

The application of hydroxyapatite-based treatments to salt-bearing porous limestones: A study on sodium sulphate-contaminated Lecce Stone

Gabriela Graziani^{1,2*}, Enrico Sassoni¹, George W. Scherer³ and Elisa Franzoni¹

¹ Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Italy

² Laboratory of NanoBiotechnology (NaBi), Rizzoli Orthopaedic Institute, Bologna, Italy

³ Department of Civil and Environmental Engineering (CEE), Princeton University, USA

*gabriela.graziani2@unibo.it

Abstract

Salt weathering is among the most severe phenomena affecting porous limestone, often leading to the loss of precious material from historical sculptures and building façades. Together with exerting a weathering action, salts can also hamper the success of consolidation treatments, by interfering with consolidants' penetration and/or curing reactions. On site, application of consolidants on non-contaminated stone is rarely feasible, especially in the case of porous limestones; for this reason, testing application of consolidants on salt laden stone is of particular relevance to guarantee their successful application in the field.

In this paper, two hydroxyapatite (HAP)-based treatments have been applied to Lecce Stone, a very porous organogenic limestone, highly susceptible to salt weathering. The two treatments differ for DAP concentration, application procedure and presence/absence of ethanol in the formulation. Prior to treating, specimens were subjected to salt crystallization cycles in a sodium sulphate solution, to cause salt contamination and induce weathering. They were then desalinated, purposely leaving a percentage of salts in the stone (SO_4^{2-} after desalination $\sim 0.15\text{-}0.3$ wt%). Phase formation and distribution as a result of different contamination levels were investigated, and the efficacy of the treatments in

comparison to ethyl silicate was determined, as it is currently the most used consolidant for this lithotype. Finally, the durability of the most promising treatment to further salt crystallization was evaluated, again in comparison with ethyl silicate.

Promising results were obtained, as the presence of sodium sulphate did not prevent the HAP-based consolidants from uniformly distributing in the stone, sealing cracks and forming insoluble phosphate phases. Interestingly, the application on non-desalinated stone revealed that the nature and the amount of the phases that form as a result of the treatment are dependent on the amount of salts in the stone. Finally, most promising HAP-based formulation was found to enhance the stone's durability towards further salt crystallization, also compared to ethyl silicate.

Keywords: salt weathering, cultural heritage, calcium phosphates, limestone

1. Introduction

Salt weathering is among the main causes of stone deterioration, especially for porous limestone, that can undergo severe damage, such as flaking, scaling and pulverization, all leading to the loss of significant amounts of material and of architectural/sculptural details. Together

with causing weathering, salts inside the stone may interfere with consolidants' penetration and hardening reactions, thus possibly having a negative impact on the treatments' outcome: for this reason, desalination procedures are normally performed prior to consolidation. However, even after desalination some salts may remain inside the stone, interfering with the success of consolidation. Therefore, the effects of the application of consolidants on salt-bearing stones needs to be investigated.

Treatments based on hydroxyapatite (HAP) (produced by treating the stone with an aqueous solution of diammonium hydrogen phosphate, DAP) have been proposed for limestone consolidation, exhibiting remarkable efficacy, compatibility and durability.^{1, 2} However, tests carried out so far mainly focused on uncontaminated samples, which is rarely the case on site. Salt-related issues could arise for real specimens because not only HAP but also metastable calcium phosphate (CaP) phases and, possibly, phosphate salts could form, depending on the substrate contamination³; moreover, HAP might easily incorporate foreign ions, possibly altering its crystallinity and solubility.^{4, 5}

In the literature, the presence of foreign ions has been found to promote HAP growth, but also to cause the formation of soluble phases, depending on substrate composition, nature of contaminants and surface roughness.⁶ For this reason, the investigation of application of a hydroxyapatite-based treatment on salt-laden stone is of particular interest.

In this study, we studied the effects of applying HAP-based treatments on salt-contaminated Lecce stone, a porous organogenic limestone characteristic of Baroque Architecture of southern Italy. This stone contains significant amounts of silica, aluminum, phosphorus and magnesium, which could also have an impact on the formation of hydroxyapatite

or soluble phases.^{4, 5} Stone samples were contaminated by sodium sulphate, which is one of the most widespread and noxious among the salts that can be found on site, then were treated with two different HAP-based formulations, previously developed by the authors for limestone and marble consolidation.^{1, 2, 3, 6} The effects of the treatments on phase formation were analyzed and compared to those obtained by ethyl silicate, currently the most used product for the consolidation of limestone and, in particular, of Lecce Stone.

