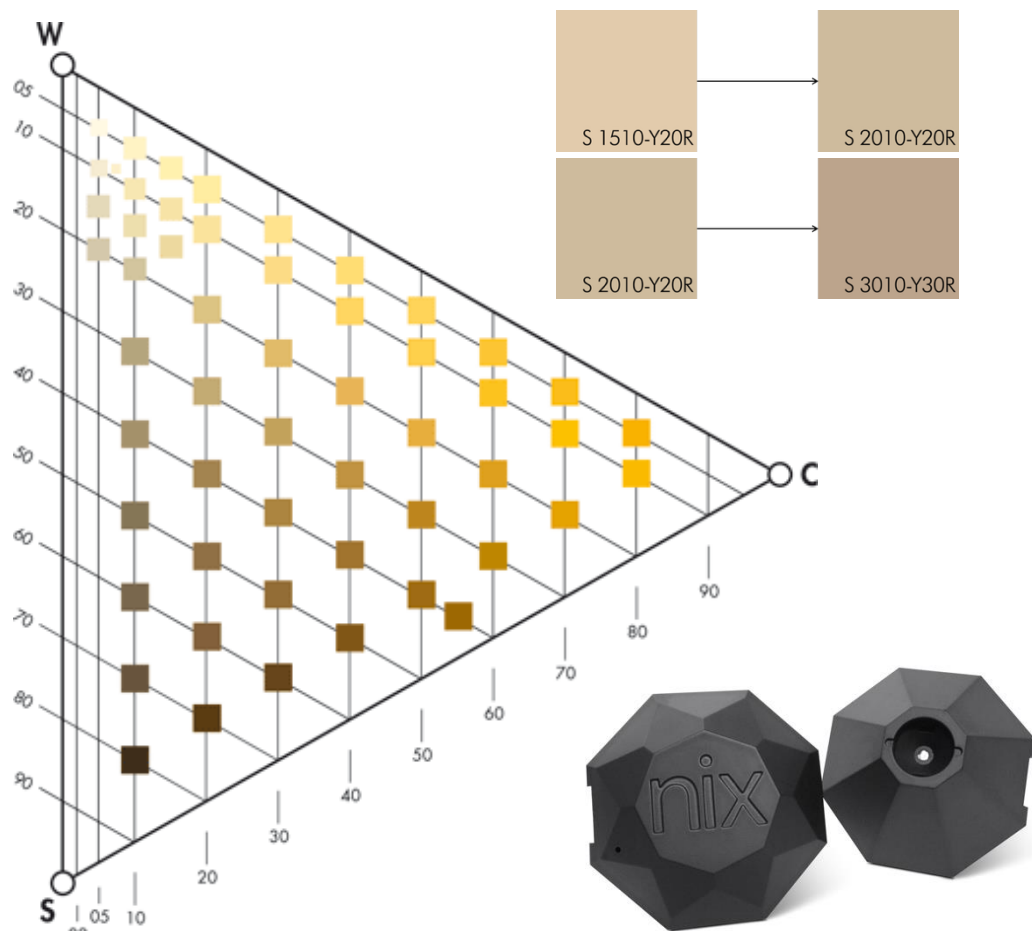


Medium

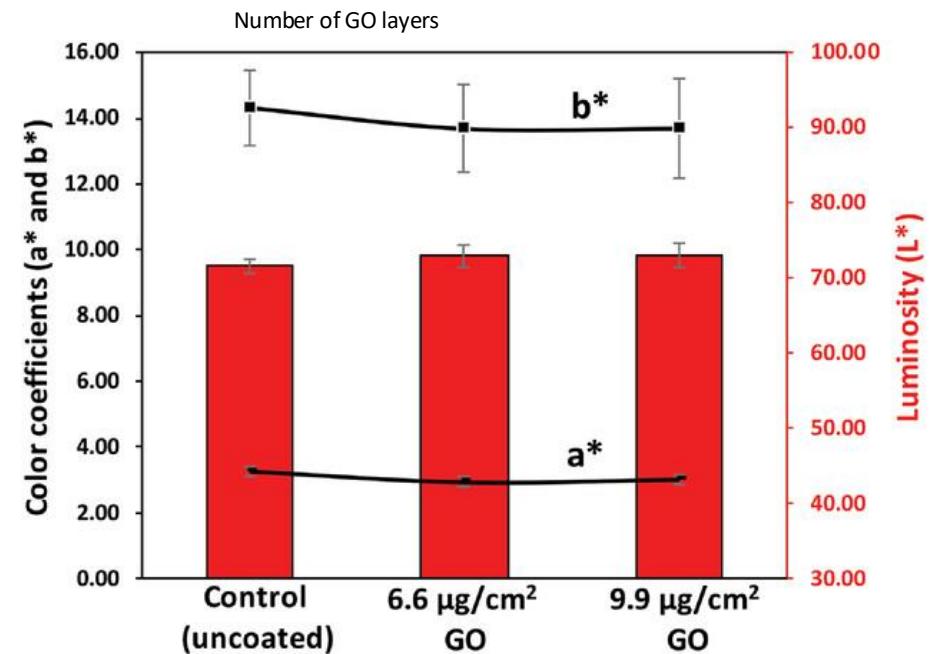
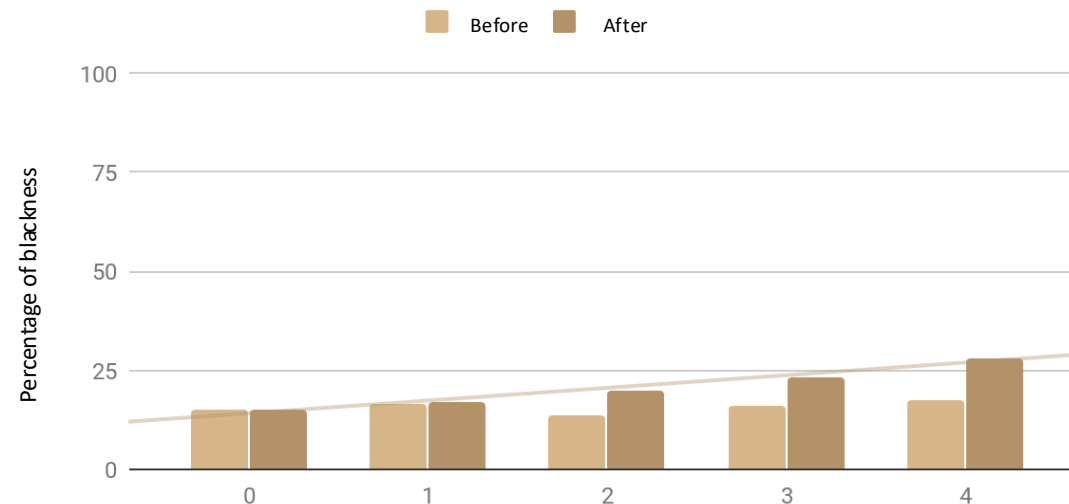


Interpretation: Carbon Nanostructures and Nanotechnology Group (G-CNN) of the Institute of Carbochemistry of the CSIC of Zaragoza

