DTC LAZIO
DISTRETTO TECNOLOGICO BENI E ATTIVITÀ CULTURALI
CENTRO DI ECCELLENZA

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

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TECNOLOGIE DI ANALISI, DIAGNOSTICA E MONITORAGGIO PER LA CONSERVAZIONE E IL RESTAURO DI BENI CULTURALI

Surface protection of “Sperone” of Villa Mondragone by nanostructured materials in the framework of ADAMO project

***Claudia Pelosi*, Giorgia Agresti, Luca Lanteri, Gianluca Rubino, Franca Persia, Giuseppe Bonifazi, Silvia Serranti, Giuseppe Capobianco**

UNIVERSITÀ DEGLI STUDI DELLA Tuscia

SAPIENZA UNIVERSITÀ DI ROMA

ENEA

WP 5 – Analysis of the materials used in conservation and restoration of cultural heritage and evaluation of treatments

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GOALS

- Tests on commercial products used in restoration
- Tests on innovative materials
- Development of protocols for evaluating the effectiveness of treatments

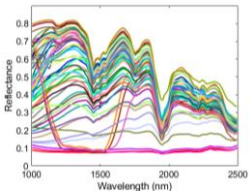
tattoo WALL digital murals

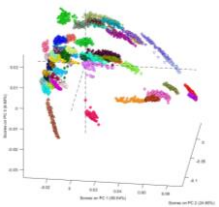
TASK LIST

- **Task 5.1** – Experimental tests of treatments of stone and wood materials through artificial ageing protocols [TUS, RM1, ENEA].
- **Task 5.2** – Development and validation of methods for conservation of ancient bronzes [RM3]
- **Task 5.3** – Validation and characterization of multi-functionalised nanostructured materials for the restoration of stone artworks [RM3, RM1]

DELIVERABLES

- **1**. Report with the first results of the comparison between the performance of traditional restoration materials and new innovative nanostructured products applied on the case studies selected by WP1.
- **2.** Promotion of new products for restoration.
- **3.** Report of two case studies describing the potentiality of the application of new materials for targeted action.
- **4**. Report on new non-invasive and non-destructive methodologies for the identification and classification of materials and for the evaluation of consolidant and protective treatments.





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Scientific papers:

- G. Bonifazi, G. Capobianco, C. Pelosi, S. Serranti, Hyperspectral imaging as powerful technique for investigating the stability of painting samples, Journal of Imaging, 5(8), 2019.
- L. Lanteri, G. Agresti, C. Pelosi, A new practical approach for 3D documentation in ultraviolet fluorescence and infrared reflectography of polychromatic sculptures as fundamental step in restoration, Heritage, 2(1), 2019, 207-215.

The remains of the villa of Quintili (2nd century A.D.) under Villa Mondragone

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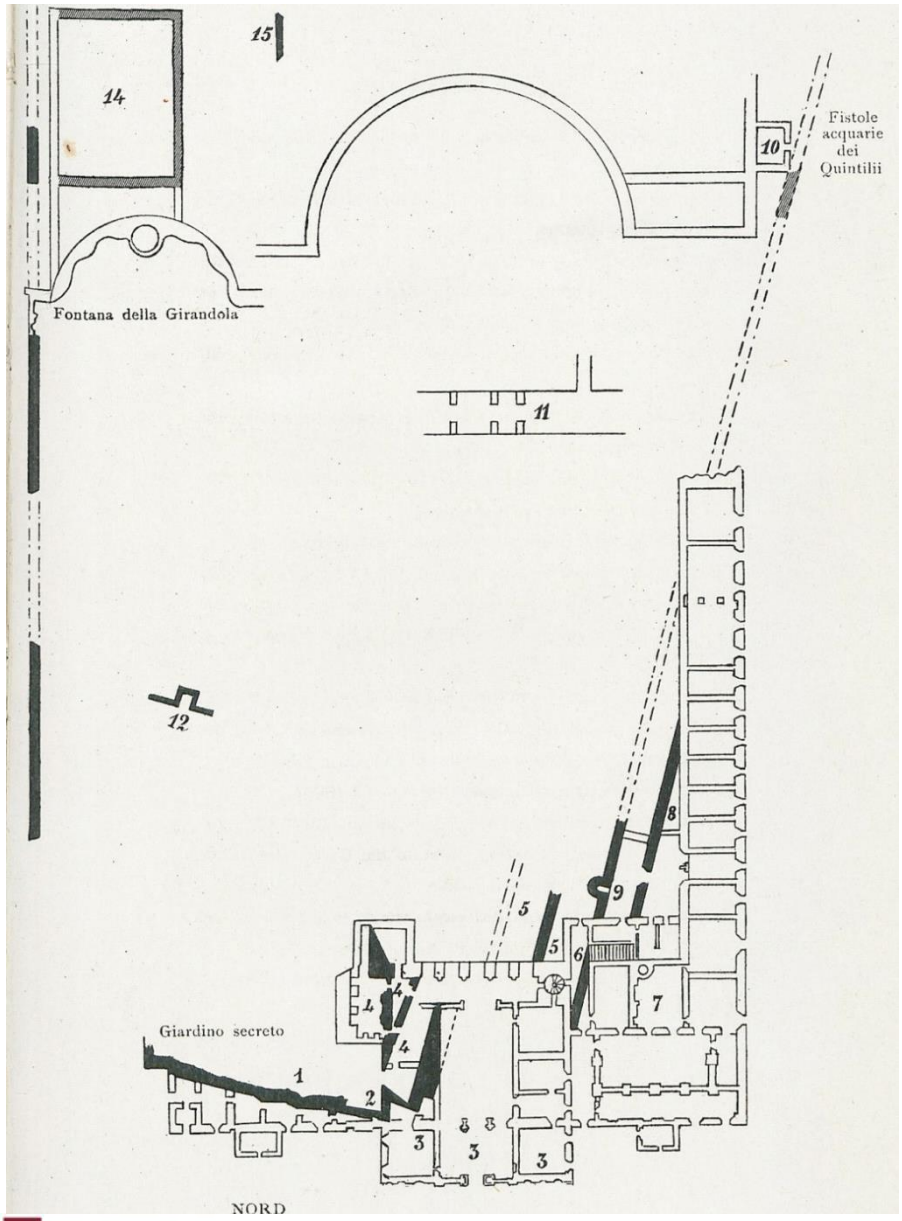

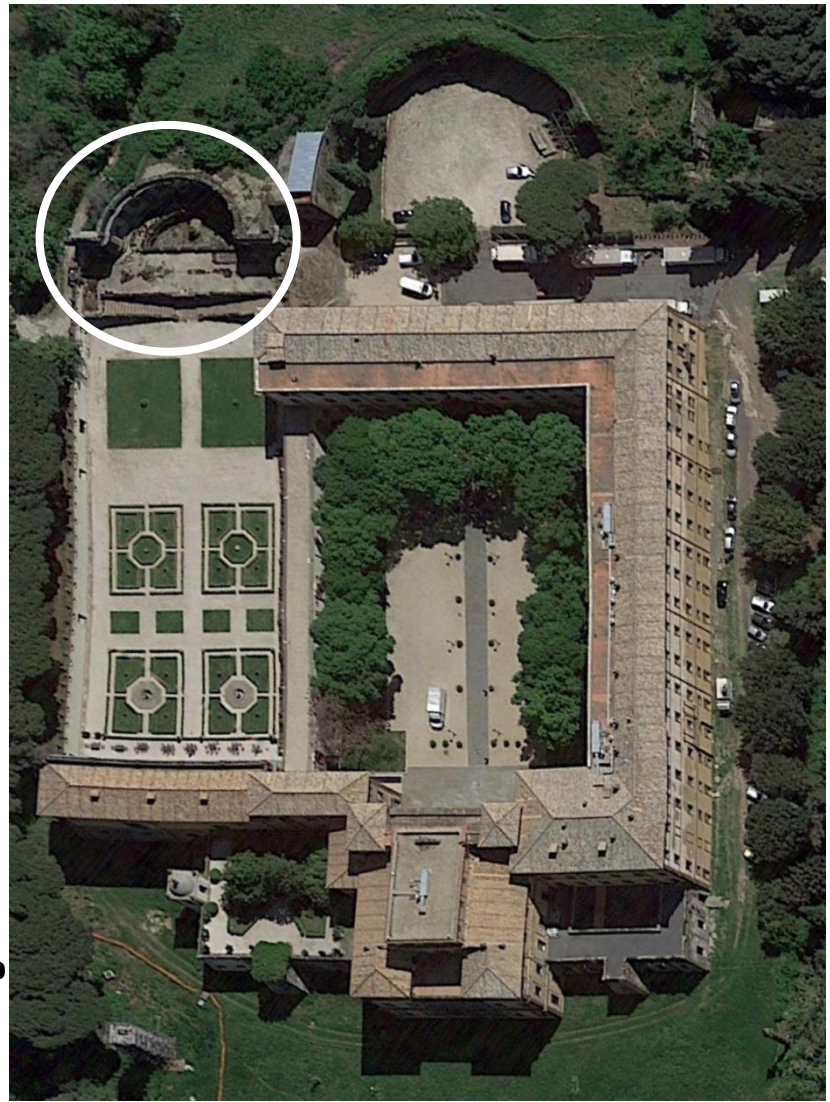

F. Grossi Gondi, *Di una villa dei Quintili nel Tuscolano*. Bullettino della Commissione Archeologica Comunale di Roma, 1898