2. Materials and Methods

2.1. Materials

Tests were carried out on Lecce Stone (LS), which has non-uniform microstructure and mechanical properties, even within a single stone slab. Cores 5 cm in height and 2 cm in diameter were used for all the tests, except for the evaluation of the durability after consolidation, for which 5x5x5 cm³ cubes were used, given the low resistance of the stone to salt weathering. All cores and cubes were cut from one quarry slab.

Samples were contaminated by cycles of sodium sulphate crystallization (samples "SALT"), performed as follows:

- 1) Wetting phase (24 h): samples were immersed to a depth of about 1 cm in a 14 wt% solution of sodium sulphate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) in deionized water;
- 2) Drying phase (22 h): samples were dried in ventilated oven at 50°C;
- 3) Cooling (1h) and measuring of weight and dynamic elastic modulus (total: 2 h).

Two cycles were performed on the cores, 5 on the cubes. The number and

duration of the cycles were selected based on preliminary tests, with the aim of contaminating the stone with a suitable amount of salts, without causing rupture, and conserving a morphology suitable for mechanical testing. Salt content as a result of the cycles was measured by ion chromatography (IC).

To reproduce the conditions on site, where stone is normally desalinated before the application of the consolidant (even if a fraction of salts usually remains in the stone), part of the cores and all the cubes were partially desalinated after contamination. This also allowed evaluation of the impact of different levels of salt contamination on phase formation (samples "DESALT"). Desalination was performed by applying a deionized water poultice (water:cellulose pulp ratio 1:5, thickness ~1 cm). The poultice was kept sealed for 24 hours to allow solubilization of the salts, then left to dry in contact with the samples to allow advection of the salts towards the external surface. Residual salt content was evaluated by IC performed on the ground stone after salt extraction and filtering. The investigation of phase formation and of mechanical properties after treatment was also carried out on uncontaminated, uniformly weathered samples. For this purpose, a batch of stone cores (samples "HEAT") was artificially weathered by heating at 400°C for 1h, according to a procedure previously developed by the authors for promoting cracks formation in the stone.^{1,2}

2.2. Treating procedure

Two HAP-based treatments were tested that were previously developed for the consolidation and protection of limestone and marble, respectively:

1) Treatment "3M": A 3 M DAP solution is applied by brushing (10 strokes) followed by the application of a lime-water poultice (1.7 g/l Ca(OH)₂, lime-

water:poultice ratio 1:6). Limewater poultice is applied with the aim of providing further calcium ions to boost HAP formation and to remove possible soluble phosphate remaining in the stone after treatment;

2) Treatment "0.1M": A 0.1 M DAP solution also containing 0.1 mM CaCl₂ and 10 vol% ethanol is applied, followed by the application of a 0.1 M DAP + 0.1 mM CaCl₂ solution without the addition of ethanol. Both solutions are applied by brushing (10 strokes)⁷. This procedure was developed for the consolidation of marble, for which it was found that ethanol promotes HAP formation (and thus better efficacy) with lower amounts of precursors.

Ethyl silicate (ES) was also tested for comparison's sake, as it is currently the most used product for consolidation of Lecce Stone. For ES treatment a commercial formulation (Estel 1000, CTS, Italy, composed of 75 wt% ethyl silicate and 25 wt% white spirit D40, also containing 1 wt% dibutyltin dilaurate as a catalyst) was applied by brushing (10 brush strokes). After treatment, samples were left to cure for 1 month in room conditions prior to testing. A deionized water poultice was applied to ethyl silicate-treated cubes before performing durability cycles (water:poultice ratio 5:1, poultice kept on the samples for 48h), to remove possible hydrophobicity linked to residual ethoxy groups, that could interfere with the uptake of saline solution.⁸ The poultice was not applied to ES-treated cores to avoid desalination and because they did not need to be subjected to any characterization test involving absorption of water or saline solution.

Stone cores were treated on the whole external surface, while cubes were treated on one face perpendicular to the bedding planes.