Colorimetry



Darkening of the samples



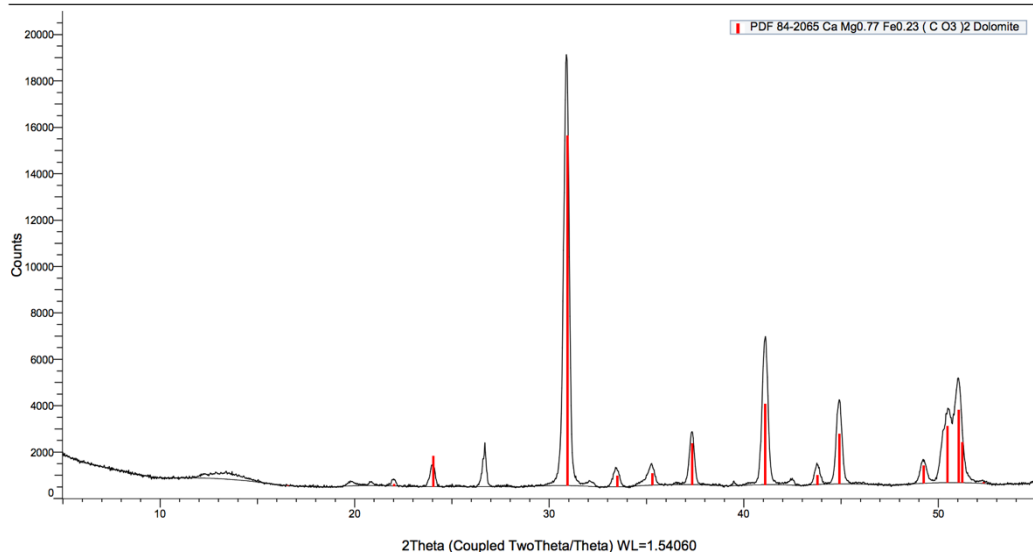
Analyses carried out

XRD: X-ray Diffraction

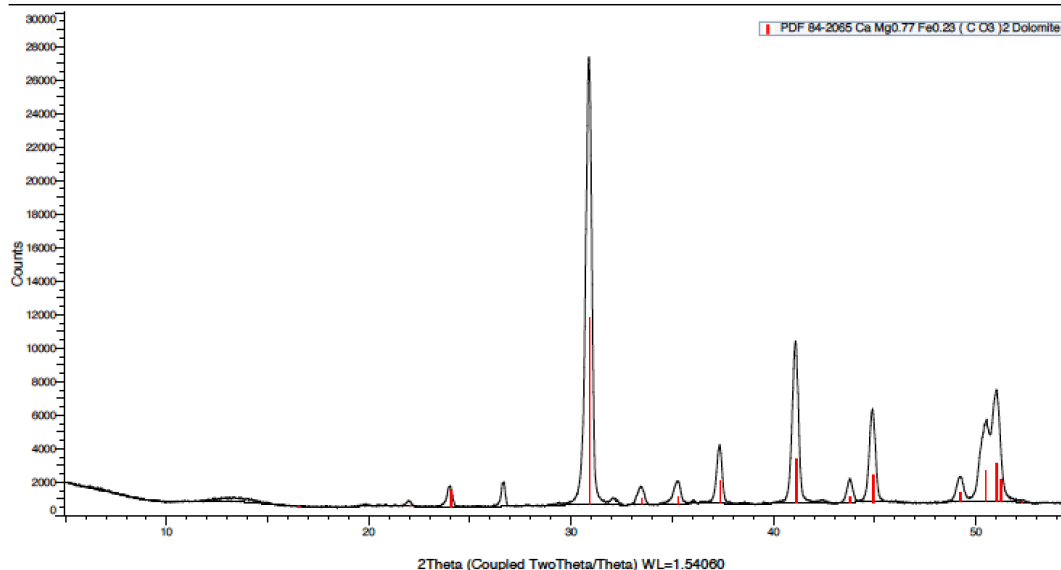


Small

MR-001 (1804180) (Coupled TwoTheta/Theta)



MR-001_G (1804181) (Coupled TwoTheta/Theta)



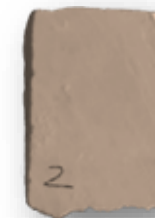
Raman Spectroscopy

XPS: X-ray Emitted Photoelectron Spectroscopy

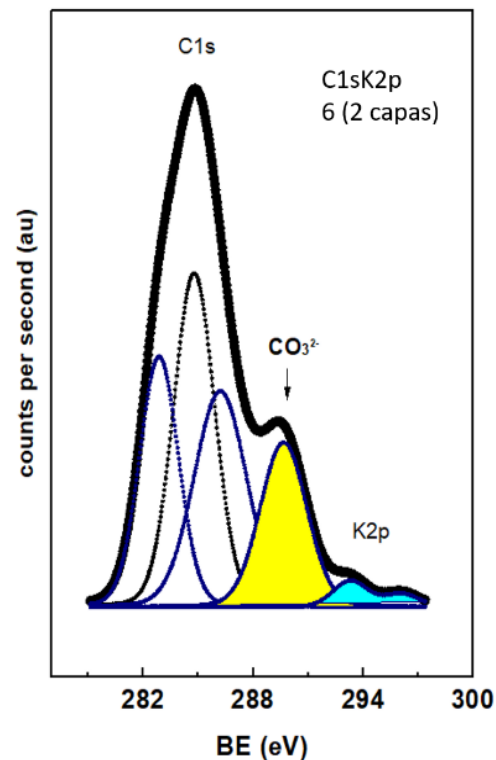
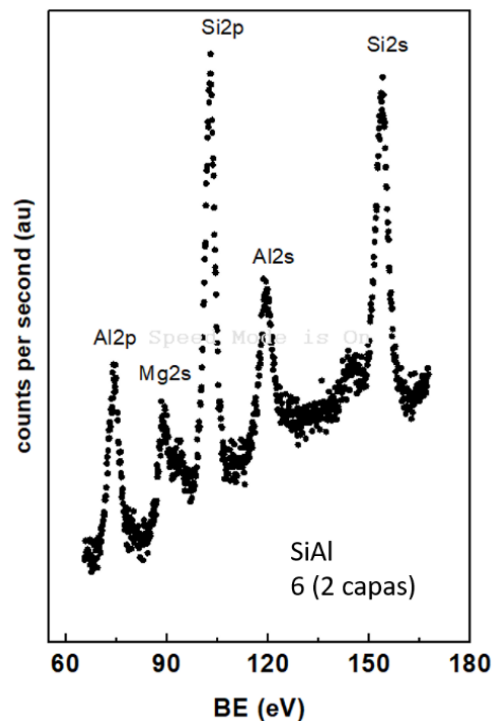
Interpretation (XRD and Raman): G-CNN from the
Institute of Carbochemistry of the CSIC of Zaragoza

Interpreting (XPS): Dr. José Luis García Fierro, Institute of
Catalysis and Petrochemistry of the CSIC of Madrid

