

Nanostructured materials for restoration and conservation: Nanotech and Cappadocia (Turkey) projects

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<http://www.unitus.it/it/dipartimento/deim/chi-siamo-informazioni/articolo/laboratorio-di-diagnostica-per-la-conservazione-e-il-restauro-deim>



Improving the stability of some natural organic dyes and pigments encapsulating them with nano-silica via layer-by-layer assembly technique for their possible use in conservation applications.

**[PRIN Project (Prof. U. Santamaria):
Nanotechnologies and surface functionalization
for made in Italy (Made in Italy – Nanotech)].**

A. Lo Monaco, M. Marabelli, C. Pelosi, R. Picchio, *Colour measurements of surfaces to evaluate the restoration materials*, Proceedings of SPIE Volume 8084, Monaco 23-26 May 2011, DOI: 10.1117/12.889147, 80840-P1-14.

U. Santamaria, F. Morresi, G. Agresti, C. Pelosi, *Studi analitici della policromia antica e sperimentazione sul nano incapsulamento di coloranti con nanosilici*. In: P. Liverani e U. Santamaria (Eds.), *Diversamente bianco, la policromia della scultura romana*, Edizioni Quasar, Roma, 2014, pp. 33-49.



ENCAPSULATION OF PIGMENTS WITH NANO-SILICA THROUGH LAYER-BY-LAYER ASSEMBLY*

MATERIALS

Commercial pigments

- Madder lake (Zecchi 2200E)
- Ultramarine blue (Zecchi 0105)
- Burnt Sienna (Zecchi 813)
- Raw umber (Zecchi 797)
- Ivory black (Zecchi KR12000)

Poly-electrolites

- PsS poly (sodium 4-styrene sulfonate)
1 gL⁻¹ in distilled water
- PDADMAC poly diallyl-dimethylammonium chloride)
1 gL⁻¹ in distilled water with 0.3M sodium chloride (NaCl).

Sycol 40 (now Zargun PARNASOS ZG260011, 40% nano-silica in water
-Colorobbia-)

*J. Yuan, W. Xing, G. Gu, L. Wu, *The properties of organic pigment encapsulated with nano-silica via layer-by-layer assembly technique*, *Dyes and Pigments*, 76 (2008), 463-469

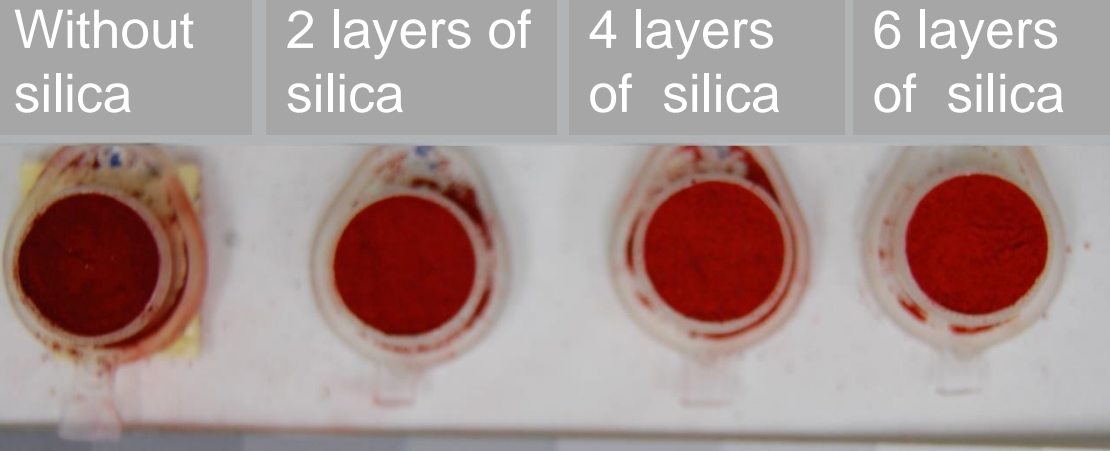
EXPERIMENTAL

1. Addition of PsS - anion- to the commercial pigment. Then, 1 hour in ultrasonic bath to obtain a homogeneous mixture.
2. Four alternating cycles of PsS and PDADMAC – cation - were performed. Between each cycle the mixture was washed with distilled water.
3. Alternating cycles with Sycol 40 (nano-silica) and PDADMAC were executed, separated by a washing with distilled water.
Each cycle is made of two phases:
PHASE 1, the sample is maintained for one hour in ultrasonic bath to homogenize the mixture;
PHASE 2, the samples were centrifuged for 15 minutes at 15.000 rpm to separate the solid and liquid phases
4. At last the prepared products were put in an oven at 40°C for water evaporation