2.4. Evaluation of the treatments' effects

Phase formation was examined by FT-IR. For a better understanding of the effect of the presence of salts on the HAP based treatments, FT-IR was performed on heated (HEAT), desalinated (DESALT) and non-desalinated (SALT) samples, to highlight the impact of different levels of salt contamination. FT-IR was also performed on ES-treated samples to verify whether the presence of salts interferes with ES curing.

Phase morphology and distribution were evaluated by SEM/EDS, to understand whether the presence of salts prevents consolidants from penetrating deeply into the stone and to evaluate the treatments' capability of sealing cracks.

Mechanical properties after treatments were evaluated in terms of dynamic elastic modulus (5 samples were taken for each condition). Dynamic elastic modulus was selected as it is non destructive and allows testing of the same samples before and after salt contamination and

treatment, which mitigates the impact of the high heterogeneity of the stone on the evaluation of the treatments' performance. To have a preliminary evaluation of the efficacy of the treatments, dynamic elastic modulus was also measured on samples artificially weathered by heating (instead of salt weathering), so as to determine their effects on uniformly weathered and uncontaminated stone.

For the durability tests, after desalination and treatment, 4 stone cubes for each condition were subjected to 10 additional salt crystallization cycles, performed exactly as during the contamination phase. The effects of the cycles were evaluated by measuring weight loss and dynamic elastic modulus after each cycle and after 10 cycles and desalination.

3. Results and Discussion

Morphology and composition of Lecce Stone was investigated by SEM/EDS (*Figure 1*). Untreated stone consists of a cement

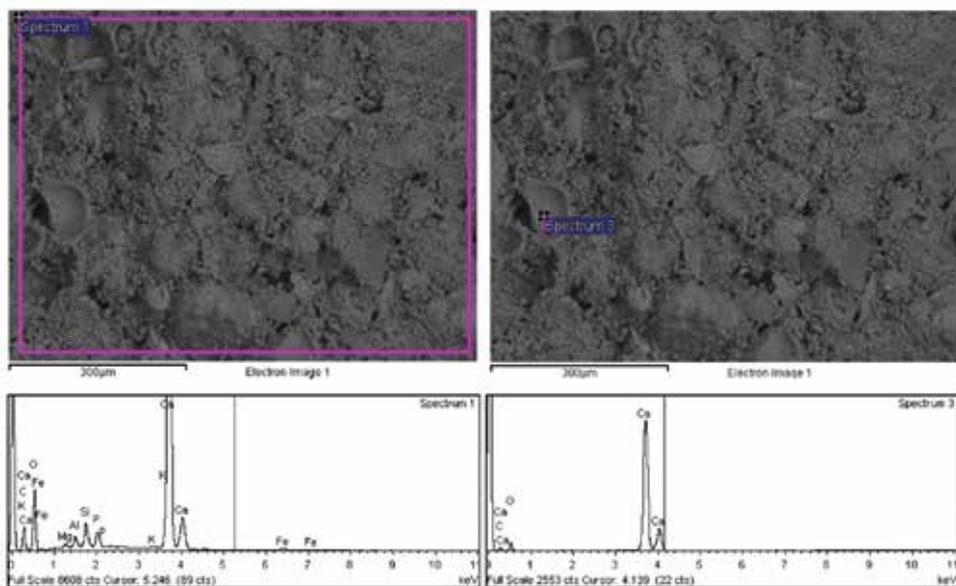


Figure 1: SEM images and EDS spectra of untreated Lecce Stone

mainly constituted by calcite with traces of phosphorous, magnesium, aluminium, iron and silicon, that envelops fossil shells only composed of calcium carbonate (*Figure 1*). To have a preliminary evaluation of the treatments' efficacy prior to application on contaminated stone, they were first applied to samples artificially weathered by heating, that also exhibit more uniform weathering (*Table 1*). Significant efficacy is obtained for the application on heated stone, especially for treatment 3M that causes higher increases in Ed compared to ethyl silicate. Remarkably, both ES and 3M fully restore

about 0.15-0.30 wt% of salts remain in the stone, depending on the specimen and the initial contamination, their residual presence being confirmed by FT-IR and EDS spectra (*Figure 2 and 3*). Interestingly, salt content after the application of treatment 3M significantly decreases (average SO_4^- content = 0.0244 wt%), indicating that the application of a limewater poultice allows for some desalination of the stone, which can be considered an advantage of this treatment. Salt content in 0.1M and ES samples, instead, remains substantially unaltered in all the examined areas of the samples.