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Experimental setup

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- Preparation of the samples for protective treatments, according to EN16581:2018.
- Polarizing microscopy for stone characterization
- μ-XRF for element mapping
- Choice of products and tests according to EN17114:2019.
- FT-IR spectroscopy for product characterization
- Application of protective products and colour measurements for evaluating their effects on surface colour
- Colour measurements before and after ageing
- Hyperspectral imaging before and after ageing
- UV and relative humidity ageing

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The selected case of Villa Mondragone: sampling of Sperone stone

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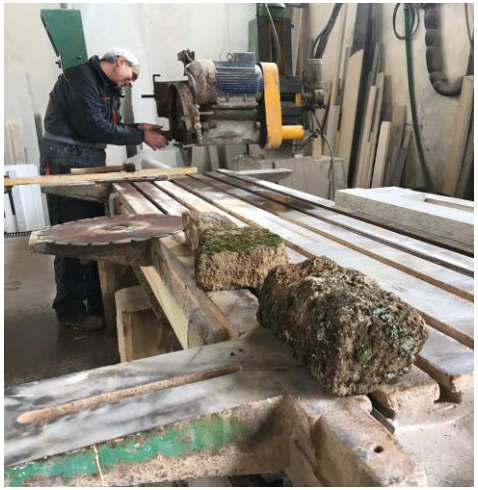

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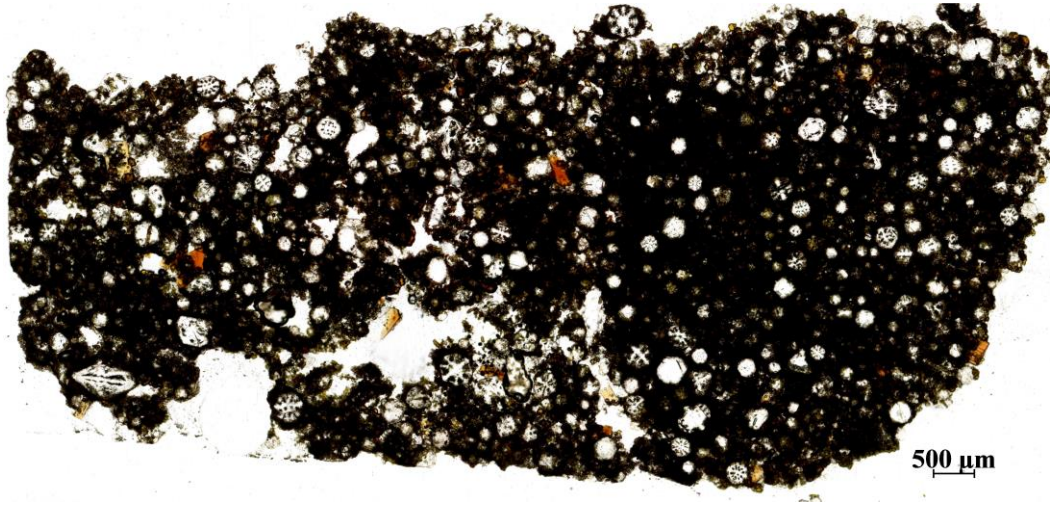
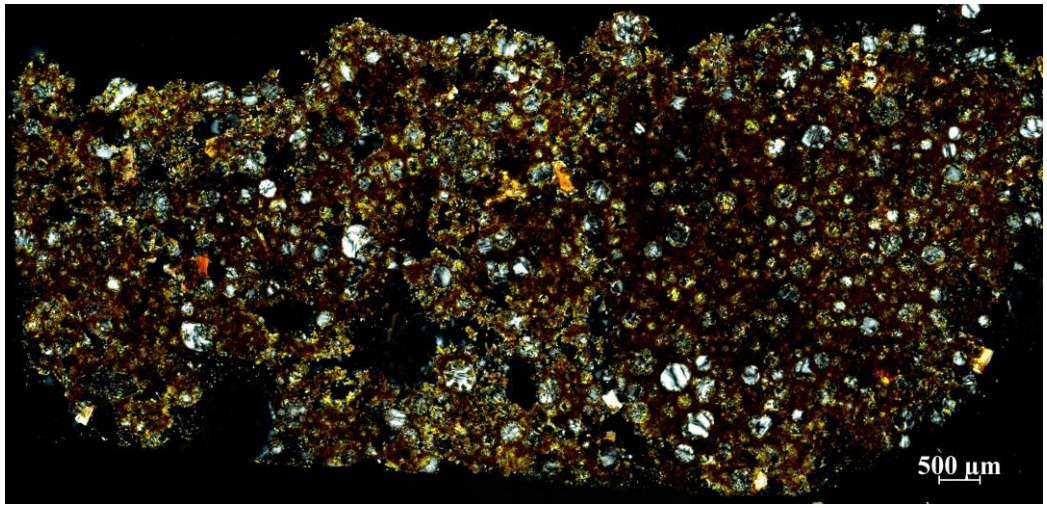
Thin section under polarizing microscope





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"Sperone" is a deposit of welded volcanic scoriae forming a portion of the Tuscolanio - Artemisio caldera rim, near the town of Tuscolo. "Sperone" has well distinguished macroscopic petrographic features with respect to tuffs being an aggregate of rounded, subcentimeter sized, poorly vesicular scoriae, resembling a scoriaceous lava rather than a pyroclastic-flow or hydromagmatic-surge deposit. Indeed, "Sperone" is a clast supported deposit, which lacks the fine ash matrix characteristically occurring in the "peperini".

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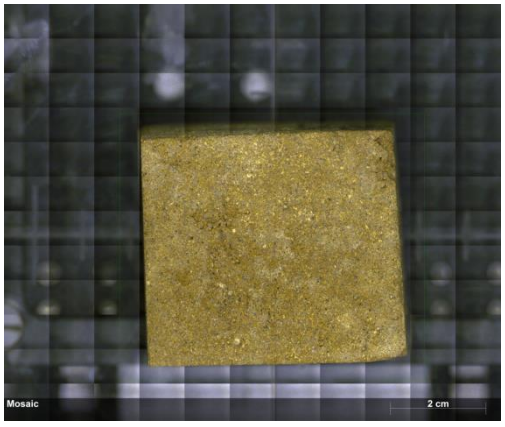
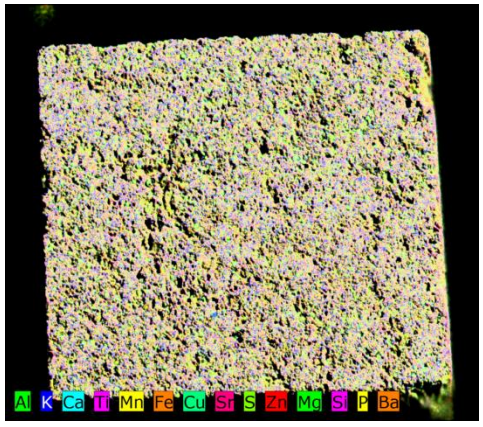
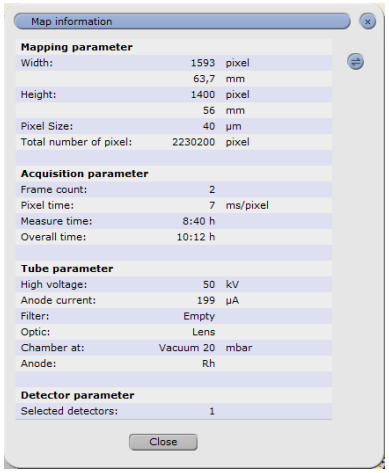
J. Farr et al., Geochemical identification criteria for "peperino" stones employed in ancient Roman buildings: A Lapis Gabinus case study, J. Archaeol. Sci.: Reports 3 (2015) 41–51