MADDER LAKE



Madder lake without any treatment

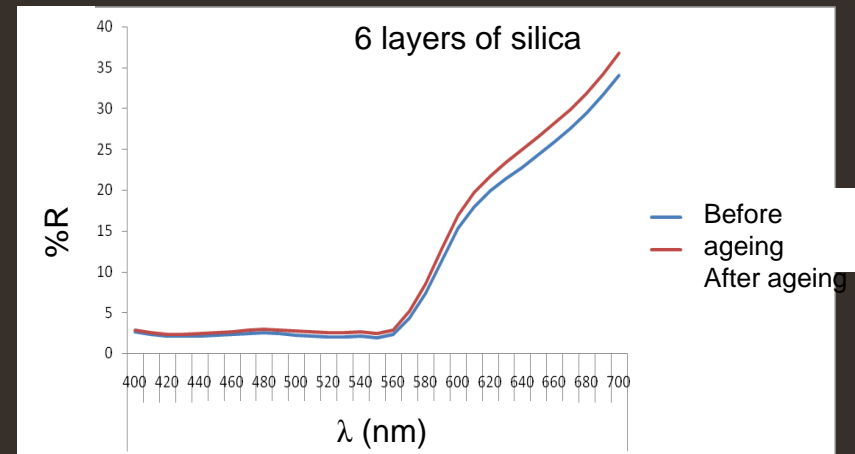
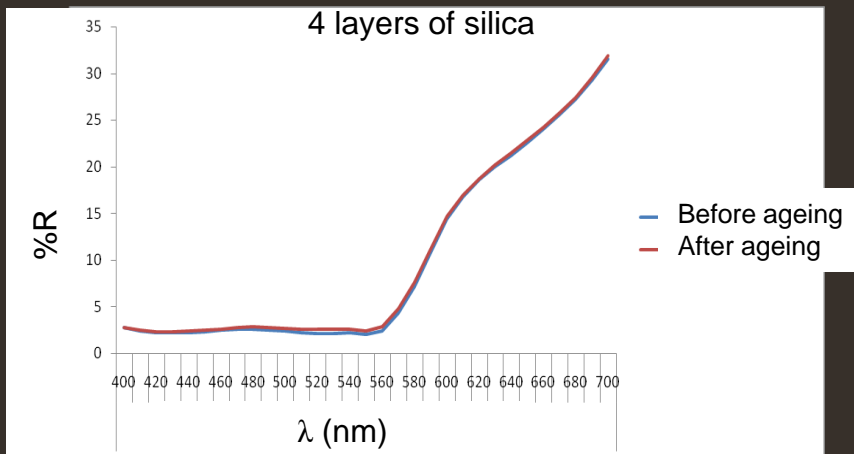
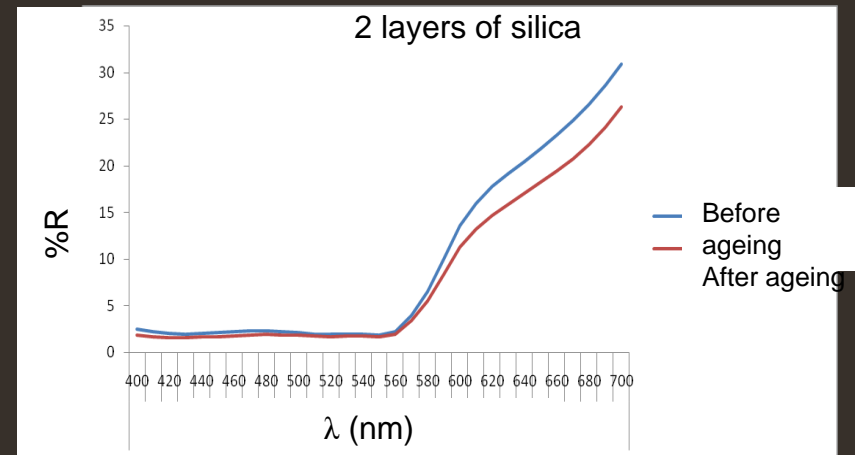
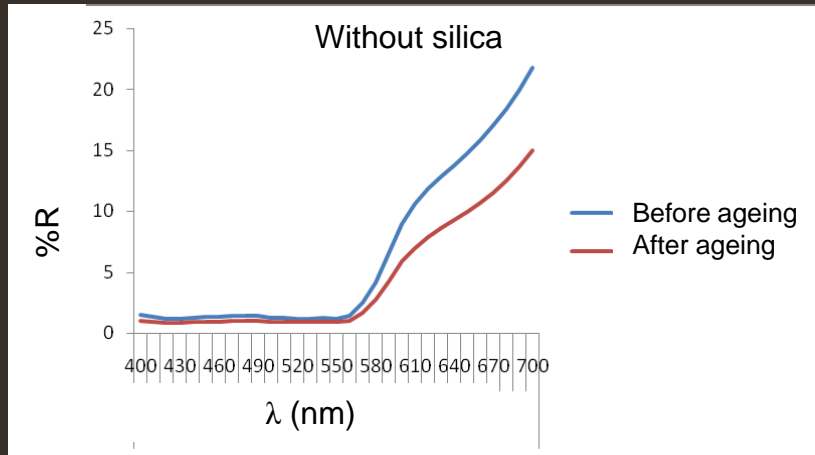


Madder lake treated with poly-electrolyte and 2, 4, 6 layers of nano-silica

In order to evaluate the chromatic changes caused by ageing, the powders of Madder, both treated and untreated with nano-silica, were artificially aged under UV lamps for 900h.

The powders were examined by reflectance spectrophotometry before and after the artificial ageing.

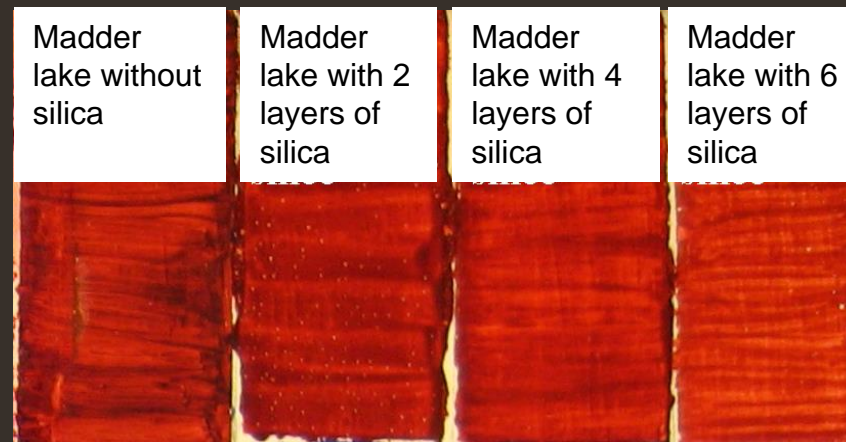
Comparison of the reflectance spectra before and after the artificial ageing



CHROMATIC COORDINATES BEFORE AND AFTER THE ARTIFICIAL AGEING

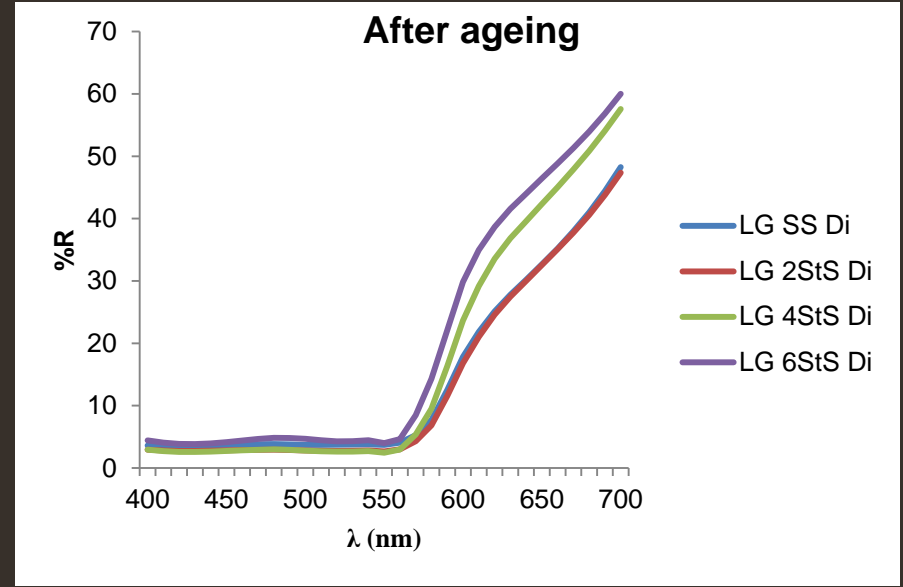
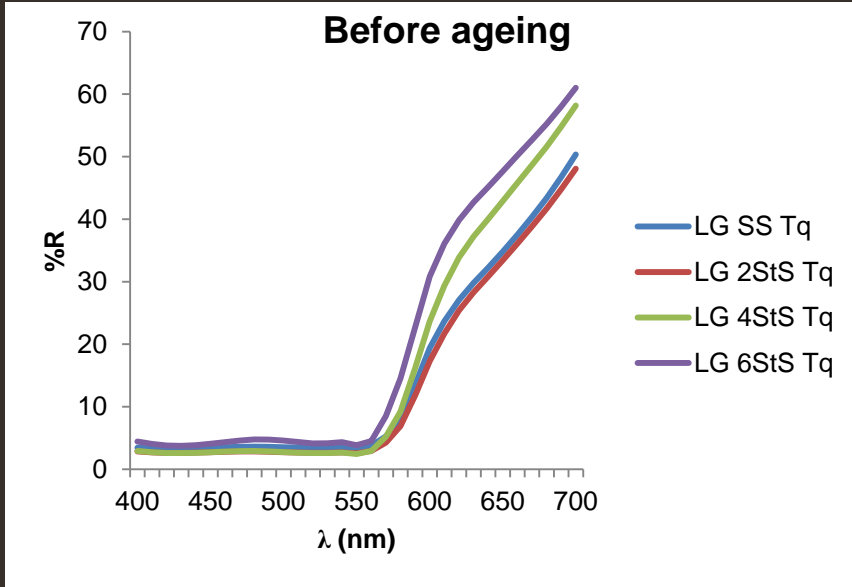
Treatment typology		MADDER LAKE						
		L*	a*	b*	C*	h°	ΔE	ΔC
Without silica	Before	23.11	29.82	20.01	35.92	33.87	7.02	4.93
	After ageing	18.12	25.68	17.33	30.99	34.01		
2 layers of silica	Before	28.96	33.69	22.02	40.25	33.17	3.86	2.93
	After ageing	26.65	30.71	21.21	37.32	34.63		
4 layers of silica	Before	30.04	33.55	21.89	40.06	33.13	1.75	1.14
	After ageing	30.82	32.00	22.16	38,92	34.70		
6 layers of silica	Before	30.46	35.47	23.59	42.60	33.62	2.48	0.19
	After ageing	32.68	34.70	24.37	42.40	35.08		