Ed [GPa]					
	Before heating	After heating ("HEAT")	ΔEd	After heating and consolidation	ΔEd
3M	10.5±0.6	7.7±0.4	-27%	12.5±0.8	+62%
0.1M	10.6±1.2	7.8±0.6	-26%	9.1±0.7	+17%
ES	12.8±0.5	9.3±0.2	-27%	13.0±1.1	+40%

Table 2: Dynamic elastic modulus on samples artificially weathered by heating. Values for stone before heating are different between the different batches of samples because of the heterogeneity of the stone.

the initial dynamic elastic modulus of unweathered stone. A lower increase is obtained by treatment 0.1M, which however can still be considered promising, particularly in view of the much lower amounts of precursors used.

Lecce Stone exhibits a very low resistance to salt weathering, significantly variable between different slabs and even different areas of the same slab. For this reason, two salt crystallization cycles were selected to achieve salt contamination without causing rupture in the stone. As a result of the cycles, about 1.43 wt% sulphates (expressed as SO_4^-) are deposited inside the stone, the total amount being quite variable between different specimens. After desalination,

Phase formation after treatments is reported in *Figure 2*. FT-IR spectra confirm the presence of residual sulphate in desalinated stone. No formation of soluble calcium phosphates phases nor phosphate salts or other soluble compounds is detected for any of the treated specimens. For sample 3M the application on non-desalinated ("SALT"), compared to desalinated stone ("DESALT"), leads to a higher formation of reaction products. However, given the position of the bands, it seems that octacalcium phosphate (OCP) is the phase that forms in the presence of higher amounts of salt (samples "SALT"), while HAP forms in its absence and for lower levels of contamination (samples "HEAT" and "DESALT").⁹