Analysis of the stone: XRF mapping







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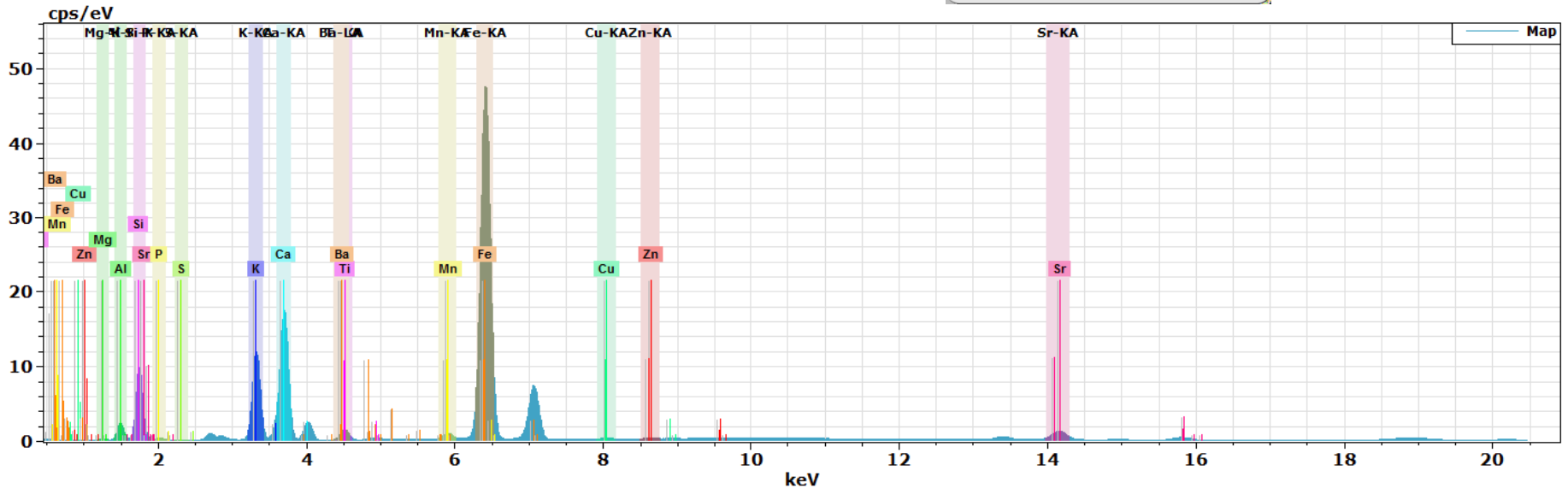

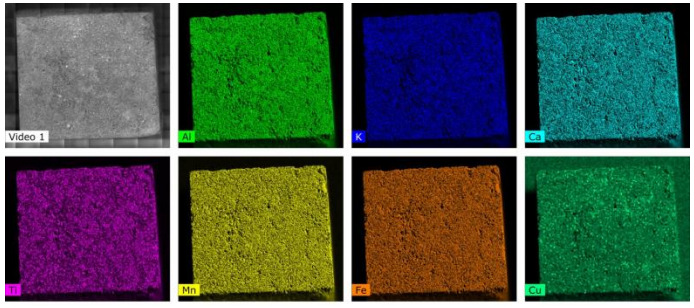

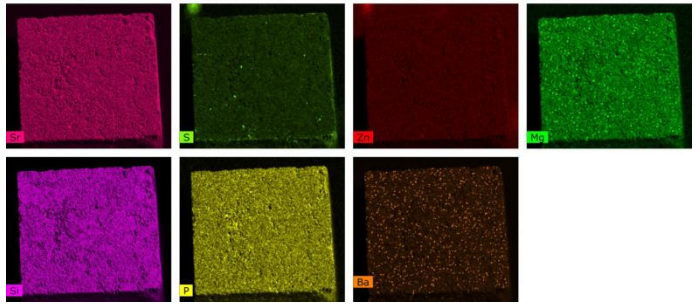

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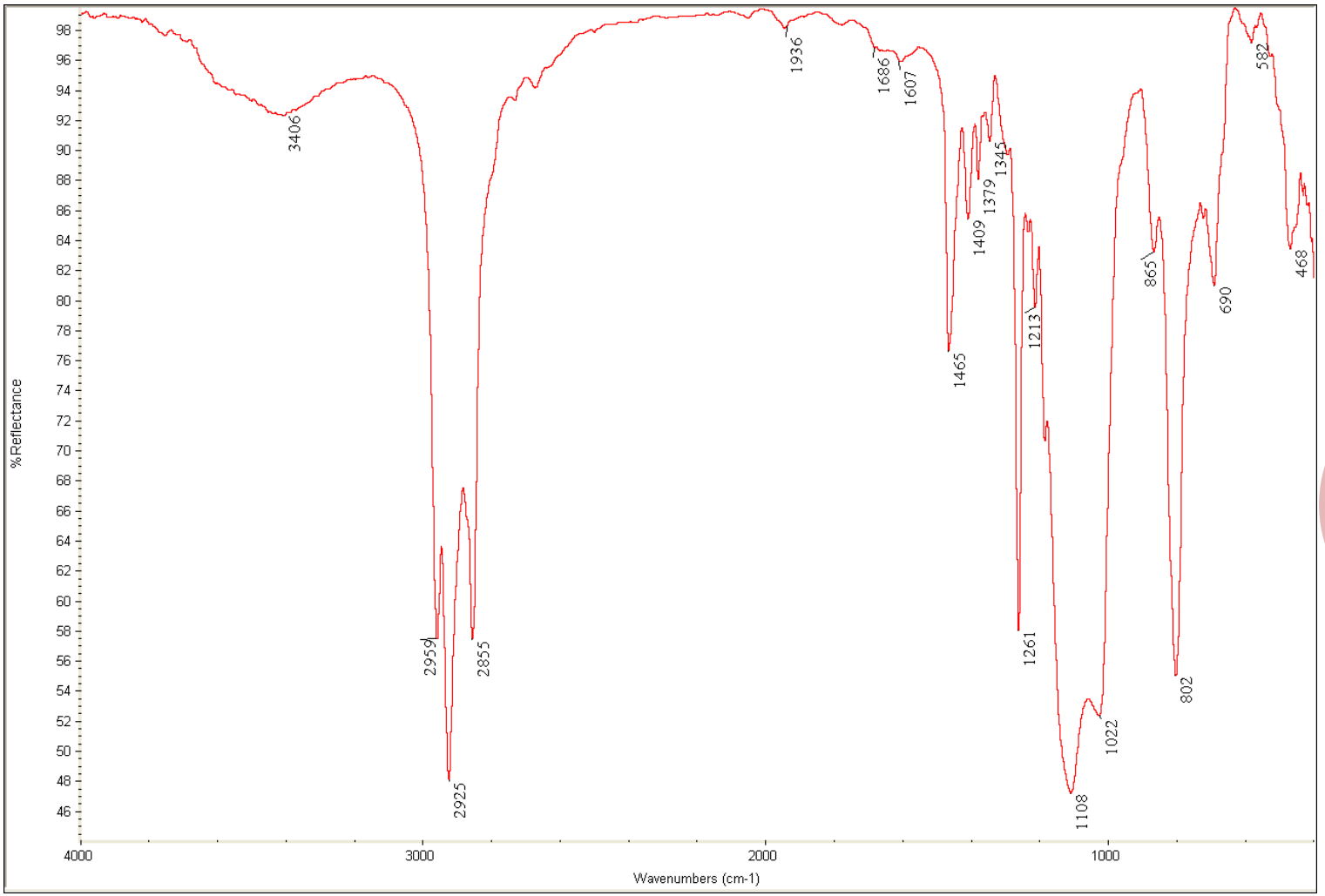
The choice of protective products

Reference	Commercial products	Stone
Fluorinated elastomers		
D. Colangiuli et al, 2015	Fluoline PE (CTS): water dispersion (10% w/w) of low molecular weight perfluoropolyether	Trani's rock
C. D. Vacchiano et al , 2008	Kimistone Antismog (KIMIA): modified fluorinated polymers in water solution	Yellow and grey tuff
Siloxanes in organic solvent		
C. D. Vacchiano et al , 2008	Antipluviol S (MAPEI): siloxanes in organic solvent (aromatic hydrocarbons)	Yellow and grey tuff
C. D. Vacchiano et al , 2008	Kimistone Idrorep (KIMIA): siloxanes in organic solvent	Yellow and grey tuff
C. D. Vacchiano et al , 2008	Sikagard 700S (SIKA): alkyl-alkoxy-siloxanes in organic solvent	Yellow and grey tuff
G. Cappelletti et al, 2015	Alpha®SI30 (SIKKENS): oligomeric poly-siloxane with 0.1M of $Ti(OC_3H_7)_4$ in 100 mL ethanol	Marble "botticino", Carrara, Angera (dolomitic marble)
Siloxanes in water solution		
C. D. Vacchiano et al , 2008	Kimistone Ibasil (KIMIA): siloxanes in water solution	Yellow and grey tuff
L. de Ferri et al, 2011	Glymo [3-(2,3-epoxy-propoxy)-poly-trimethoxy-silane] or 3-glycidoxypropyl-trimetoxisilane, $C_9\ H_{20}O_5\ Si$	Marmo botticino, Formazione Macigno (La Spezia), granito bianco (Montorfano)
Emulsions with nano-structured materials		
L. D'Orazio, A. Grippo (2016)	Idrocap 994: linear aliphatic poly-carbonate urethane (ICAP-SIRA) with addition of TiO_2 (5, 10, and 15% w/v) nanoparticles.	Yellow and grey tuff
L. de Ferri et al, 2011	Aeroxide LE1 [1,1,1-Trimethyl-N-(trimethylsilyl)-silanamine], particle dimension about 14 nm (DEGIUSSA-EVONIK) mixed with Dynasilan 40 (DEGIUSSA-EVONIK). The solutions are prepared in ethanol and catalysed with HCl.	Marble "botticino", "Formazione Macigno" (La Spezia, Italy), white granite (Montorfano)
	Aeroxide LE1 [1,1,1-Trimethyl-N-(trimethylsilyl)silanamine], particle dimension about 14 nm (DEGIUSSA-EVONIK) mixed with Glymo [3-(2,3-epoxy-propoxy)-poly-trimethoxy-silane] or 3-glycidoxypropyl-trimetoxisilane ($C_9\ H_{20}\ O_5$ Si) (DEGIUSSA-EVONIK) in ethanol as solvent.	
Other products		
Lucia D'Arienzo et al (2008)	Fluormet CP, vinyliden fluoride acrylic polymer (CTS); Cloisite 30B, stratified montmorillonite modified through N,methyl-N,tallow-N,N0,2-hydroxyethyl-ammoniumchloride (90 meq/100g clay) (SOUTHERN CLAY PRODUCTS). Tests were executed with Fluormet CP 3,7% in acetone alone and also by dispersing Cloisite 30B in Fluormet CP (1, 2, 4%)	Yellow and grey tuff