APPLICATION OF THE NANO-ENCAPSULATED PIGMENTS ON A CANVAS PREPARED WITH A TRADITIONAL MIXTURE OF GYPSUM AND GLUE



The paintings were artificially aged under UV for 900 hours .
Colour changes were evaluated by reflectance spectrophotometry applied
before and after the ageing

MADDER LAKE



	L*	$\Delta L^* = 0.570$	a*	$\Delta a^* = 2.443$	b*	$\Delta b^* = 2.540$	$\Delta E = 3.570$	C*	$\Delta C = 3.408$
LG SS Tq	35.563		37.980		23.705			44.772	
LG SS Di	34.993		35.537	21.165	41.363				
	L*	$\Delta L^* = 0.168$	a*	$\Delta a^* = 0.970$	b*	$\Delta b^* = 1.010$	$\Delta E = 1.410$	C*	$\Delta C = 1.355$
LG 2StS Tq	33.280		39.472		24.668			46.545	
LG 2StS Di	33.112		38.502	23.658	45.190				
	L*	$\Delta L^* = 0.035$	a*	$\Delta a^* = 0.455$	b*	$\Delta b^* = 0.075$	$\Delta E = 0.462$	C*	$\Delta C = 0.415$
LG 4StS Tq	37.165		45.573		31.382			55.337	
LG 4StS Di	37.200		45.118	31.307	54.922				
	L*	$\Delta L^* = 0.283$	a*	$\Delta a^* = 1.043$	b*	$\Delta b^* = 0.930$	$\Delta E = 1.426$	C*	$\Delta C = 1.387$
LG 6StS Tq	42.562		43.938		31.470			54.043	
LG 6StS Di	42.278		42.895	30.540	52.657				

PRIN Project: Arte e Habitat rupestre in Cappadocia (Turchia) e nell' Italia centromeridionale. Rocca, architettura scavata, pittura: fra conoscenza, conservazione, valorizzazione.

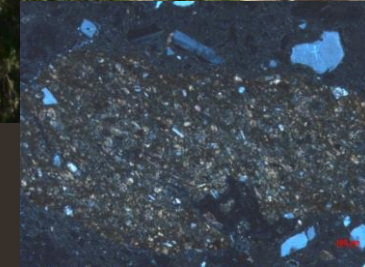
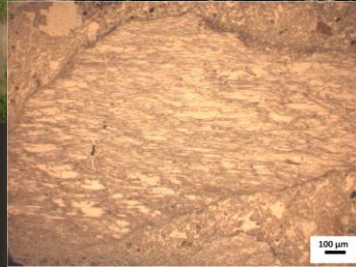
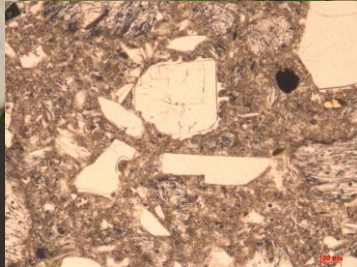
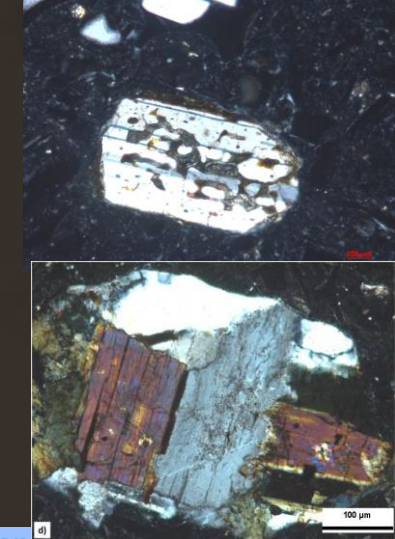
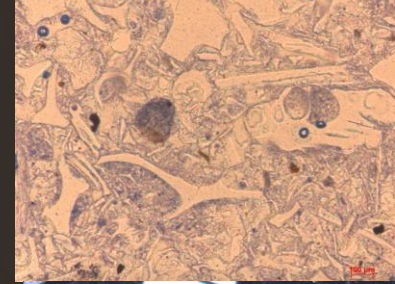
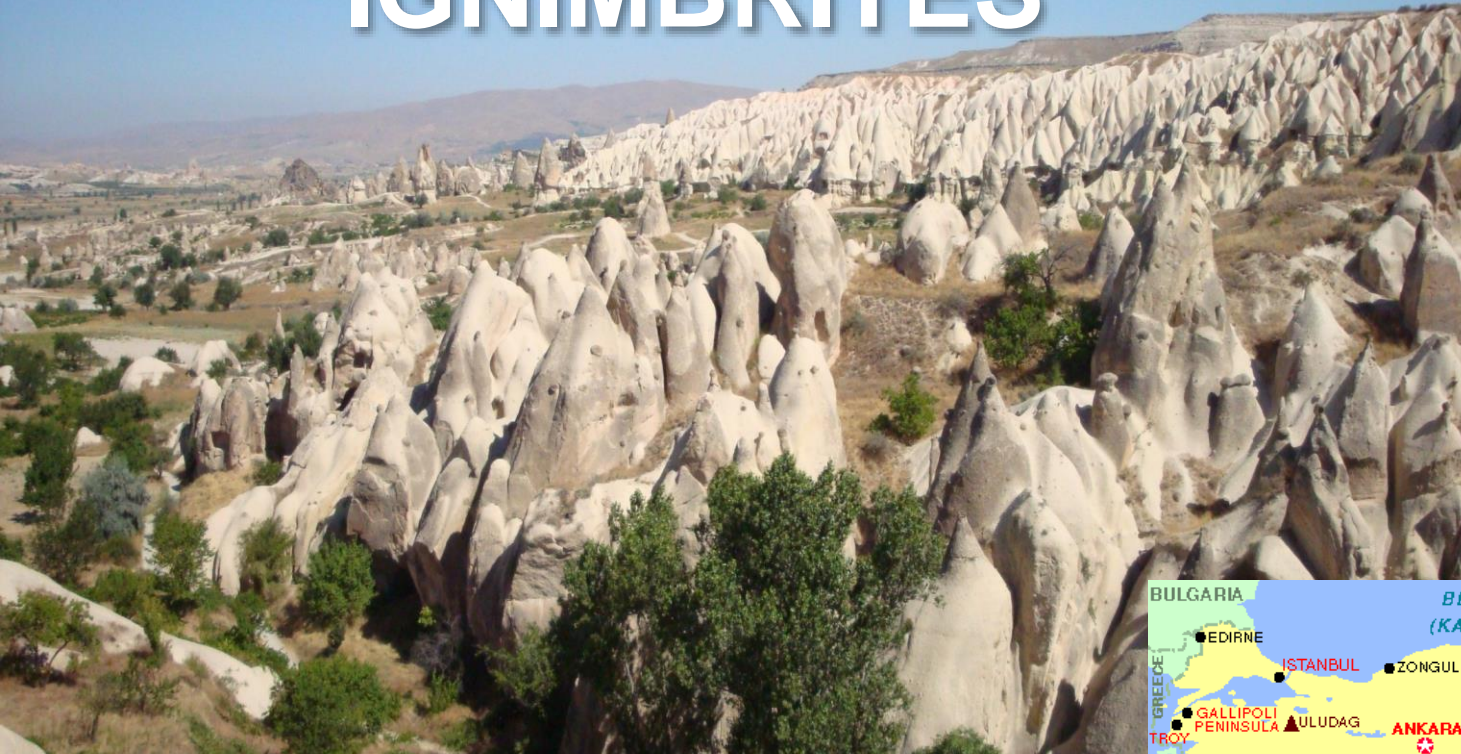
Rupestrian art and habitat in Cappadocia (Turkey) and in central and southern Italy. Rock, excavated architecture, painting: between knowledge, preservation and enhancement