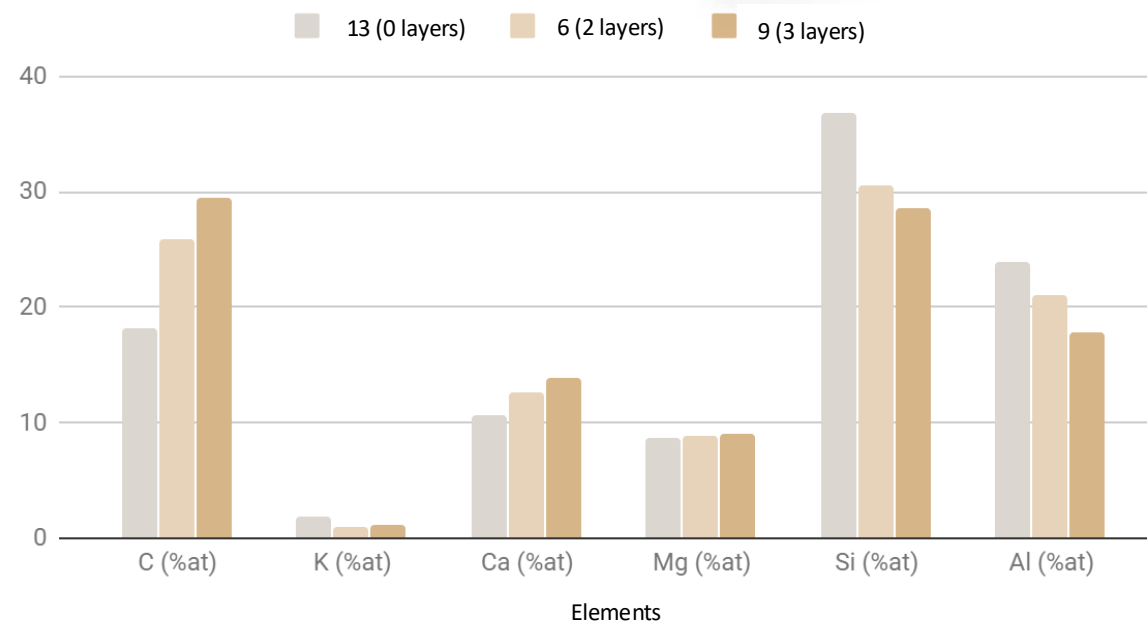
XPS: X-ray Emitted Photoelectron Spectroscopy



Small



Atomic composition (%)

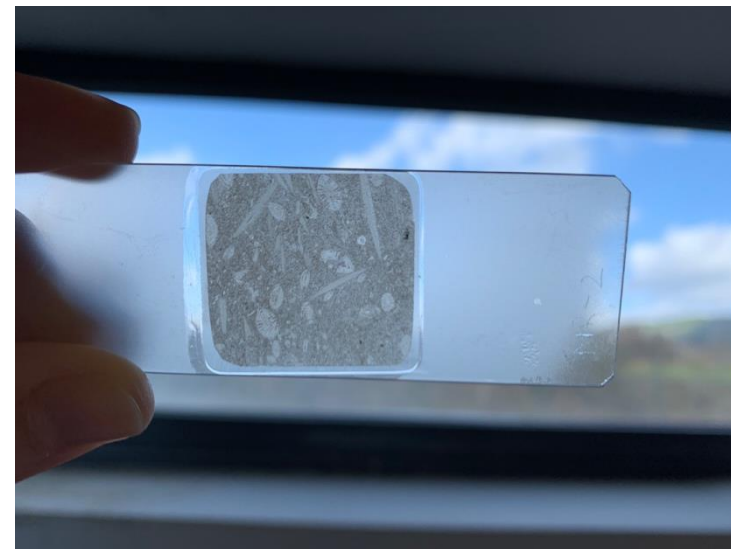


Collaboration: Dr. José Luis García Fierro, Institute of Catalysis and Petrochemistry of the CSIC of Madrid