FT-IR spectroscopy for product characterization



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Silo N7

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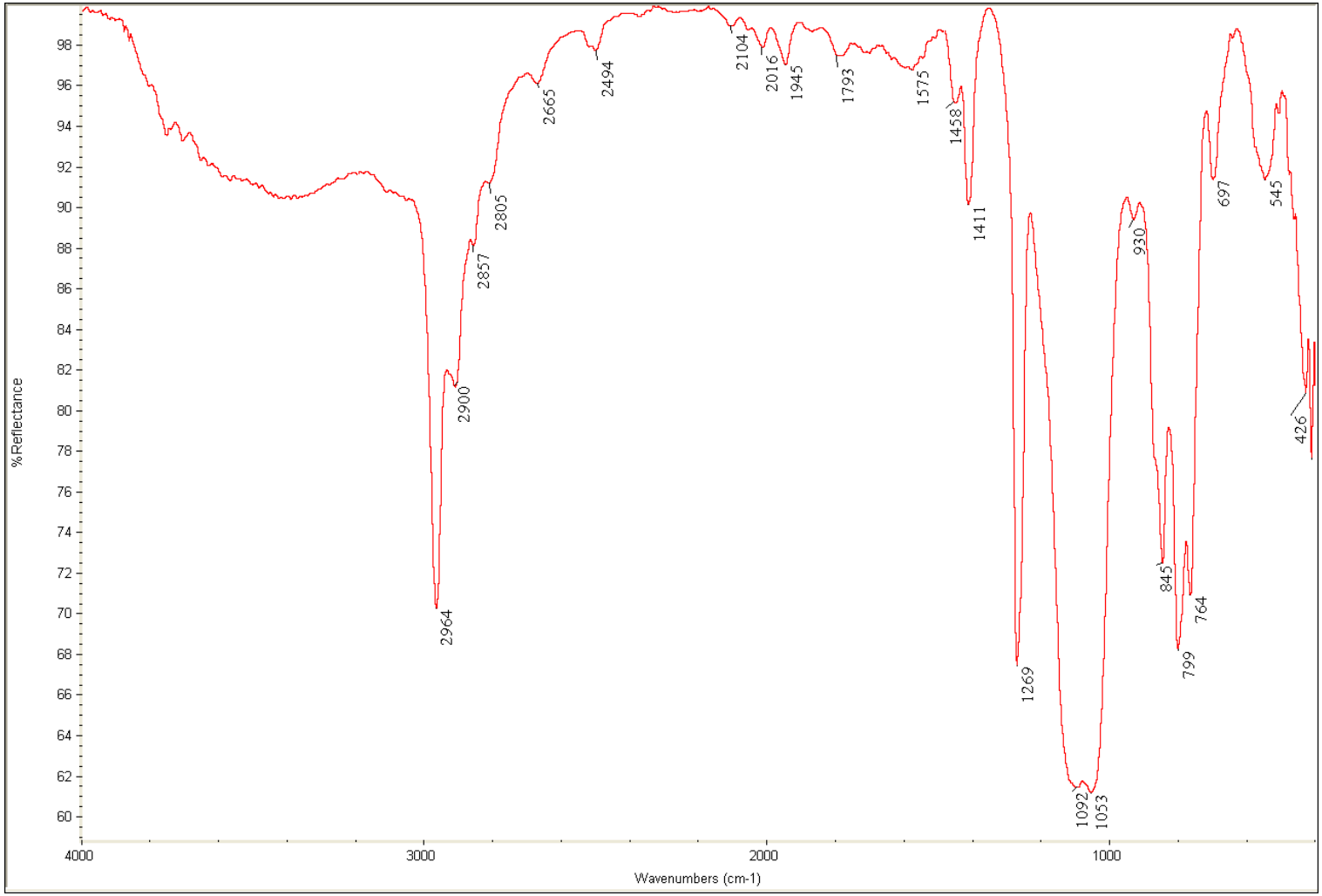
Nano silica based protective functionalized with poly-siloxanes.

FT-IR spectroscopy for product characterization



Rhodorsil H224

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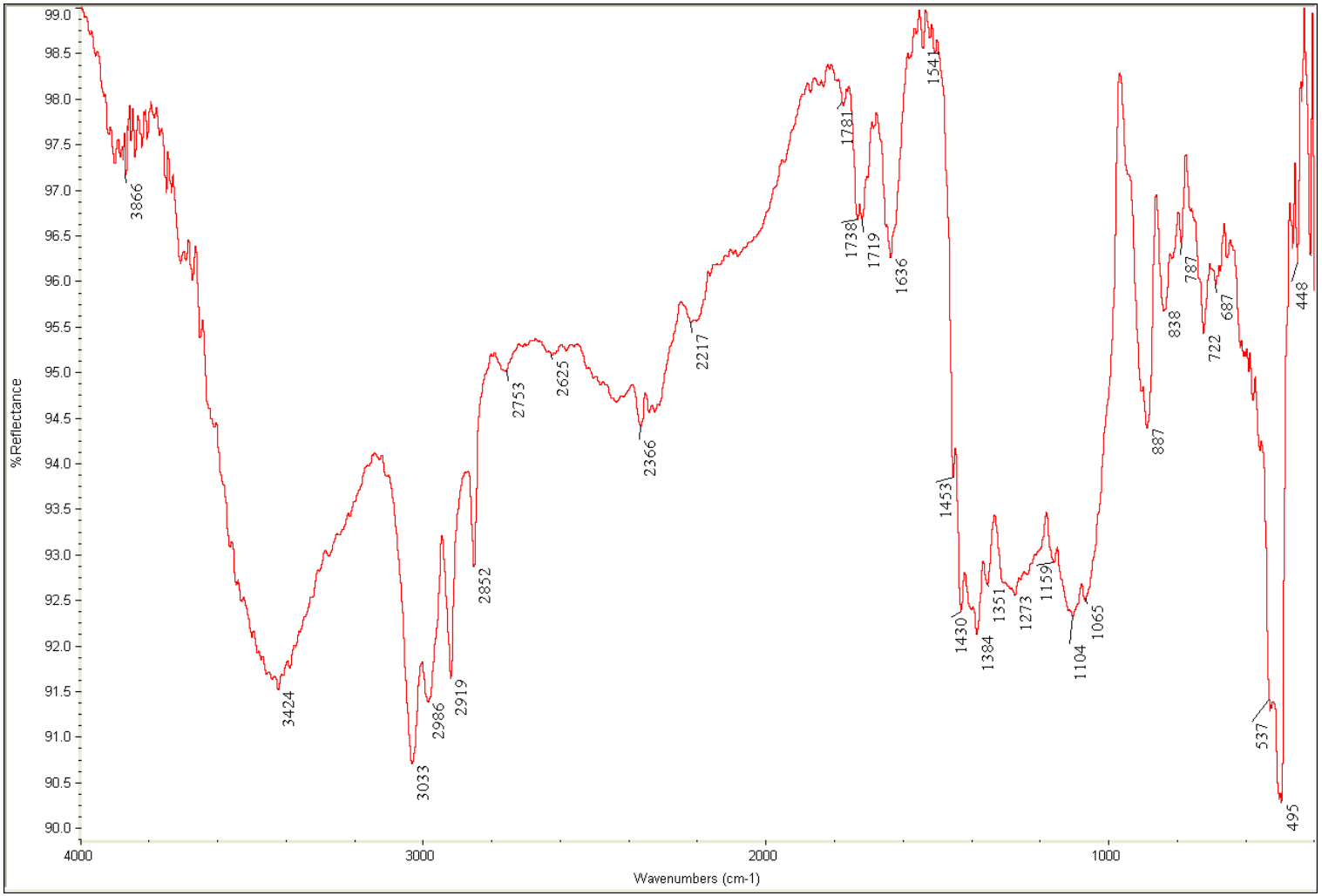
FT-IR spectroscopy for product characterization



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Fluoline HY

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Application of protective products

	Silo N7	Rhodorsil H224	Fluoline HY
CHARACTERISTICS			
Chemical composition	**Functionalized nanoparticles**	**Alkyl polysiloxane polymer**	**Fluorinated copolymers**
Solvent	water	aliphatic hydrocarbons	acetone / butyl acetate
Physical state	liquid	liquid	liquid
Colour	white	colorless or slightly yellow	colorless
Viscosity	at 20°C 1 mPa.s	at 25°C mm^2/s	Brookfield 20-100 cP
EXPERIMENTAL			
Mixture	1:1 in demineralized water	6% in white spirit	TQ
Method	brush	brush	brush
Number of treatments	2 (consecutive)	2 (2^{th} treatment after 3 days)	2 (2th treatment after 3 days)
Number sample	8	8	8

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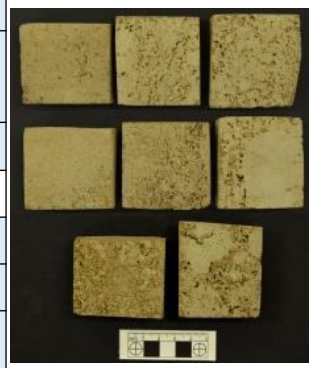

Not treated

Silo N7 is a new sperimental product kindly supplied by CTS for testing. It is not commercialized yet.