Coordinatore Nazionale: Prof. Maria Andaloro

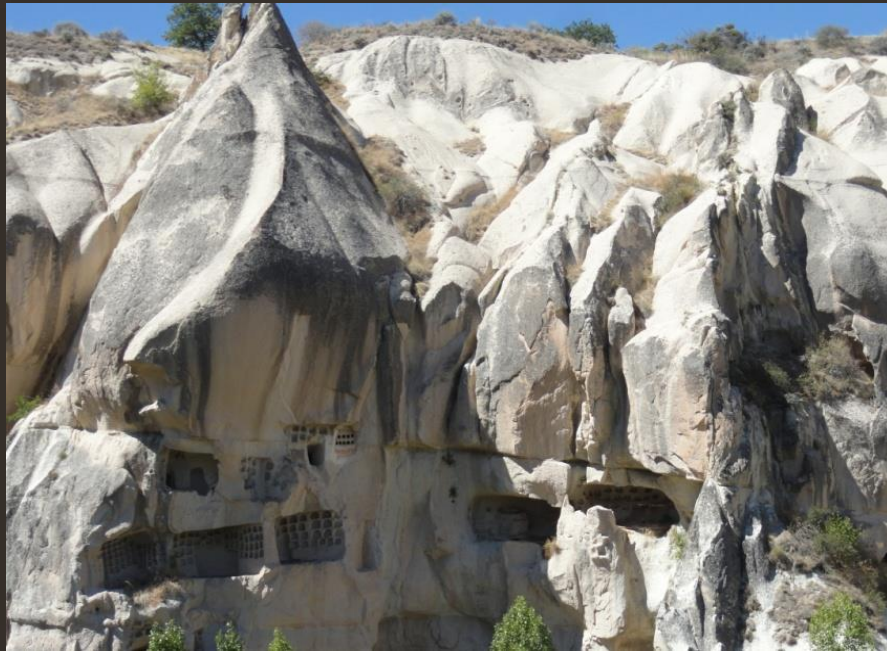
*Application of products based on silica and nano-silica for the consolidation of the rock support in the rupestrian churches of Cappadocia (Turkey).
University of Calabria*

- M. F. La Russa, S. A. Ruffolo, N. Rovella, C. M. Belfiore, P. Pogliani, C. Pelosi, M. Andaloro and G. Mirocle Crisci, *Cappadocian ignimbrite cave churches: stone degradation and conservation strategies*, Periodico di Mineralogia, 83 (2), 2014, 187-206.
- C. Pelosi, G. Agresti, M. Andaloro, P. Baraldi, P. Pogliani, U. Santamaria, M.F. La Russa, S.A. Ruffolo, N. Rovella, *Micro-Raman and micro-stratigraphic analysis of the painting materials in the rock-hewn church of the Forty Martyrs in Şahinefendi, Cappadocia (Turkey)*, Archaeometry, 58(4), 2016, 659-672, doi: 10.1111/arcm.12184.

CAPPADOCIA AND IGNIMBRITES



“Fairy Chimneys” characterize the Cappadocian landscape. They were commonly carved and changed into dwellings or rupestrian churches with precious wall paintings.



AIMS OF THE WORK

To test innovative consolidating products, evaluating their effectiveness against the decay phenomena affecting the rocks constituting the rupestrian churches

Evaluation of the conservation state of the rupestrian churches and observation of the main degradation phenomena

Mineralogical, petrographic and physical characterization of ignimbrites

Application of consolidants and evaluation of their performance in lab and in the sites

Tokalı Church Cappadocia (Turkey), X century A.D.



GÖREME TOKALI KİLİSE'DE RESTORASYON VE KONSERVASYON ÇALIŞMALARI
RESEARCH, RESTORATION AND CONSERVATION IN THE TOKALI KİLİSE - GÖREME