Collaborations



Collaborations



Production of thin sheets

Collaborations



Pycnometry and permeability

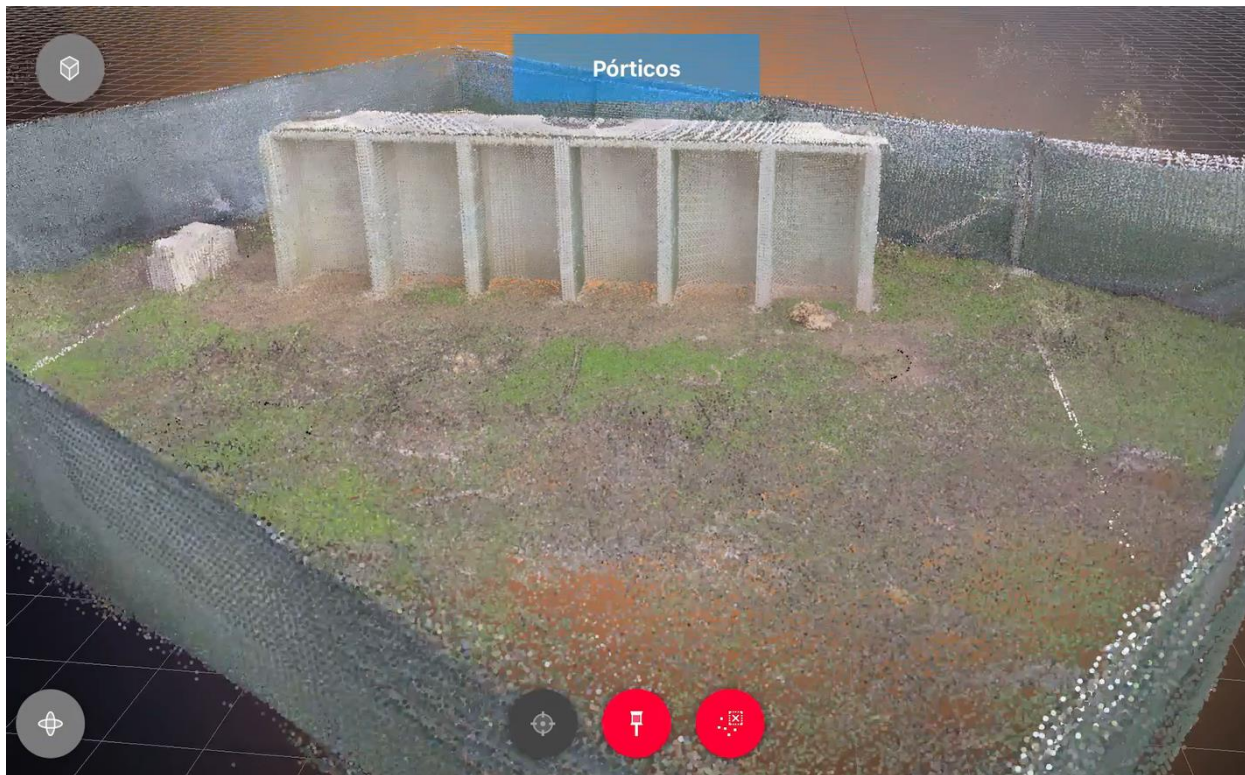
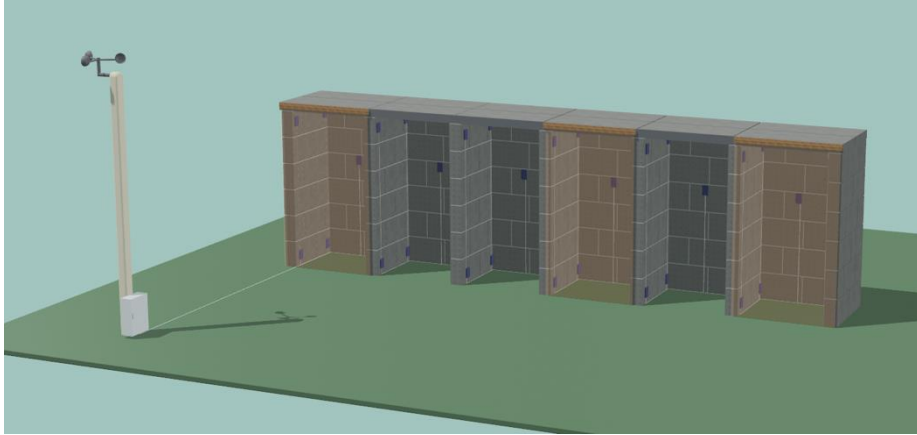




Portico

Visibility

Assess cracks, damage, wear and tear



Hydrophilic materials

Concentrations have been studied in standardised tests. The problem is that the tests are not designed for hydrophilic materials. Water-repellent tests have also been carried out.



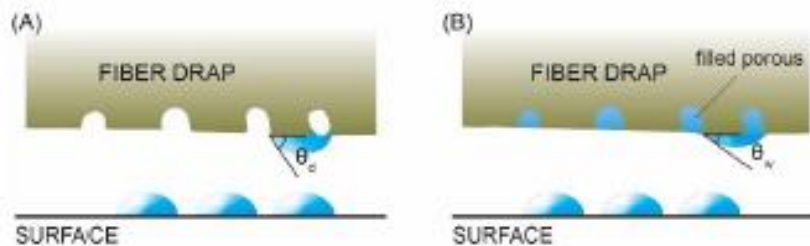
Article

Adaptation of a Standard Method for Water Absorption Testing of Stone Materials: The Case of a Hydrophilic Protective Coating

Gabriel Búrdalo-Salcedo ^{1,*}, Indira Rodríguez ¹, María Fernández-Raga ^{1,*}, Sagrario Fernández-Raga ², Carlos Rodríguez-Fernández ² and José Miguel González-Domínguez ³