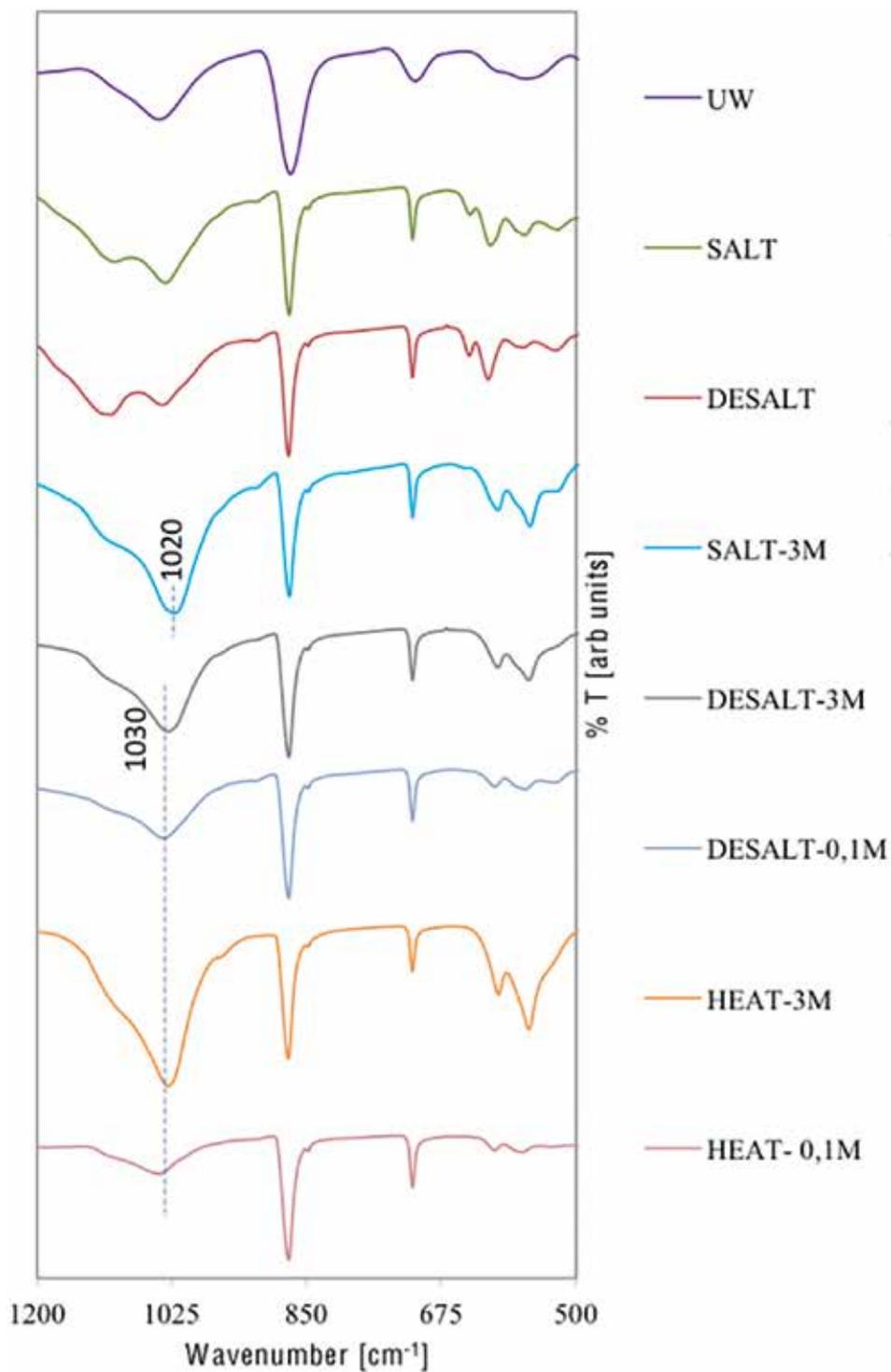


Figure 2: FT-IR spectra on untreated and treated specimens, for different levels of salt contamination

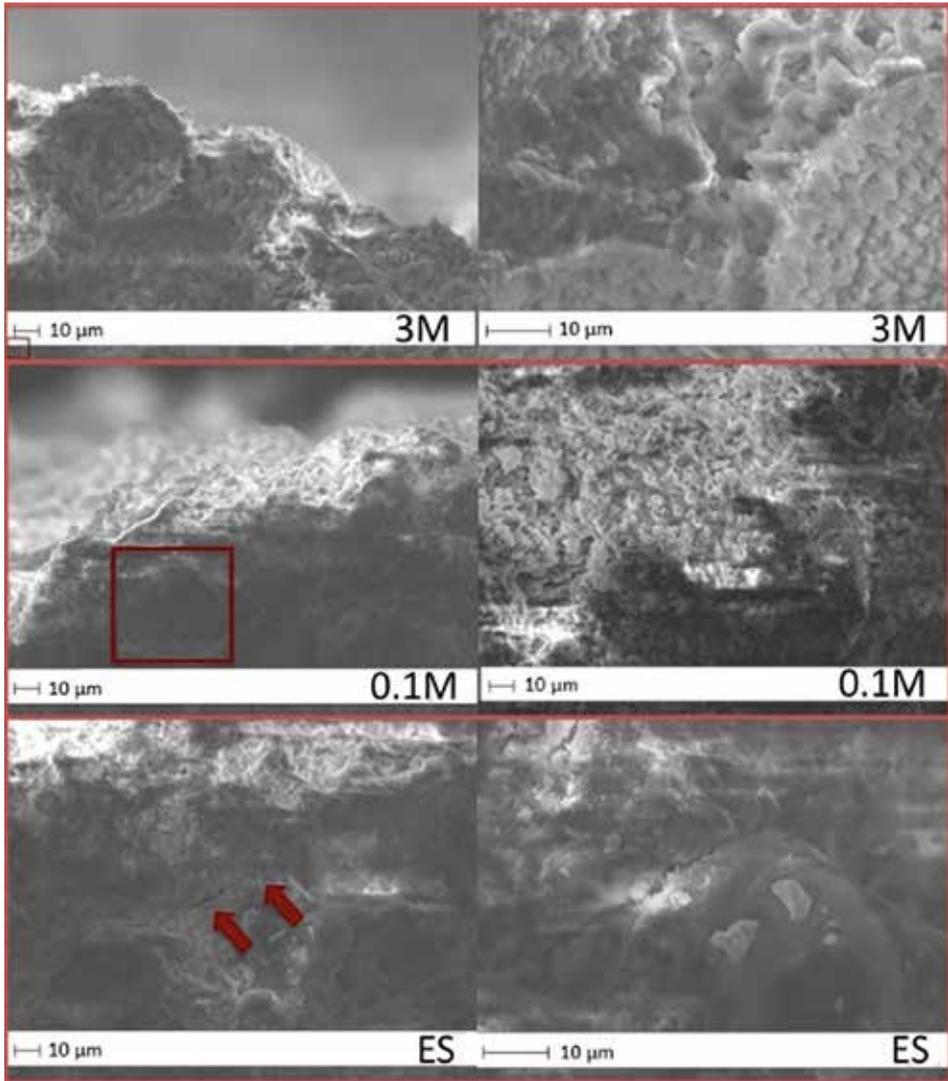


Figure 3: SEM images of treated samples' cross sections. In figure, the red square indicates significant formation of phosphate phases in correspondence of one shell, the arrows indicate a crack that remains unselaed after ethyl silicate treatment.

The formation of higher amounts of calcium phosphates in the presence of higher amounts of salts could be due to increased surface area and roughness (increase in surface roughness being caused by salt damaging the stone), similar to what was found in ¹⁰ for ammonium oxalate treated samples, where more calcium oxalate was found to form on non-desalinated samples because of the

higher specific surface and the different surface texture of the samples. Conversely, the formation of OCP instead of HAP is possibly due to the fact that different ions (including Na) can exert opposite impact on phase formation, and on crystallinity and solubility of reaction products, so not only the ions themselves but also the relative amount of each ion can have an effect on phase formation ⁴⁻⁵.

In general, the effect of salts could be due to the fact that their presence and the damage they cause affect surface roughness, specific surface and the presence of sites available for nucleation. This indicates that the level of salt contamination has an impact on phase formation; however, despite OCP being a metastable phase (eventually converting in HAP), it is far less soluble than calcite, hence its formation is not considered a drawback of the treatment. The absence of any band corresponding to sodium sulphate, in agreement with IC, confirms that salts were removed by the application of the lime-water poultice during the 3M treatment. Treatment 0.1M leads to the formation of HAP (see the presence of the phosphate stretching bands at 600 and 560 cm^{-1} , and the shift in the main band with the appearance of a shoulder at $\approx 1100 \text{ cm}^{-1}$), but a significantly lower amount of phosphate phases forms compared to 3M, in contrast to what was reported for marble.⁷ However, because the stone itself contains phosphate fractions, the lower phase formation complicates the exact discrimination between HAP and other calcium phosphate phases. Data for SALT-0.1M treatment are not reported here, as no significant differences can be assessed between the spectra for SALT and DESALT samples. Sample ES exhibits a broad band in the 1040-1100 cm^{-1} area, probably resulting from the overlapping of the bands at 1037 cm^{-1} (Lecce Stone), 1080 cm^{-1} (Si-O-Si of hydrolyzed ES)⁹ and 1104 cm^{-1} (sodium sulphate). No bands at 1170 cm^{-1} are present, indicative of Si-O-C.¹¹

Phase morphology and distribution in treated samples was evaluated by SEM/EDS. In sample 3M, phosphate phases were detected both on the surface and in depth in the samples, indicating that the presence of salts does not prevent a uniform penetration of the consolidant. Interestingly, phosphate formation is higher adjacent to and inside the shells, which exhibit no ion-contamination,

suggesting that HAP nucleation could be inhibited by ions contained in the stone matrix (probably magnesium, which is known to be an HAP growth inhibitor^{4,5}). For Lecce stone, therefore, the presence of trace elements in the stone seems to have a stronger impact on HAP formation than sodium sulphate has.

Consistently, also in sample 0.1M, phosphate formation is favoured on the shells, indicating that, even with ethanol in the solution phase, formation is lower in ion-doped areas of the stone. The formation of calcium phosphates is generally lower compared to 3M and it is quite non-uniform (in some areas P is not detected by EDS). However, because the stone itself contains phosphorous in variable concentrations, it is not possible to detect the formation of phosphate phases unless a large amount forms. The treatment, however, is effective in sealing cracks, also in depth in the sample, again indicating that the presence of salts does not prevent the penetration of the consolidant. The ability of the HAP-based consolidants to seal cracks is reflected in their ability to fully restore the dynamic elastic modulus of untreated stone (see Table 2). The lower phase formation in 0.1M treatment compared to 3M, however, combined with the lower increase of dynamic elastic modulus, indicates that the formulation needs further optimization for being applied to Lecce Stone, and that a higher concentration of DAP should be used, given the high porosity of the stone (experiments are in progress). However, because HAP is found to form and seal cracks also in depth in the sample, it seems that ethanol has a positive impact on HAP formation. SEM images on ethyl silicate treated samples indicate abundant phase formation, but also reveal the presence of unsealed cracks that were not noticed in HAP-based treatments. For these samples, EDS analysis did not provide meaningful information, as a high and very variable