NEVŞEHİR ARKEOLOJİ MÜZESİ

ARCHAEOLOGICAL MUSEUM OF NEVŞEHİR

NEVŞEHİR ARKEOLOJİ MÜZESİ MÜDÜRÜ / DIRECTOR OF THE MUSEUM OF NEVŞEHİR
MURAT GÜLYAZ

TUSCİA ÜNİVERSİTESİ - TOKALI PROJECT

UNIVERSITY OF TUSCİA - TOKALI PROJECT

ARAŞTIRMA VE RESTORASYON PROJESİ BAŞKANI / DIRECTOR OF THE RESEARCH
PROJECT AND RESTORATION
MARIA ANDALORO

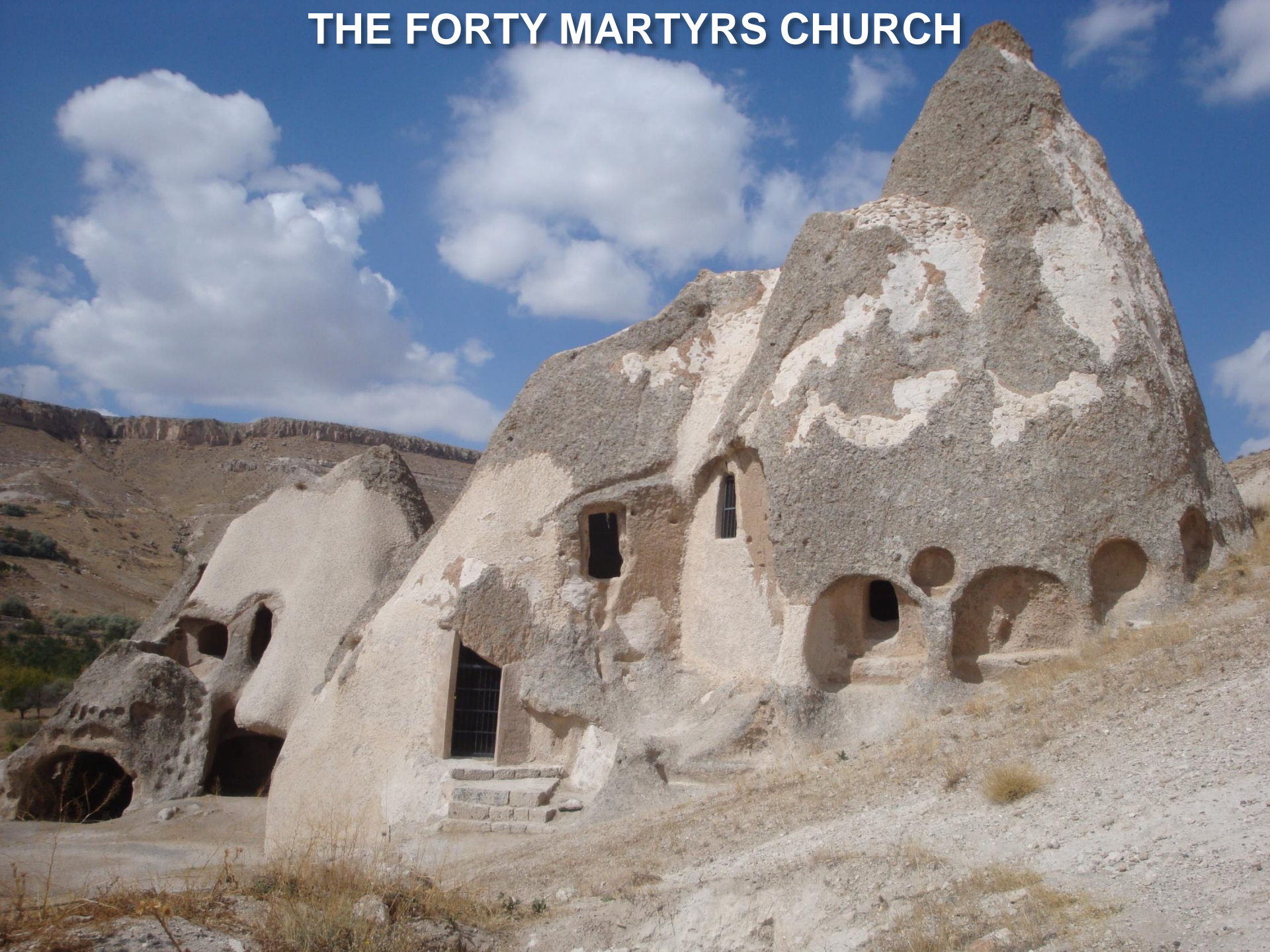


Nanoinnovation2016. Section TS.VII.E: Nanotechnology and nanomaterial for cultural heritage.
Rome, September 22, 2016

Tokalı Church Cappadocia (Turkey), X century A.D.



THE FORTY MARTYRS CHURCH



Şahinefendi The Forty Martyrs Church (XIII centuries). Before conservation



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Şahinefendi The Forty Martyrs Church (XIII centuries). After conservation



Şahinefendi The Forty Martyrs Church (XIII centuries). After conservation

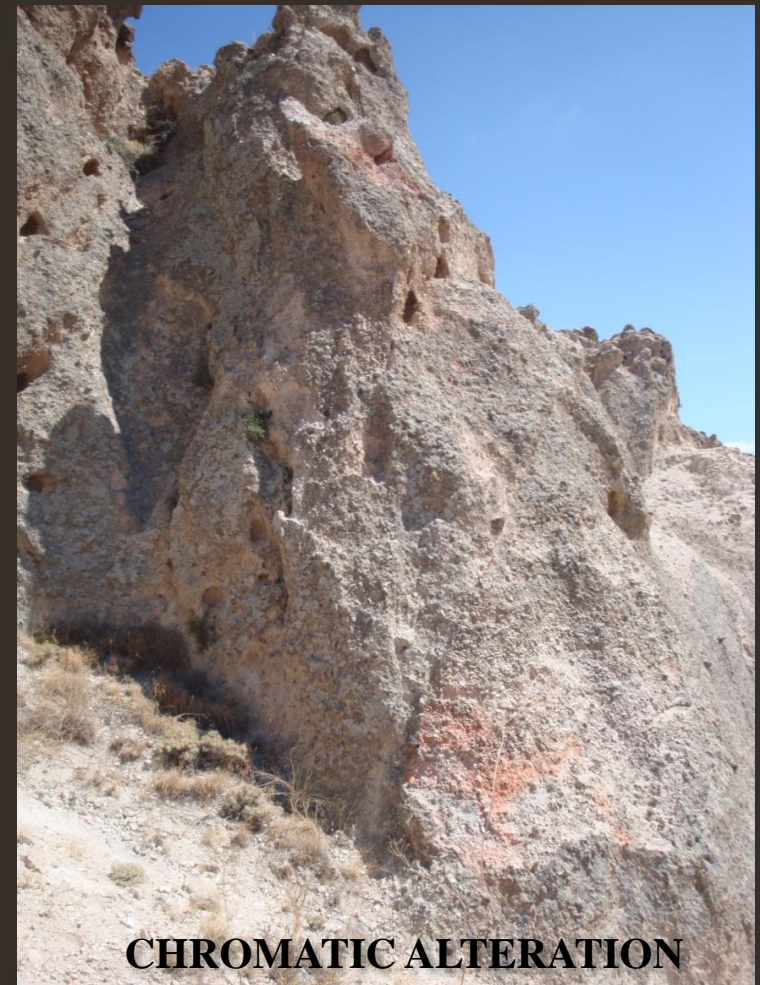


DEGRADATION PHENOMENA

Estimated weathered zone^{1,2}: depth ~8-10 cm; around joints ~ 20 cm.



LICHENIAN COLONIZATION



CHROMATIC ALTERATION

¹Topal T. & Doyuran V., *Analyses of deterioration of the Cappadocian tuff, Turkey*, Engineering Geology, 34, 1998, 5–20.

²Türkmenoğlu A.G., Gokturk E.H., Caner E.N., *The deterioration of tuffs from the Cappadocia region of Turkey*. Archaeometry, 33, 1991, 231-238.