Treated with Silo N7

Treated with Rhodorsil H224

Treated with Fluoline HY

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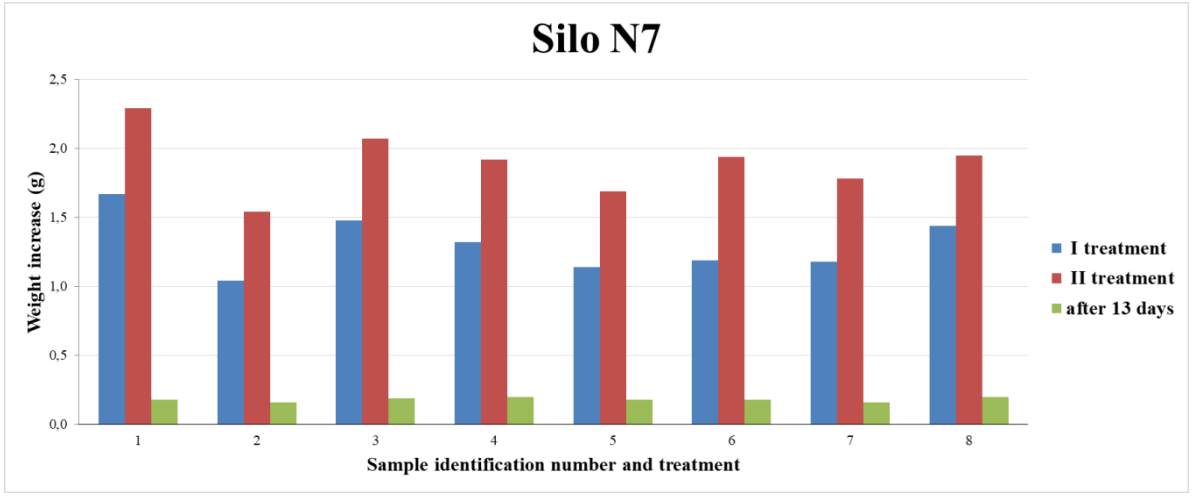
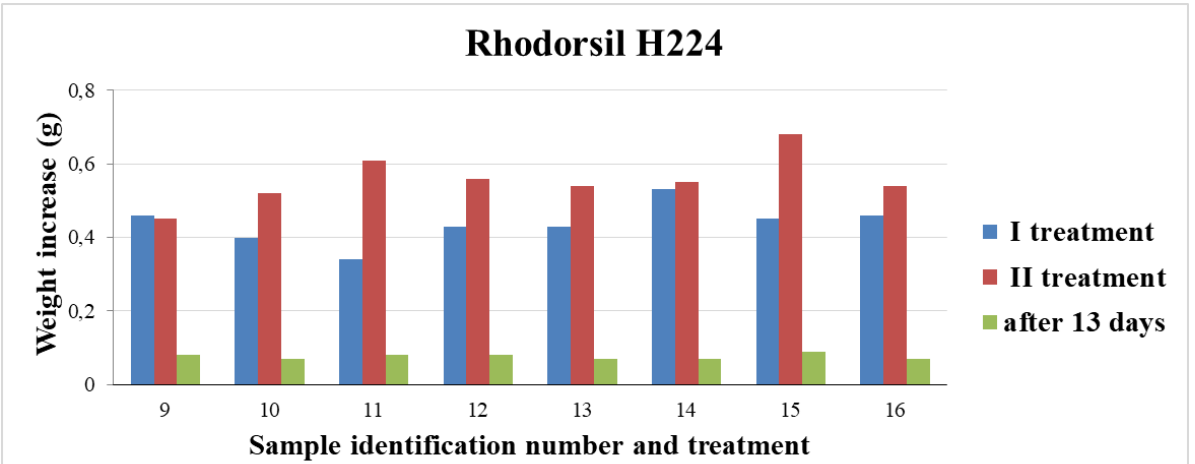
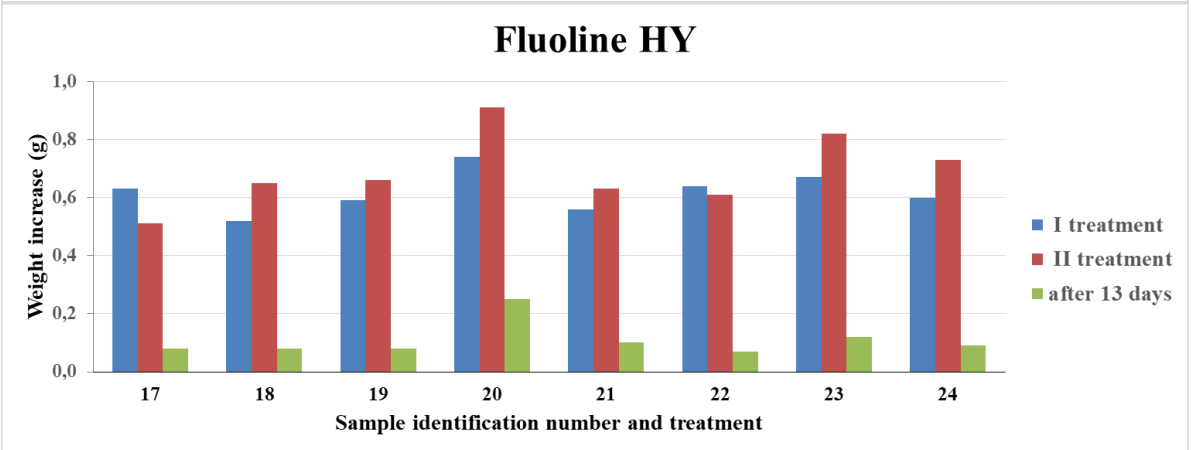
Silo N7



Rhodorsil H224



Fluoline HY



Weight variation after protective application

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Colour measurements for evaluating their effects on surface colour characteristics: Silo N7

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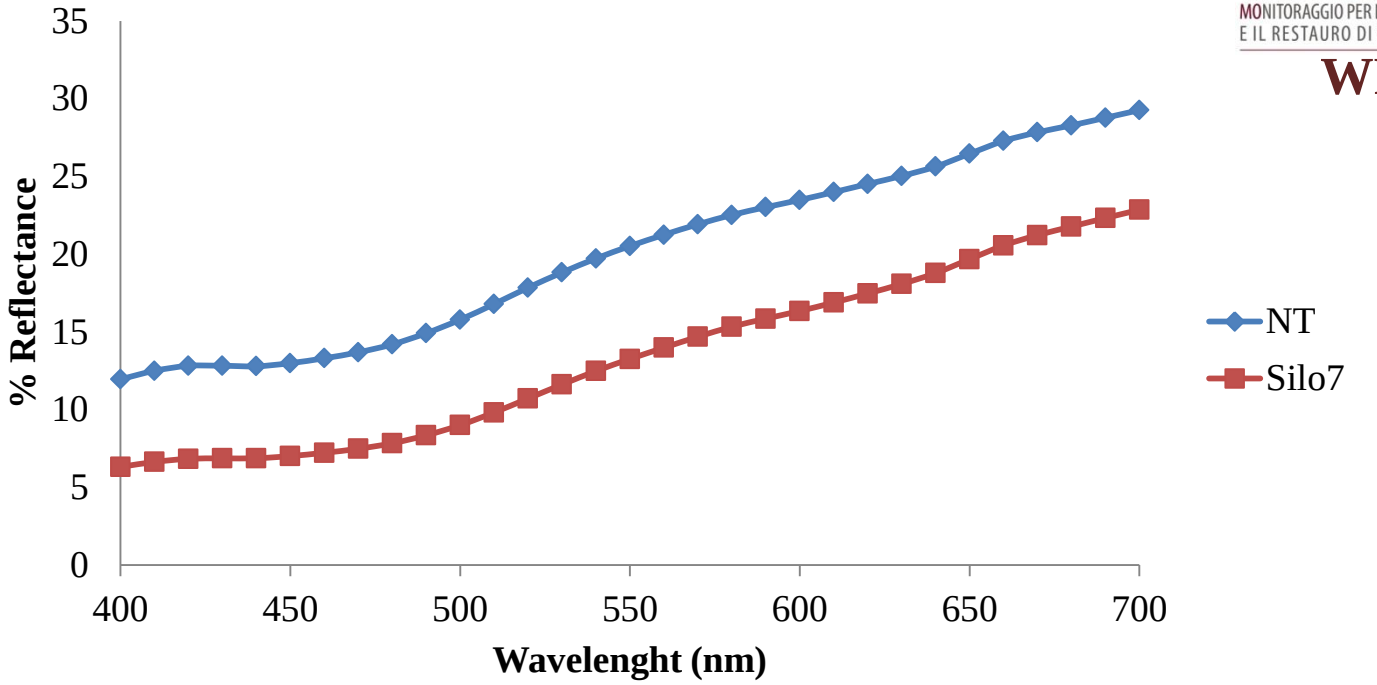
Not treated (NT)