Ed [GPa]					
	Before salt weathering cycles	After 2 cycles and desalination	Δ Ed	After consolidation	Δ Ed
3M	16.5±0.3	16.2±0.6	-2%	17.8±0.3	+10%
0.1M	10.9±0.3	10.8±0.2	≈	11.4±0.3	+6%
ES	11.1±0.3	10.7±0.6	-4%	13.9±0.4	+30%

Table 2: Dynamic elastic modulus of samples subjected to salt crystallization cycles

Ed [GPa]			
	Before salt weathering cycles	After 10 cycles and desalination	Δ Ed
Untreated	18.1±0.4	14.2±0.3	-22%
3M	18.1±0.4	16.0±1.1	-12%
ES	17.4±0.3	13.6±0.7	-22%

Table 3: Durability of treated samples in terms of dynamic elastic modulus

amount of silica is contained in the stone itself.

The efficacy of the treatments was evaluated by dynamic elastic modulus (see Table 2). Weathering resulted mainly in the pulverization and consequent detachment of the external layers of the samples, but did not cause significant decrease in the elastic modulus of the non-detached parts. None of the HAP-based treatments provides dramatic increases in dynamic elastic modulus compared to the values after weathering. The increase is higher for samples treated by ethyl silicate, which, however, exhibit the highest amount of residual salts in the pores, which could cause some pore occlusion resulting in increases in Ed not ascribable to a consolidating effect. However, the values after treatment exceed those of the unweathered specimens, thus indicating that low increases in dynamic elastic modulus are registered

because the stone was not severely damaged by weathering cycles, which were aimed at investigating the effects of salt contamination rather than causing significant damage to the stone. However, because phosphate formation was found to occur also deep in the samples (Figure 3) and because only HAP and OCP and no other CaP phases were detected by FT-IR (Figure 2), it can be concluded that no pore occlusion occurred, which would prevent the consolidant from penetrating deeply into the stone, and no formation of metastable phases took place as a result of salts contamination, which were the main concerns regarding the application on salt weathered stone. This implies that higher increases in mechanical properties can be obtained for more severely damaged samples (experiments are in progress).

To better investigate the effect of the 3M treatment compared to ES, their ca-

pability of increasing stone durability towards further weathering cycles was evaluated (*results in Table 3*). Untreated specimens were also considered for comparison's sake. As can be seen in Table 3, 3M samples experience the lowest decrease in dynamic elastic modulus after the cycles, thus indicating that this treatment has the best durability. This also indicates that, despite apparent low efficacy obtained for the cores (caused by limited weathering level of the specimens), still this treatment is promising as it enhances the stone durability towards salt weathering better than ethyl silicate does.

4. Conclusions

The application of two HAP-based treatments was tested on Lecce Stone contaminated by sodium sulphate. The following conclusions can be derived:

- 1) The presence of salt in the stone does not prevent penetration of the HAP-based consolidants nor cause formation of phosphate salts instead of calcium phosphates;
- 2) Depending on the amount of salts contained in the stone, either HAP or OCP are obtained, both suitable for consolidation of limestone;
- 3) Increasing levels of sodium sulphate affect the nature of the phases that form, but promote the formation of higher amounts of calcium phosphates. Instead, other ions contained in the stone (possibly magnesium) affect the nucleation of HAP, leading to a nonuniform coverage of the substrate, and to the preferential formation of HAP in uncontaminated shells.
- 4) Comparing the 0.1M and 3M treatments, the latter exhibits better efficacy, as it results in more calcium phosphate formation. The 0.1M treatment, however, still guarantees sealing of cracks even in the depth of the sample, which suggests that optimization of this treatment is worth pursuing;
- 5) Treatment 3M is promising as it increases resistance of the stone to further salt weathering, whereas ethyl silicate treatment does not.

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