DEGRADATION PHENOMENA



FRACTURINGS AND FALLS



ARGILLIFICATION; SOILING; DETACHMENT



SCALING

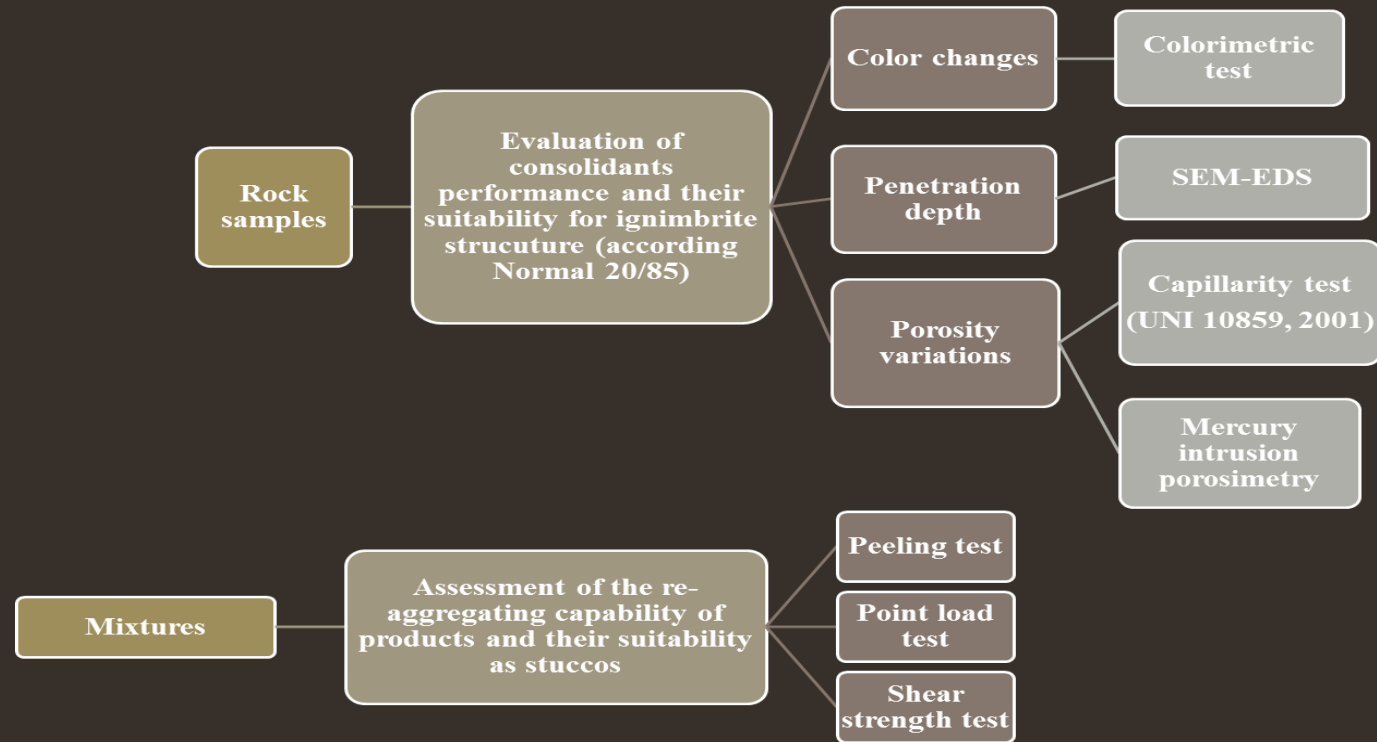


CONSOLIDATION STRATEGY AND TESTS

• ***NanoEstel***, an aqueous suspension of silica nanoparticles (30% concentration) having an average size of 30 nm, distributed by CTS

• ***ESTEL 1000***, composed of TEOS (tetraethyl orthosilicate) diluted in white spirit (a mixture of aliphatic hydrocarbons having a boiling point of 145–250 °C), distributed by CTS

• ***ESTEL 1100***, composed of tetraethyl orthosilicate and oligomers of polydimethylsiloxane diluted in white spirit, distributed by CTS



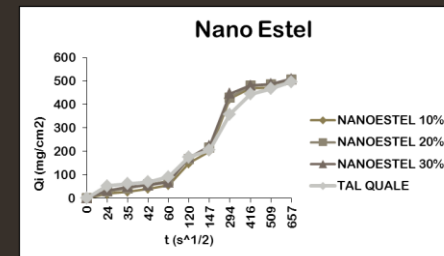
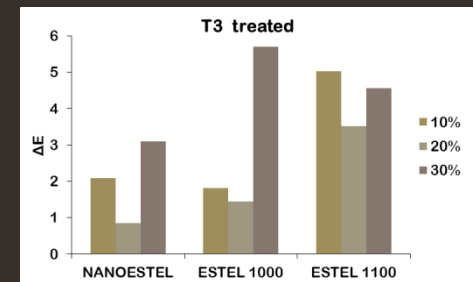
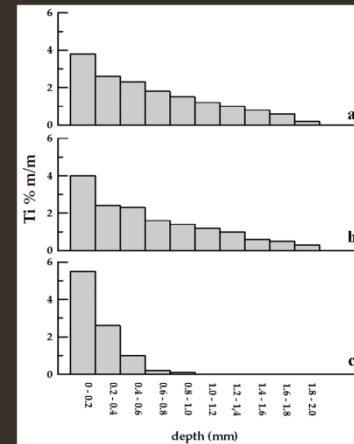
MAIN RESULTS ON LABORATORY SAMPLES



- Samples sized 5x5x2 cm
- Application by brush
- Concentrations 15, 20 and 30%
- Amount 0.5 G

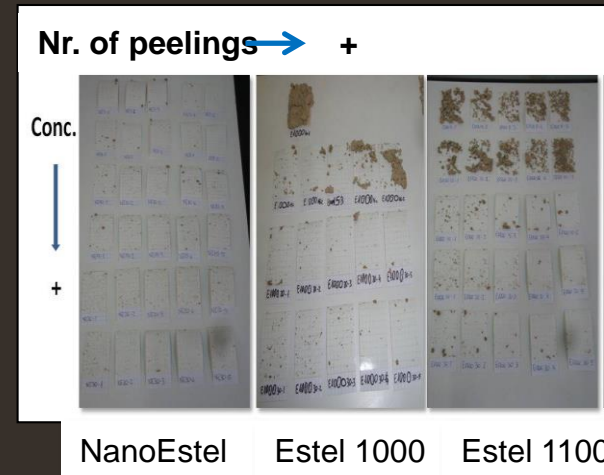
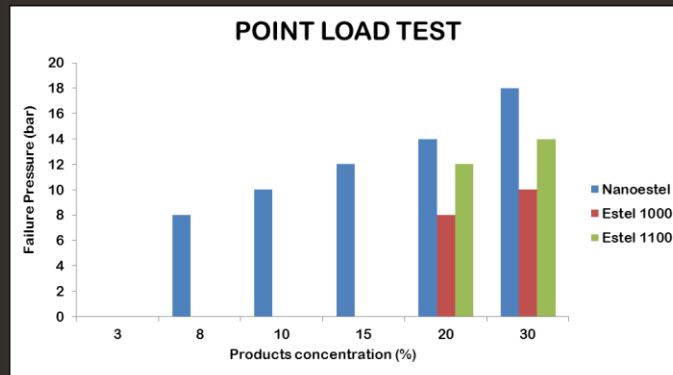
• The SEM-EDS analysis revealed a reasonable penetration of 30 wt% consolidants, better for Estel1000 and 1100 than NanoEstel.

• Colour changes are negligible for NanoEstel, especially with 20% of concentration



• NanoEstel achieved better results in the capillary absorption test, suggesting that the product leaves the stone porous structure substantially unaltered.

MAIN RESULTS ON LABORATORY SAMPLES



- **PHASE 1:** Crushing rock and separation of granulometric fractions , respectively, <2 mm and ranged between 2 mm to 10 mm.
- **PHASE 2:** Preparation of mixtures shaped 5x5x5 cm constituted by 66 g of coarse fraction and 66 g of fine fraction blended with 50 ml of binder.
- peeling test; point load test.
- NanoEstel seems to give the best results in terms of re-aggregating capabilities.