Silo N7



		L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
NT	Average	51.8	4.43	15.1	-9.15	2.29	3.24	9.97
	StDev	3.27	0.74	1.07				
Silo N7	Average	42.7	6.72	18.3				
	StDev	3.49	0.85	1.38				

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Colour measurements for evaluating their effects on surface colour characteristics: Rhodorsil H224

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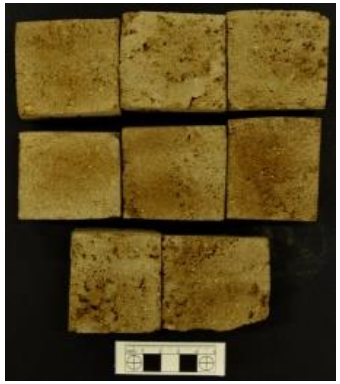
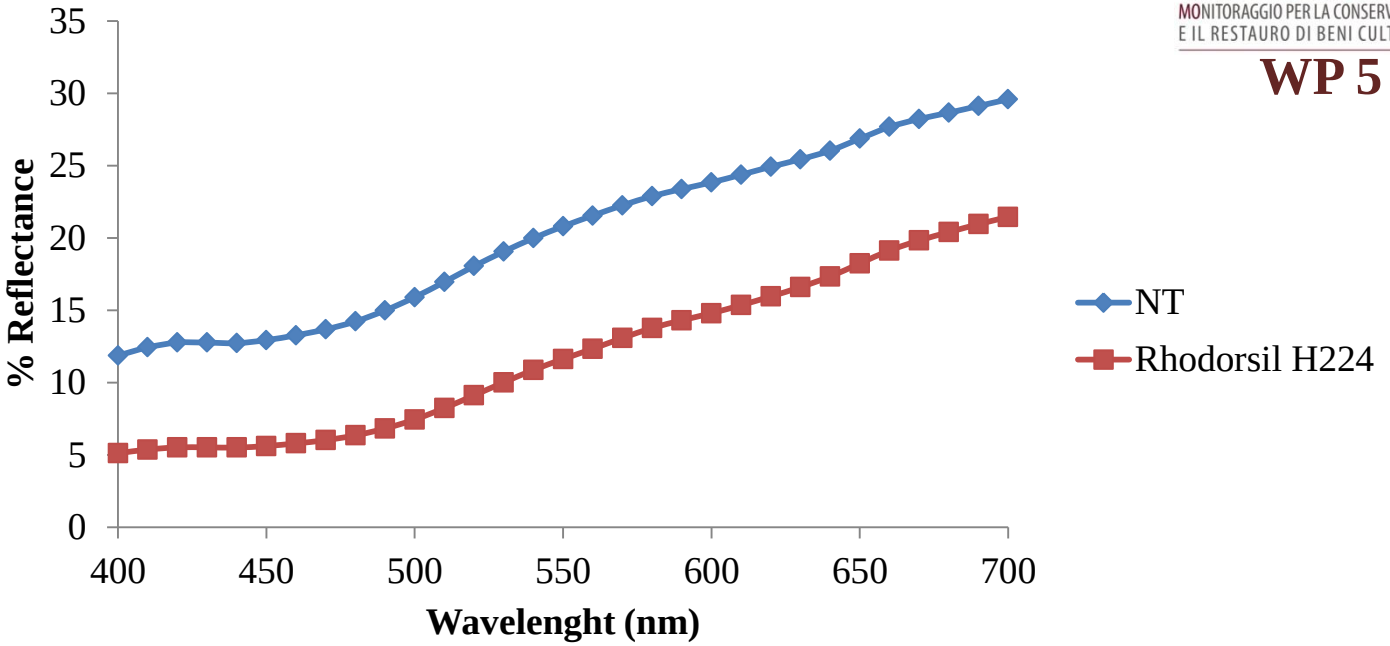
Not treated (NT)



Rhodorsil H 224



		L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
NT	Average	52.0	4.47	15.7	-12.0	3.21	4.26	13.1
	StDev	4.35	0.63	0.89				
Rhodorsil H224	Average	40.1	7.68	20.0				
	StDev	4.75	1.05	1.08				

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Colour measurements for evaluating their effects on surface colour characteristics: Fluoline HY

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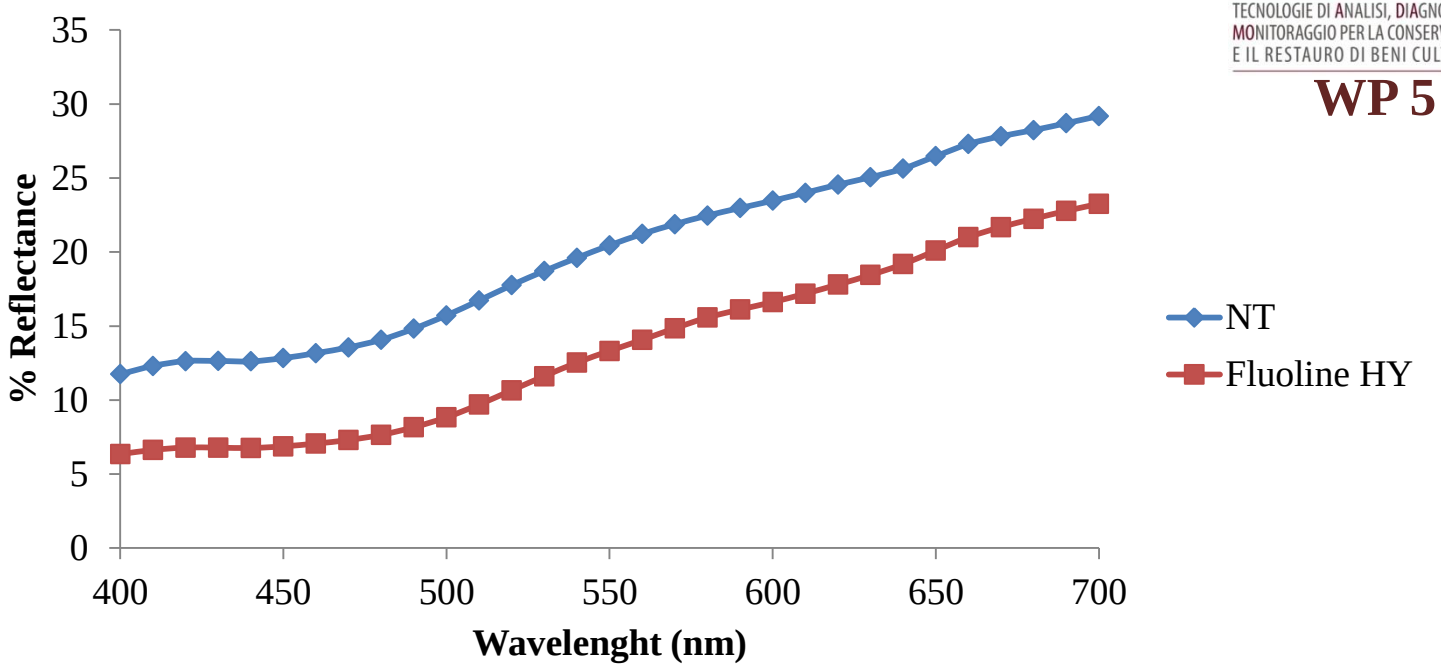
Not treated (NT)

Fluoline HY



		L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
NT	Average	51.8	4.46	15.4	-8.90	2.69	3.59	9.97
	StDev	3.12	0.70	1.00				
Fluoline HY	Average	42.9	7.15	18.9				
	StDev	2.95	0.66	1.20				