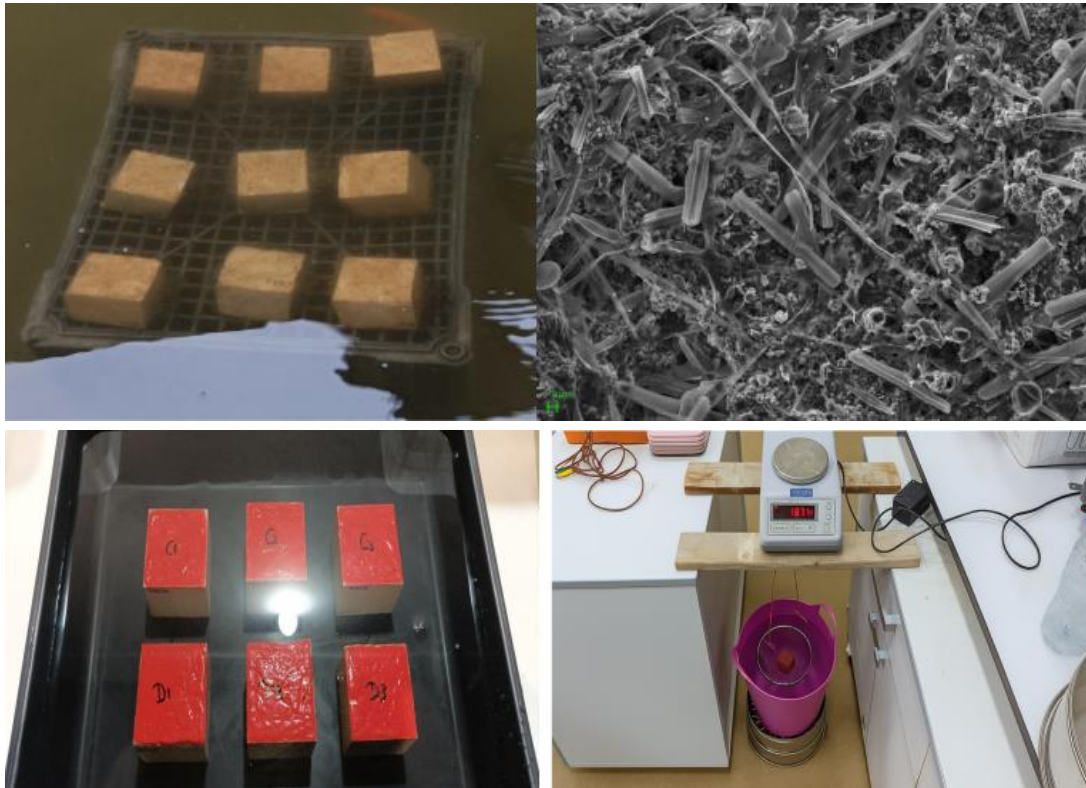
Main conclusions:

- Standard water absorption protocols must be mandatorily adapted because they do not account for the presence of protective coatings on stone materials.
- The modified methodology must strictly control the drying temperature, use distilled water, and employ surgical cloths for the surface cleaning of samples.
- It is strongly recommended to use the same samples for all comparative analyses to mitigate the significant influence of the stone's intrinsic heterogeneity.



Ongoing research: diatoms coatings

- Development of new coatings in different lithologies, concretes, and metals, such as the use of diatoms to improve the durability of materials.



Article

Study About the Influence of Diatoms on the Durability of Monumental Limestone

Daniel Merino-Maldonado ^{1,*}, Rebeca Martínez-García ^{1,*}, Víctor Baladrón-Blanco ¹, Jesús de Prado-Gil ¹, Fernando J. Fraile-Fernández ¹, María Fernández-Raga ², Covadonga Palencia ² and Andrés Juan-Valdés ³

Main conclusions:

- Diatom-treated samples exhibited higher overall porosity and water absorption compared to control samples.
- The surface side most exposed to biodeposition showed reduced water absorption, suggesting improved anti-absorption properties.
- A slightly higher resistance to frost was detected in the diatom-treated samples.