... *TO THE SITE*

Choice testing areas

Degradation state

Solar exposure

Temperature

Humidity

Application products

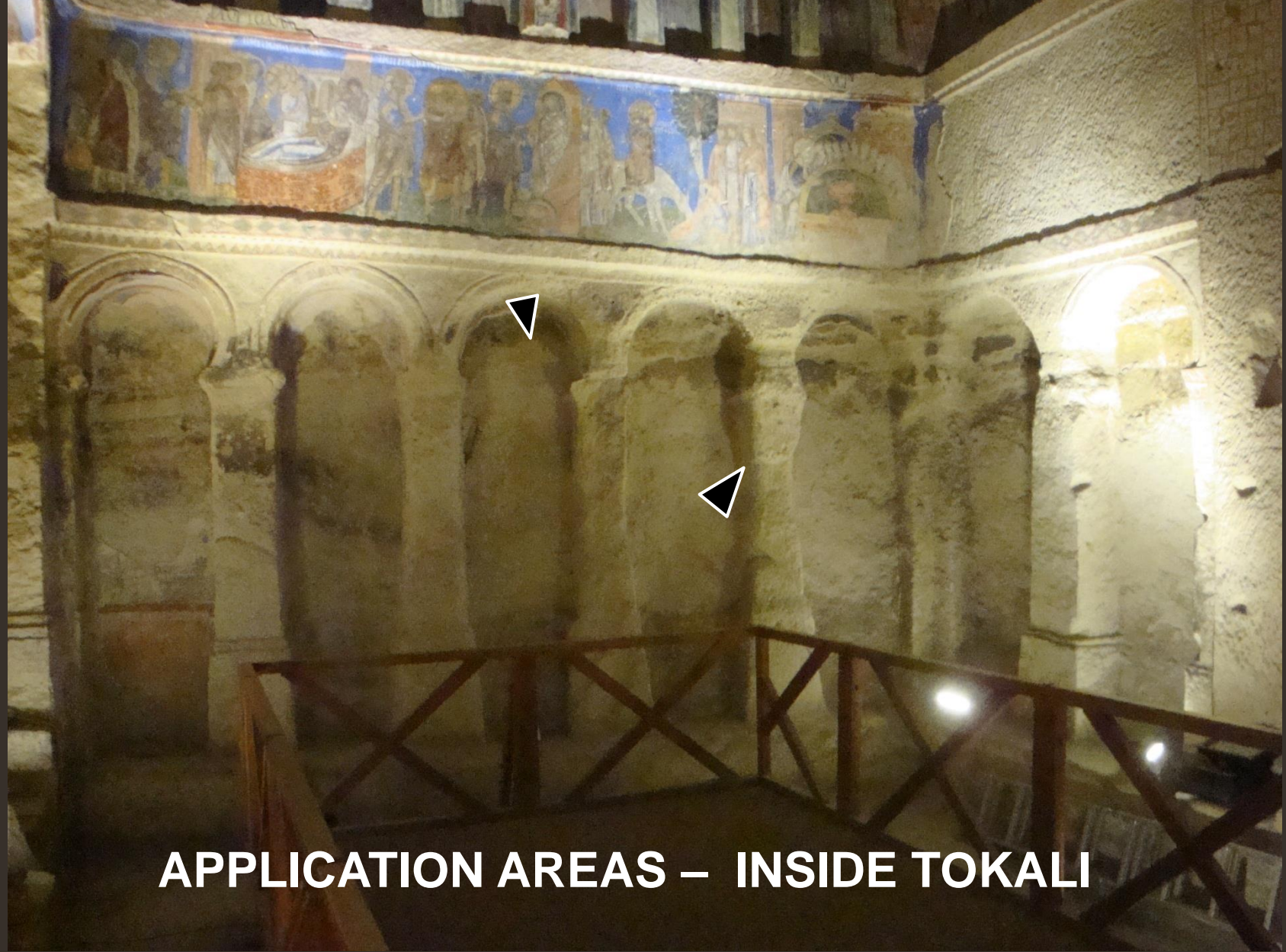
Procedures

Different Concentrations

Check analysis

Colorimetric measurements

Peeling test



APPLICATION AREAS – INSIDE TOKALI

AREAS CTK8-9

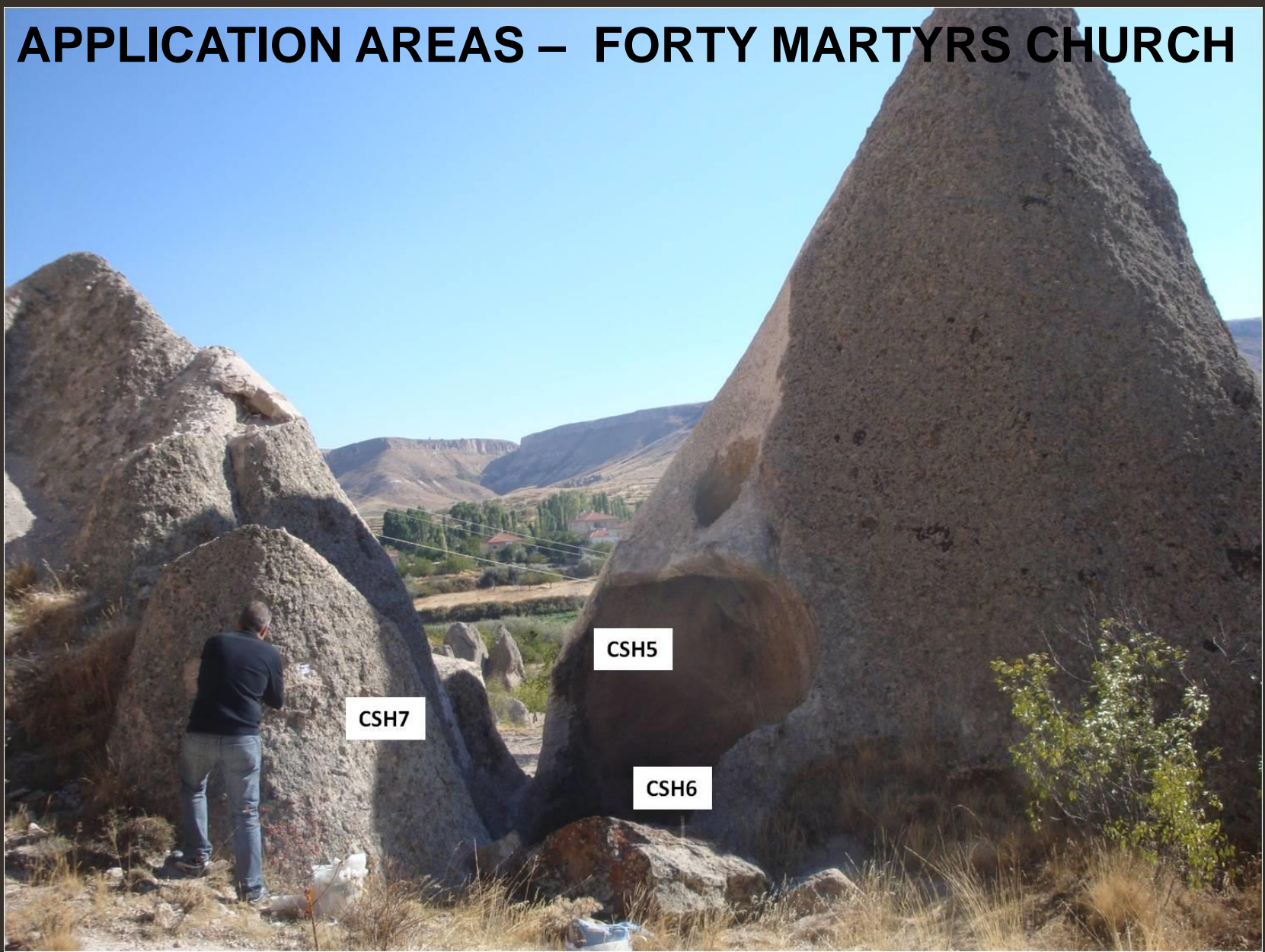


AREAS CTK6-7 AND CTK11



APPLICATION AREAS – OUTSIDE TOKALI

APPLICATION AREAS – FORTY MARTYRS CHURCH



APPLICATION AREAS – FORTY MARTYRS CHURCH

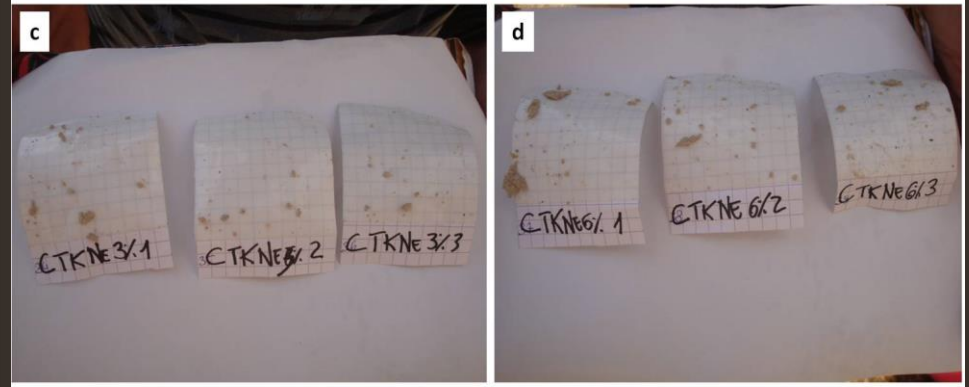
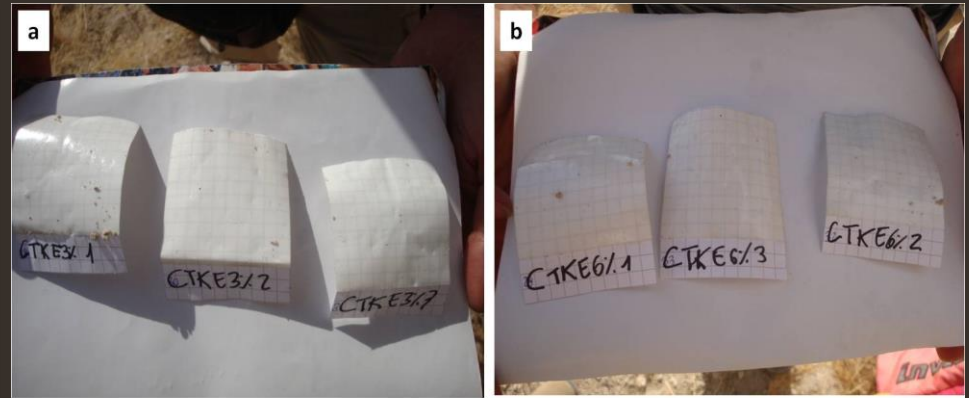