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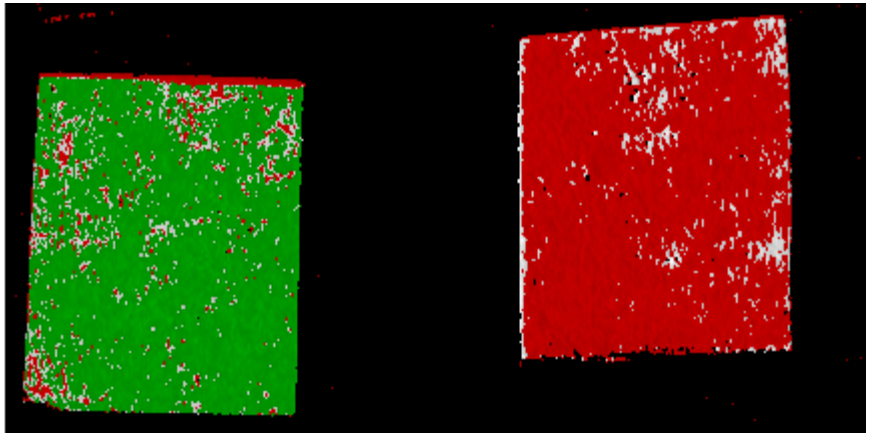
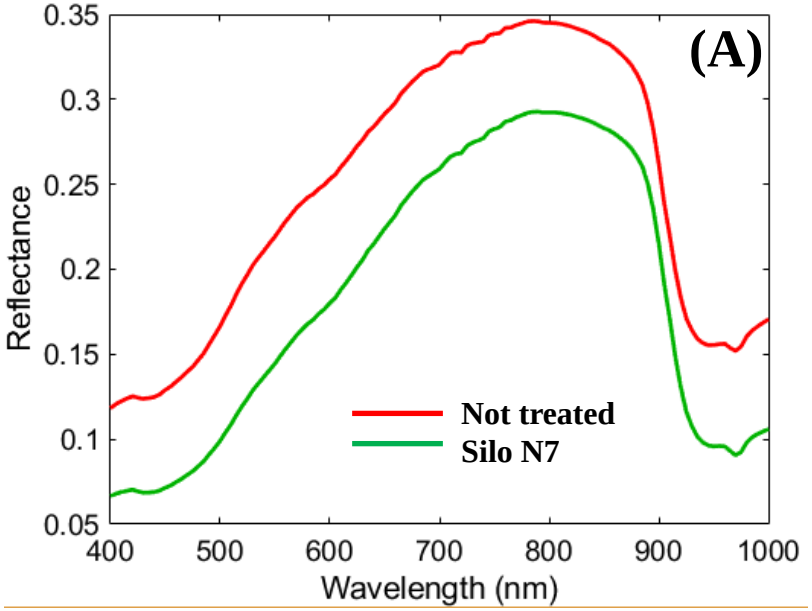
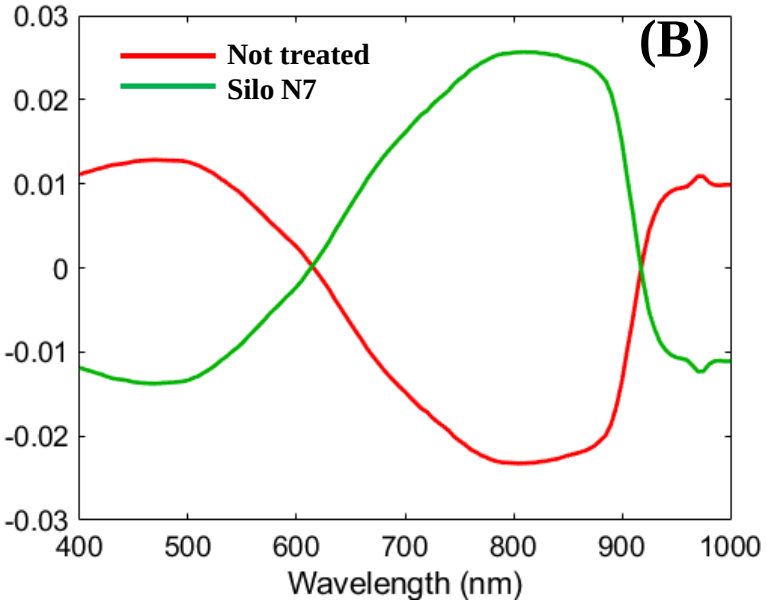
Hyperspectral imaging before ageing: VIS-NIR







(A) Average spectra in the VIS-NIR region and (B) pre-processed spectra by MSC + mc

PCA applied on the HSI data in the VIS-NIR region

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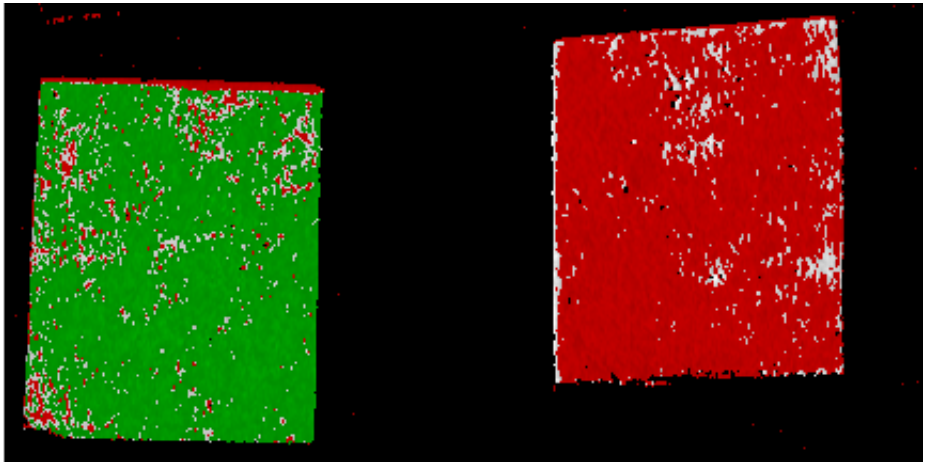

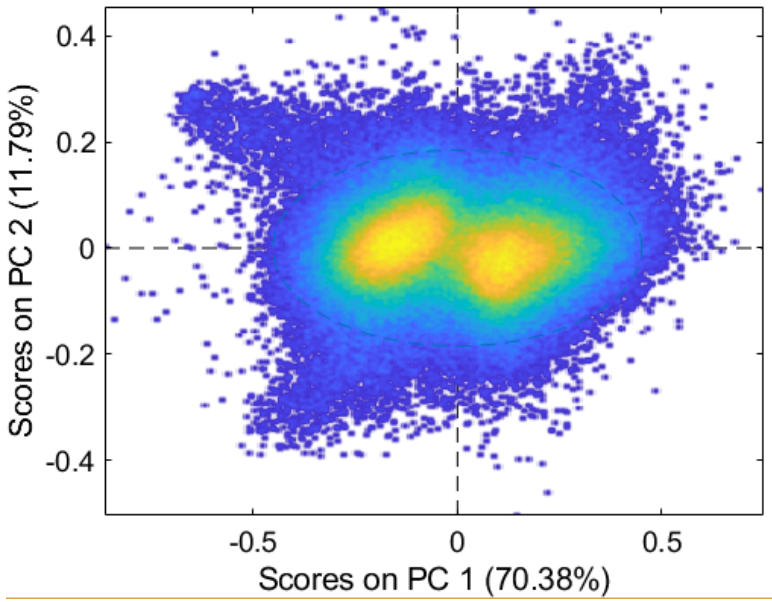

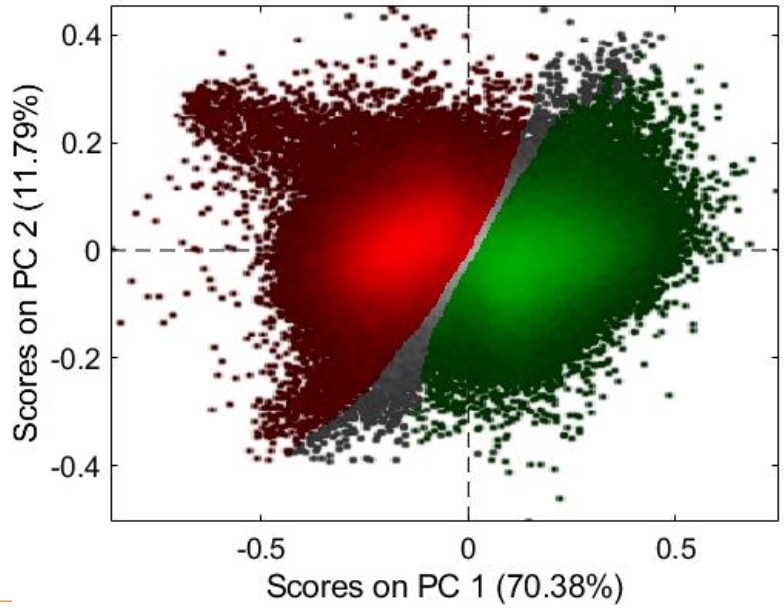

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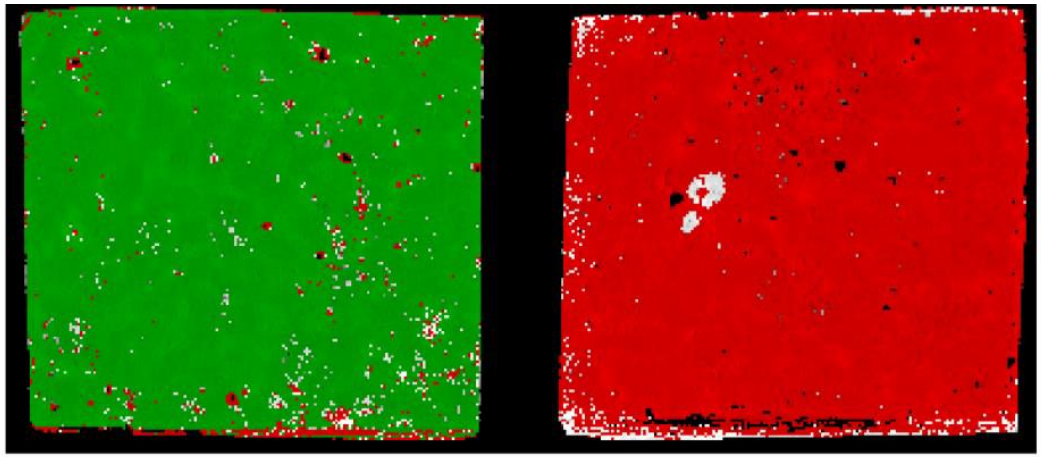
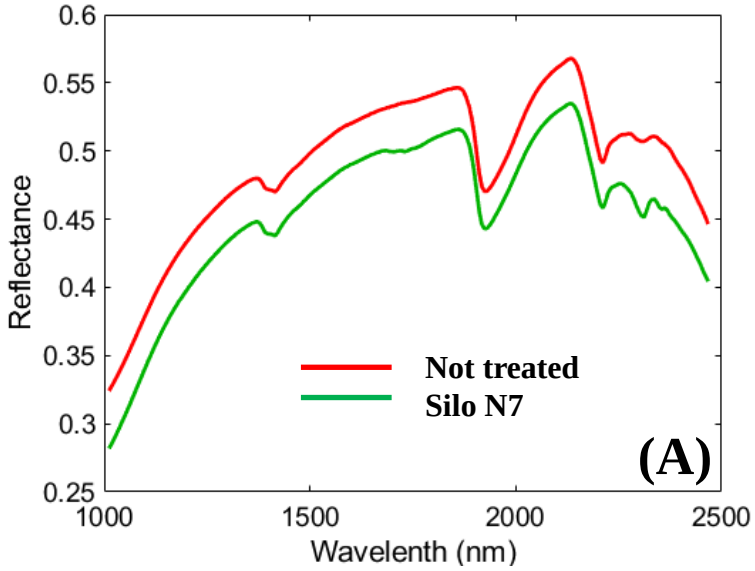
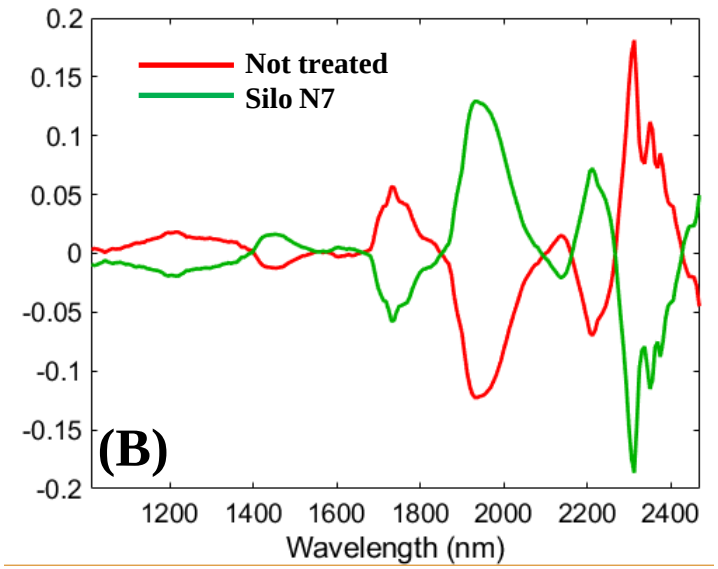
PCA shows clear separation of not treated and SILO N7 treated surface.

Hyperspectral imaging before ageing: SWIR region







(A) Average spectra in the SWIR region and (B) pre-processed spectra by Detrend + snv + mc

PCA applied on the HSI data in the SWIR region

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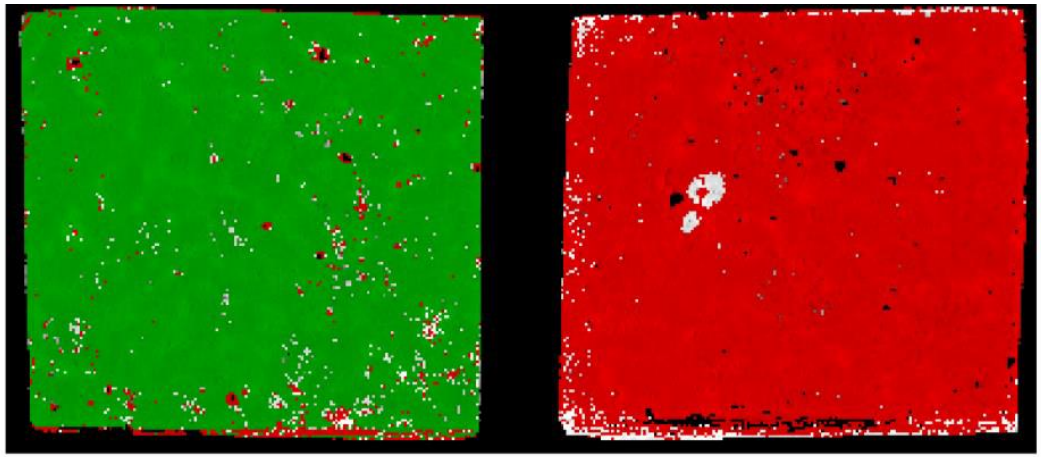

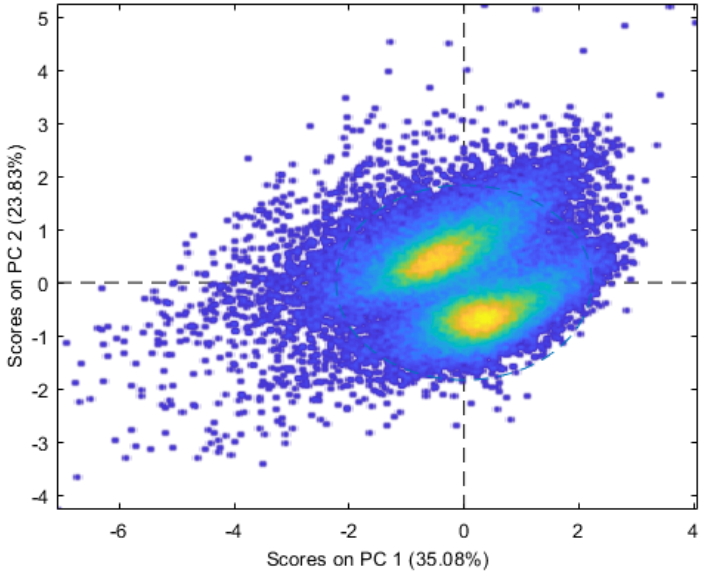

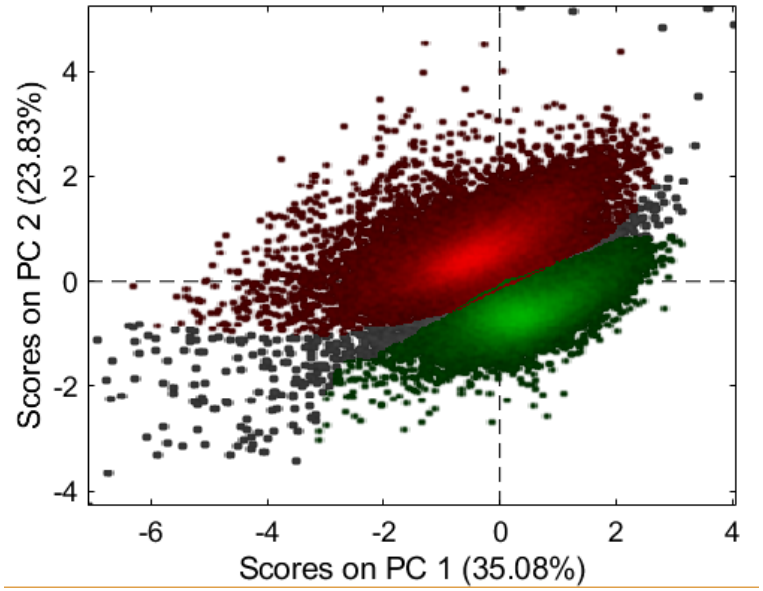

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PCA shows clear separation of not treated and SILO N7 treated surface in the SWIR region.

Conclusions … in progress

- A complete study of “Sperone”, a natural stone widely used in Villa Mondragone, has been started.
- Three protective products have been chosen, after a wide literature research, also supported by restorers expert in stone conservation.
- One of the three products is a nano-structured silica based material not commercialized yet and supplied by CTS for testing.
- Different techniques were used for products’ performance evaluation as a consequence of ageing.
- Preliminary results after treatments showed that Silo N7 and Fluoline HY caused the lowest colour changes on the stone surface. Moreover they seem to be more suitable for “Sperone” in terms of applicability and homogeneity of the treated surfaces.

Further tests to be made

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BEFORE AGEING

- Capillary test according to EN17114:2019.
- Drying Index test
- Scatch test
- Contact angle measurements

AFTER AGEING (under UV and relative humidity controlled conditions)

- Capillary test according to EN17114:2019.
- Drying Index test
- Scatch test and contact angle measurements
- Colour measurements
- HSI acquisitions

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ACKNOWLEDGEMENTS

- **A special thanks to Dr. Leonardo Borgioli for having supplied the product Silo N7 not yet commercialized and so particularly suited for experimental tests.**

- **Thanks to Lazio Region for the grant of ADAMO project.**

- **Thanks to the restorers Maria Grazia Chilosi and Mark Gittins (CBC Society) for their suggestions and indications to choose the most suitable protective products.**

- **… and thank you for your kind attention!**

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