<https://doi.org/10.3390/app15158513>

3

Honors and Awards



Research Awards

FGULEM 2018 Project

First prize in the University-Business Challenge Castilla y León 2020





universidad
de león

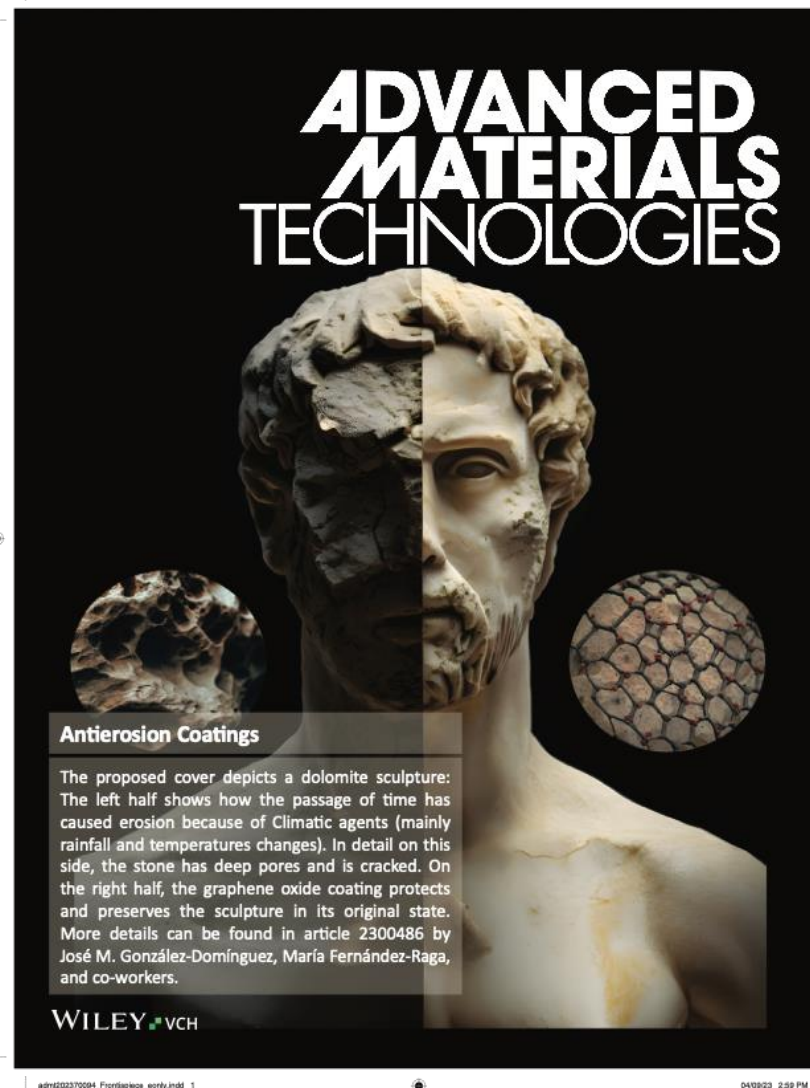
17 research papers

Agreements:

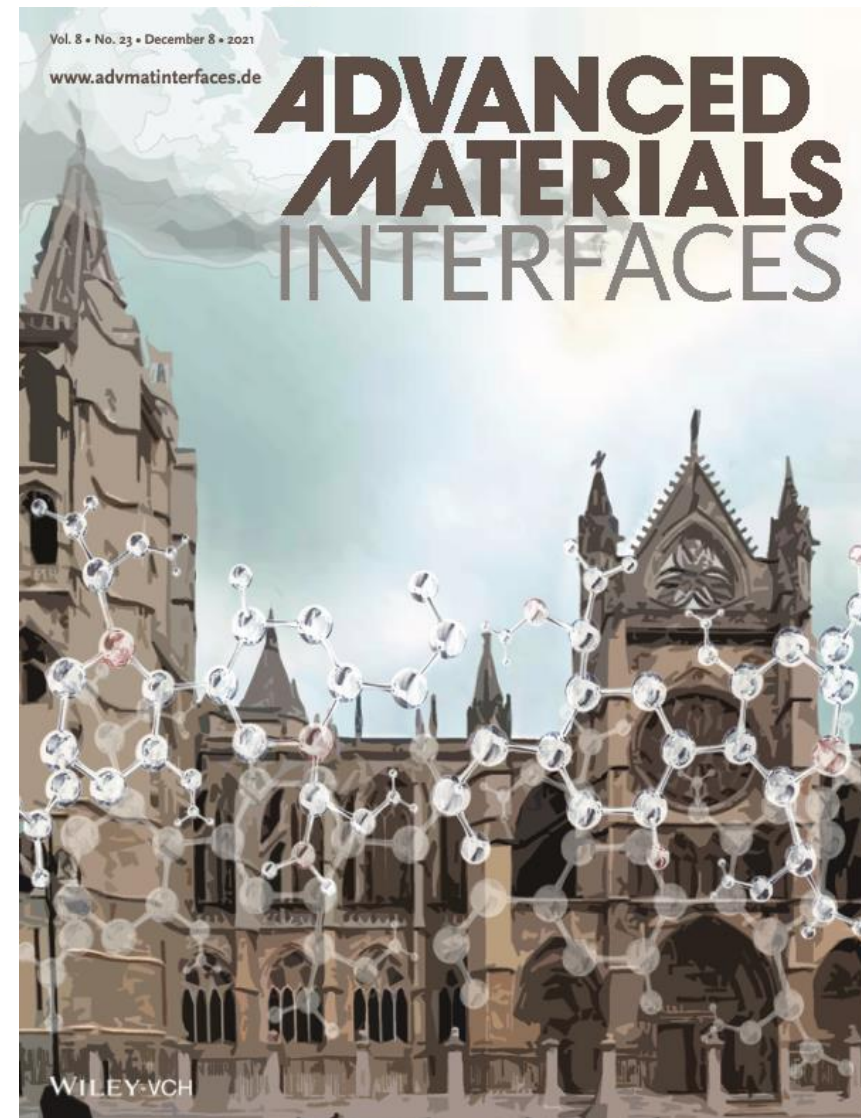
- CIUDEN (22-26)
- León City Council.
- The Chapter of El Pilar in Zaragoza.
- The Chapter of the Cathedral of Santa María in León.
- A construction company.



Funded by
the European Union



Cover selection Frontispiece
in Advance Materials Technologies 2023



Cover selection
Advanced Materials Interfaces
Vol. 8 • No. 23 • December 8 • 2021

R&D&I project and contract management

Title: NANOSHIELD I PID2020-120439RA-I00 "COMBATING THE DEGRADATION OF STONE HERITAGE DUE TO CLIMATE CHANGE WITH COATINGS MADE FROM SUSTAINABLE NANOMATERIALS"

Implementation period: 1 September 2021 - 31 August 2024.

Rating: Very satisfactory

Title: NANOSHIELD 2.0: NANOTECHNOLOGY FOR THE PROTECTION OF CULTURAL AND INDUSTRIAL HERITAGE: FROM INTERFACE TO APPLICATION (NANOSHIELD 2.0).