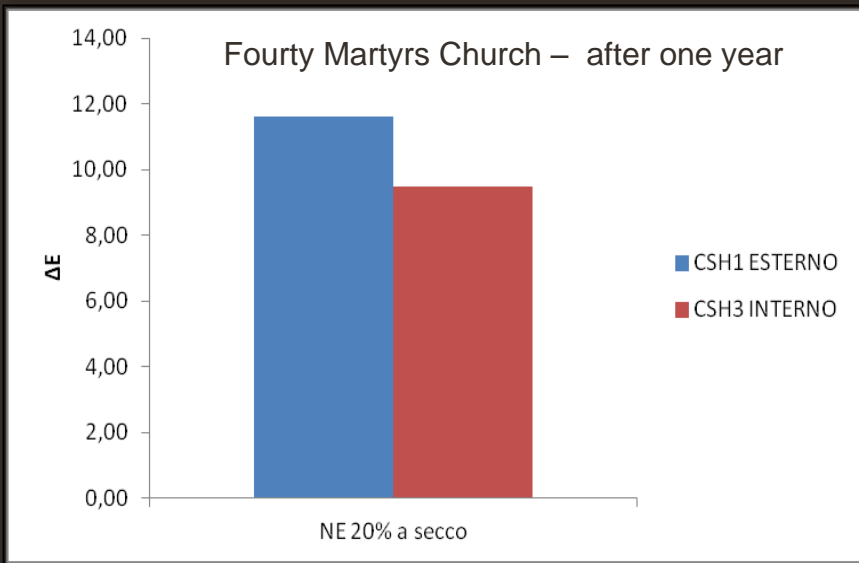
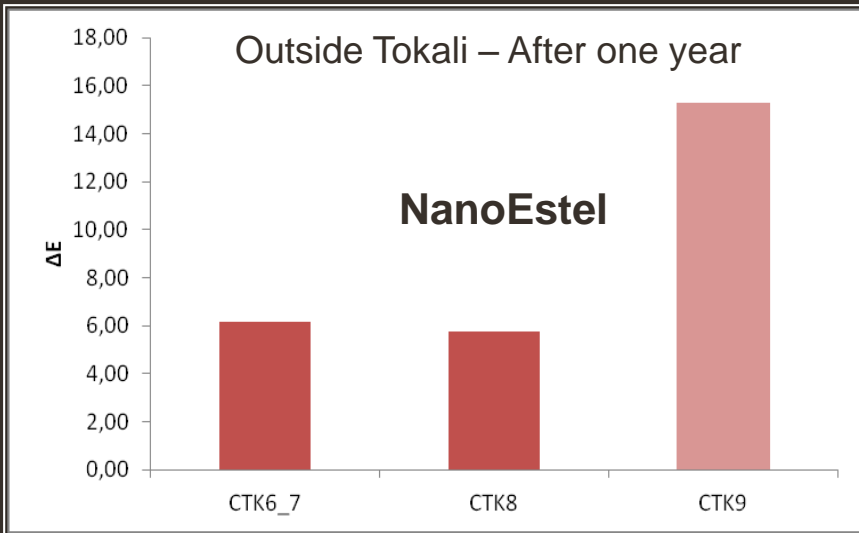


AREA CSH7



AREA CSH3

COLOUR MEASUREMENTS AND PEELING TESTS



The work demonstrated the influence of *SEVERAL FACTORS* on the consolidating products efficiency, suggesting a functional strategy for a conservative intervention.



- The structure and composition of the rocks
- The environmental conditions (solar exposure, temperature and humidity)
- The decay phenomena affecting the rocks
- The application modalities



- Consolidants amount and concentration
- Surface pretreatment