Implementation period: 1 September 2024 – 31 August 2027. + 1 FPI Doctoral Grant



4

Ongoing research



Study of Salinization or Salt movements

GO is a non-destructive technique that protects the stone and does not change its colour.

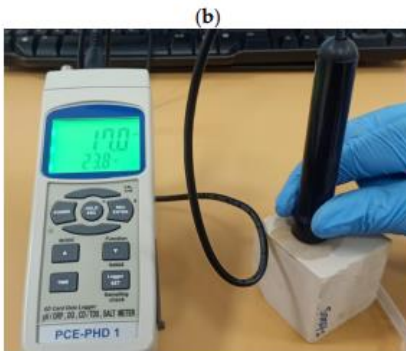
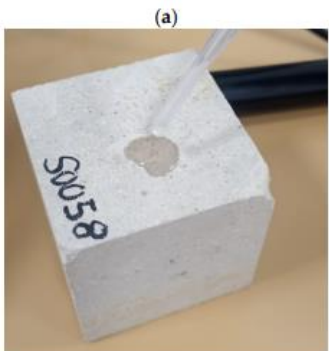
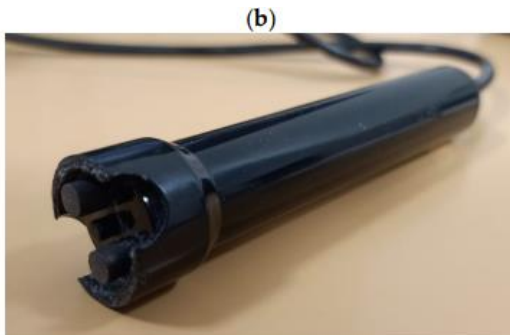
Article

Novel Methodology to Assess Salt Movement Between Mortar and Stones from Heritage in Spain

Linde Pollet ^{1,2,*}, Andrea Antolín-Rodríguez ³, Josep Gisbert-Aguilar ⁴, Gabriel Búrdalo-Salcedo ⁵, Andrés Juan-Valdés ³, César García-Álvarez ⁶, Angel Raga-Martín ⁷, Wouter Schroeyers ², Víctor Calvo ⁸ and María Fernández-Raga ^{7,*}

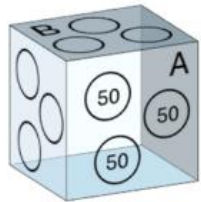
Main conclusions:

- Alkali-activated materials (AAMs) exhibit a significantly higher release of soluble salts, primarily sodium sulfate, posing a risk to adjacent porous heritage stones.
- In contrast, Blended Portland Cement (BPC) mortars showed lower salt mobility and different salt compositions.
- It is crucial to evaluate the compatibility between alternative sustainable binders and historic stones to ensure restoration materials do not inadvertently accelerate structural deterioration.

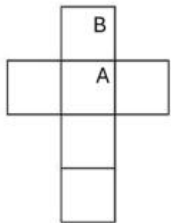


Ongoing research: Development of non-destructive testing: Spectroscopy

This allows for the detection of the type of stone and whether it has a coating.



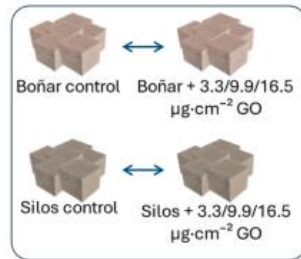
150 scans



X 6 faces



X 6 cubes



X 8 groups = 43.200 scans

Applied Surface Science Advances 30 (2025) 100864



Contents lists available at ScienceDirect

Applied Surface Science Advances

journal homepage: www.sciencedirect.com/journal/applied-surface-science-advances

Short Communication

Spectral characterization for the evaluation of a protective coating on dolomite by visible and near infrared spectroscopy

David González-Campelo^{a, *}, Víctor Calvo^{b, *}, Indira Rodríguez^{c, *}, Gabriel Búrdalo-Salcedo^{d, *}, José Miguel González-Domínguez^{b, *}, María Fernández-Raga^{a, *}

Main conclusions:

- Graphene oxide (GO) emerges as a promising protective coating that enhances the stone's resistance to weathering and preserves its aesthetic integrity.
- This study establishes vibrational spectroscopy as a powerful in situ technique for monitoring protective coatings on heritage stones.
- Using a partial least squares regression (PLSR), spectral data accurately assessed the coating presence, concentration, and uniformity of the GO on the dolomite.

Ongoing research: Development of non-destructive testing: S and P waves

Ultrasound for measuring S and P waves, enabling strength testing without destroying the sample.



Pundit for measuring S and P waves

Ongoing research: Influence of pigeon droppings and graffiti on heritage stones.



Ongoing research

- Development of new coatings in different lithologies, concretes, and metals.
- Development of testing under ageing chamber.



Thank you!

www.hieurecapro.eu | info@hieurecapro.eu

www.hieurecapro.eu | info@hieurecapro.eu

Follow us on social media:

