CONSOLIDATION OF A POROUS LIMESTONE BY MEANS OF A NEW TREATMENT BASED ON HYDROXYAPATITE

Enrico Sassoni,[1] Elisa Franzoni,[1] George W. Scherer[2] and Sonia Naidu[3]

[1] *Department of Civil, Environmental and Materials Engineering (DICAM)*
University of Bologna, Bologna, Italy
[2] *Department of Civil and Environmental Engineering (CEE)*
Princeton University, Princeton, NJ, USA
[3] *Department of Chemical and Biological Engineering (CBE)*
Princeton University, Princeton, NJ, USA

Abstract

In this study, the performance of a new inorganic consolidant, based on the formation of hydroxyapatite (HAP) by reaction between calcite and a solution of diammonium hydrogen phosphate (DAP), was investigated for the conservation of a highly porous limestone, Globigerina limestone (GL), extensively used in historical and modern architecture in Malta. The influence of the substrate deterioration level was preliminarily evaluated by comparing the effects of a 1.0 M DAP solution on unweathered GL samples and on artificially weathered ones (obtained according to previously developed methodologies). The effects of the treatment in terms of modifications in stone microstructural, physical and mechanical properties were then evaluated and compared to those brought by a commercial TEOS-based treatment. Novel methods for improving the performance of the HAP-based treatment and promoting the formation of HAP were also investigated. From the results of this study, HAP is confirmed as a very promising consolidating treatment, that can allow an increase up to +52% in tensile strength, without significantly occluding the pores and altering stone transport properties (which represents one of the limitations of the TEOS-based consolidants).

Keywords: stone, consolidation, hydroxyapatite, TEOS, water transport properties

1. Introduction

The exposure of natural stone to aggressive environments leads to several decay forms that threaten cultural heritage. In fact, stone degradation involves the irremediable loss of decorative elements and, for some structural elements, even safety concerns, thus making the development of effective consolidating materials necessary. Considering that reversibility in consolidation is fairly utopian (especially in porous stone where a deep impregnation is required), consolidants must fulfill many requirements not only in terms of consolidating efficacy, but also in terms of compatibility with the substrate and durability. From this point of view, inorganic consolidants seem quite attractive, as they are generally stable and durable, even if some drawbacks have been pointed out, such as the shallow penetration depth (e.g. for nano-particles dispersions) and the formation of a stiff and barely permeable consolidated layer (generally subject to early detachment).

To overcome some of the most common defects of consolidants, a treatment based on the formation of hydroxyapatite (HAP) in stone has been recently proposed (Naidu et

al. 2011; Sassoni et al. 2011; Sassoni et al. 2012). The treatment consists in the application of a solution of diammonium hydrogen phosphate (DAP), which reacts with calcite and forms HAP.

The reactivity of DAP with calcite makes this consolidant a good candidate for the treatment of carbonate stones, hence in this paper some treatments based on the use of DAP were tested on *Globigerina Limestone*, which is the most extensively used material in architectural heritage in Malta and which suffers from severe decay forms, ranging from pulverization, to flaking, to alveolization (Sandrolini and Franzoni 2000; Croveri et al. 2004; Misfud and Cassar 2006; Rothert et al. 2007).

Globigerina Limestone is also similar to other types of stone (Noto Limestone, Lecce Stone) widely used in baroque architecture in southern Italy, which could benefit from the HAP treatment as well.

2. Materials and methods
2.1 Materials

Globigerina limestone (GL), purchased from Xelini Skip Hire and High-Up Service (Malta), was used. The stone is a highly porous limestone, mainly made of calcite crystals and fossils (such as *globigerinae*, from which the name derives, shells and sea urchins). Stone slabs (parallel to the bedding planes) were sawn to obtain cubic, prismatic and cylindrical samples.

For the HAP-based treatment, diammonium hydrogen phosphate (DAP), purchased from Sigma-Aldrich (assay $\geq 98.0\%$, reagent grade), and de-ionized water were used.

For the TEOS-based treatment, the commercial product ESTEL 1000 by CTS s.r.l. (Italy), composed of 75 wt% TEOS oligomers (containing 1% dibutyltin dilaurate) and 25 wt% white spirit solvent, was used.

2.2 Characterization techniques

The mineralogical composition of the stone was determined by powder X-ray diffraction (XRD, Philips Diffractometer PW 1840, 40kV/20mA, Cu Kα radiation) and the carbonate content was assessed by the Dietrich-Frühling gas volumetric method (measurement of CO_2 volume released by reacting the powdered sample with HCl). The pore size distribution, total open porosity (*OP*) and pore radius corresponding to 50% intruded mercury volume (r_{50}) were assessed by mercury intrusion porosimetry (MIP, Fisons Macropore Unit 120 and Porosimeter 2000 Carlo Erba). The specific surface area (SSA) was measured using the BET method (Flowsorb II 2300 Micromeritics, USA).

The sorptivity (i.e. the rate of water sorption) was measured according to EN 15801 on cubic samples (5 cm side), the water flux being in the direction parallel to the bedding planes. The water vapor permeability was measured by determining the water vapor diffusion resistance coefficient (μ), according to EN 15803 (using a saturated aqueous solution of KNO_3), on $7 \times 7 \times 2.5$ cm^3 slabs sawn parallel to the bedding planes.

For evaluating the effectiveness of the consolidating treatments, the dynamic elastic modulus (which has the advantage of being a non-destructive measurement, that can be repeated on the same sample before and after the treatment), the tensile strength (which determines the sensitivity to deterioration processes such as freeze-thaw cycles, salt crystallization, clay swelling, etc.) and the resistance to abrasion (which represents a key parameter in Malta environmental conditions, where wind erosion causes severe damage

to stoneworks) were evaluated. The dynamic elastic modulus (E_d) and the tensile strength (σ_t) were determined on 6 cylindrical samples (5 cm height and 2 cm diameter, core-drilled perpendicular to the bedding planes), according to the methodology described by Sassoni et al. (2012). The resistance to abrasion was evaluated according to the methodology proposed by Sandrolini et al. (2000), by measuring the weight loss (W_a) of $7 \times 7 \times 2.5$ cm³ slabs after an accelerated abrasion test, based on a modified version of the PEI (Porcelain Enamel Institute) abrasion test.

The weight increase after the treatment ($\varDelta w$) was measured after drying to constant weight at room temperature. The calcium phosphate phases formed by reaction between the stone and the DAP solution were observed on a scanning electron microscope (SEM, Philips XL20) and the elemental composition was determined by dispersive X-ray spectroscopy (EDS, EDX 9800 Microanalysis). The phases were also characterized by Fourier transform infrared spectroscopy (FT-IR, Perkin–Elmer Spectrum One FT-IR Spectrometer), using the KBr pellets method. The possible presence of unreacted DAP inside stone pores was assessed by high pressure liquid chromatography (HPLC, Jasco 880-PU Intelligent HPLC Pump with CDD-6A Shimadzu Conductivity Detector), after grinding, salt extraction with distilled boiling water and filtration.

2.3 Artificial deterioration
To simulate the deterioration conditions that Globigerina limestone may experience in the field, some of the samples to be consolidated were artificially weathered according to previously proposed methodologies (Sassoni et al. 2011, Franzoni et al. 2012), by heating stone samples at 400 °C for 1 hour.

2.4 HAP-based treatment
2.4.1 Investigation of the influence of substrate deterioration level
As the conservation state of the stone may significantly affect the evaluation of a consolidant's effectiveness, the influence of the substrate deterioration level was first investigated. Four unweathered and four artificially weathered cylinders were treated with a 1.0 M DAP solution (according to Sassoni et al. 2011), applied by brushing until apparent refusal. At the end of the treatment, the samples were rinsed with de-ionized water, then wrapped with a plastic film for 48 hours and finally left to dry at room temperature until constant weight. The consolidating effect of the treatment on the two different substrates was evaluated in terms of E_d and σ_t increase.

2.4.2 Evaluation of the treatment effects and comparison with TEOS
The microstructural, physical and mechanical characteristics of artificially weathered samples were compared with those of artificially weathered samples, treated by applying a 1.0 M DAP solution by brushing as described in the previous paragraph. In particular, 6 cylinders were treated on the whole surface for determining the increase in E_d and σ_t, while the samples for the abrasion test, capillary test and water vapor permeability test were treated on one face only.

A comparison with the effects of the commercial TEOS-based treatment, applied on an analogous set of artificially weathered samples, was then performed. TEOS was applied by brushing until apparent refusal, the excess product on the surfaces at the end

of the treatment being removed using a tissue soaked in pure solvent. The TEOS-treated samples were then left in room conditions for 1 month before any characterization.

2.4.3   Investigation of novel improving treatments

With the aim of promoting and accelerating the formation of HAP and favoring its formation over other metastable phases that may form instead of HAP (Sassoni et al. 2011), the effects of adding calcium salts to the DAP solution were investigated. The potential benefit of adding calcium ions was suggested in Naidu et al. (2011), where the addition of 20 mM $CaCl_2$ to a 0.1 M DAP solution was found to enhance the formation of a uniform phosphate layer over marble surface after 24 hours of reaction, whereas, without adding any calcium salts, the phosphate layer formed in the same period of time is porous and less uniform. More recent work, reported by Naidu and Scherer in these proceedings, suggested an optimal composition of 1 mM $CaCl_2$ in 1 M DAP.

Based on the results of preliminary tests, aimed at identifying the most promising conditions, the following treatments were investigated:

(1) 1.0 M DAP with 1.0 mM $CaCl_2$ and 150 μM NH_4HCO_3
With respect to the reference treatment (1.0 M DAP), 1.0 mM $CaCl_2$ and 150 μM of NH_4HCO_3 were added, the former with the aim of favoring HAP formation thanks to the higher amount of calcium ions available for reaction, the latter with the aim of reducing the dissolution of the calcareous substrate, thanks to the presence of carbonate ions that reduce calcite solubility.

(2) 1.0 M DAP with 1.0 mM $Ca(OH)_2$ and 150 μM NH_4HCO_3
The effect of using $Ca(OH)_2$ instead of $CaCl_2$, with the advantage of not introducing chlorides inside the stone but rather innocuous OH^-, was investigated, the amount of Ca^{2+} ions being kept constant, as well as the DAP and NH_4HCO_3 concentrations.

(3) 1.0 M DAP with 2.5 mM $CaCl_2$
The effect of increasing the $CaCl_2$ concentration up to 2.5 mM was investigated. Higher concentrations (5 mM and 10 mM $CaCl_2$) were excluded as they were found to cause immediate precipitation in the beaker, right after the addition of DAP to the $CaCl_2$ solution.

(4) 6 mM DAP with 10 mM $CaCl_2$
The concentrations reported in Liu and Zhang 2011 (where a $CaCl_2$/DAP ratio of 10/6 was suggested, corresponding to the Ca/P = 10/6 ratio in stoichiometric HAP) were also considered. Upon addition of DAP to the $CaCl_2$ solution, immediate precipitation inside the beaker occurred.

(5) 1.7 g/l $Ca(OH)_2$ and then 1.0 M DAP
The effect of a preliminary introduction of Ca^{2+} ions into the stone, by impregnation with a saturated solution of calcium hydroxide, was evaluated. After 24 hours of immersion, the samples were dried to constant weight and, then, treated with the DAP solution.

(6) 3.7 DAP
The effect of increasing the DAP concentration up to the saturation one (3.7 M at 20 °C) was investigated.

(7) 3.7 DAP and then 1.7 g/l $Ca(OH)_2$

Finally, the effect of treating stone samples with a 3.7 M DAP solution and then, after drying to constant weight, impregnating them twice with a saturated solution of calcium hydroxide was investigated.

Each of the treatments described above was applied on 4 cylindrical samples that had been artificially weathered by heating. The treatment with the DAP solution, as well as the treatment with the saturated solution of calcium hydroxide, was applied by partially immersing the samples into the solution, the upper 5 mm of the samples being left uncovered to avoid entrapping air bubbles. After 48 hours of partial immersion, the samples were left dry to constant weight. The effects of the various treatments were then evaluated by measuring the variations in E_d and σ_t and by characterizing the formed phases by FT-IR.

3. Results and discussion
3.1 Materials

GL is mainly composed of calcium carbonate ($CaCO_3 = 91.4$ %) and small amounts of quartz. It has a highly porous microstructure, with quite coarse pores (Figure 1). Accordingly, the sorptivity of the stone is very high (Figure 2) and its mechanical properties are rather weak, with poor resistance to abrasion (Table 1).

3.2 Artificial deterioration

After heating at 400 °C for 1 hour, the artificially weathered stone (GL-400) exhibits a decrease in dynamic modulus ($\Delta E_d = -26.9$ %) and tensile strength ($\Delta \sigma_t = -16.7$ %), as well as an increase in weight loss after accelerated abrasion ($\Delta W_a = +10.5\%$), compared to the unweathered stone (GL) (Table 1). Even if no significant modification in the pore size distribution can be noticed after heating (Figure 1), the formation of cracks at the nano-scale (not detectable by MIP) is confirmed by the significant increase in the specific surface area detected by BET method ($\Delta SSA = +35.7$ %, Figure 1). This is consistent with the expected opening of cracks at the grain boundaries, as a consequence of the stress induced by the anisotropic deformation of calcite crystals upon heating at 400 °C (Sassoni et al. 2011; Franzoni et al. 2012). Accordingly, no significant modification in the first part of the sorptivity graph is present (Figure 2), as the initial stage is governed by the coarser pores, which remain basically unaltered after heating. However, in the second part of the curve, governed by the thinner pores, a slight increase in the rate of water sorption is present in the weathered samples (Figure 2).
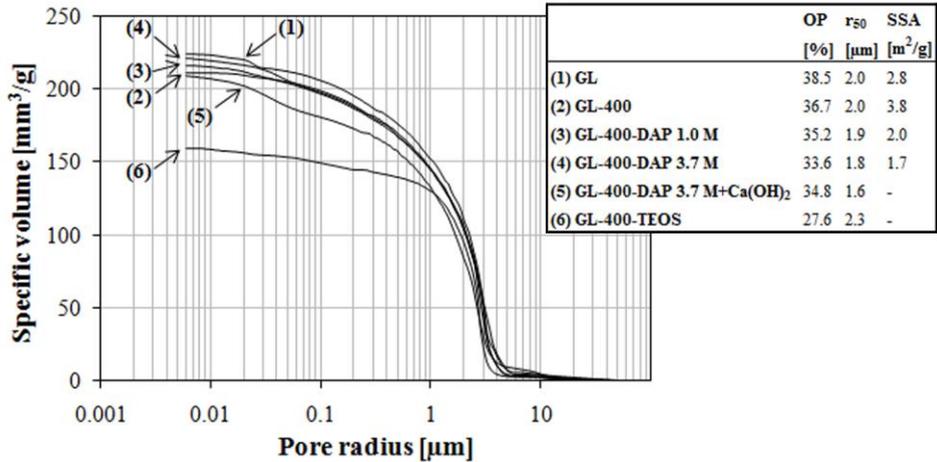
Figure 1. Pore size distribution, *OP* and *r₅₀* (MIP) and *SSA* (BET method) of GL samples unweathered, artificially weathered and artificially weathered and treated in various conditions
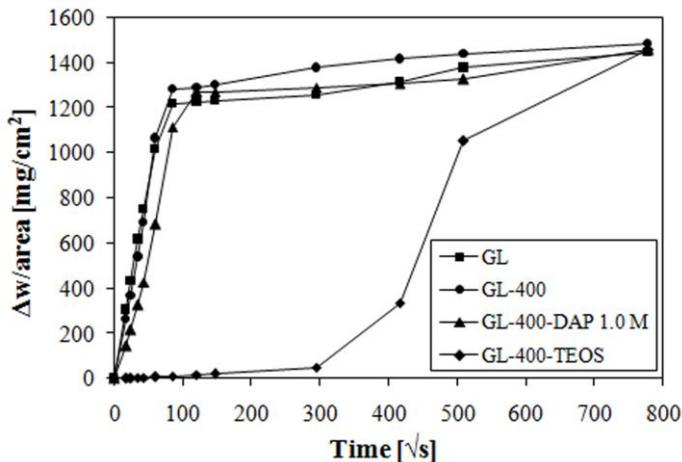

Figure 2. Sorptivity of GL samples unweathered, artificially weathered and artificially weathered and treated in various conditions

3.3 HAP-based treatment

3.3.1 Evaluation of the influence of the substrate deterioration level

Comparing the results of the application of the 1.0 M DAP treatment to unweathered and artificially weathered GL samples (GL-DAP 1.0 M and GL-400-DAP 1.0 M, respectively, Table 1), it can be noticed that the treatment proved to be significantly more effective on the deteriorated substrate than on the unweathered one. Indeed, in the latter case, E_d and σ_t exhibited no increase, while the resistance to abrasion was only slightly increased. On the contrary, the samples heated at 400 °C exhibited a significant improvement in mechanical properties after the 1.0 M DAP

treatment, particularly in terms of E_d (which is basically restored to the unweathered condition) and W_a (which is reduced by 90%).

The different performance of the treatment on the two substrates can be explained considering that, in the case of the sound stone, the microstructure is mainly characterized by coarse pores (r_{50} = 2.0 μm, Figure 1) that HAP does not occlude. On the contrary, in the case of the artificially deteriorated stone, the nano-cracks that opened after heating and that are responsible for the increase in SSA (Figure 2) can be repaired by the DAP treatment, which hence causes an improvement in mechanical properties.

Considering that the artificial deterioration method was successful in producing cracks inside the stone, which resemble the natural weathering that can be experienced in the field, the artificially deteriorated substrate can be considered as more representative of the conditions of stones needing consolidation. Hence, the consolidating performance on the deteriorated substrate can be considered as more representative of the treatment effectiveness in the field. Therefore, all the treatments in the following part of the study were performed only on artificially weathered samples (denoted by the GL-400- prefix before the indication of the treatment).

	E_d [GPa]	σ_t [MPa]	W_a [mg/mm^2]
GL	15.6 (±0.3)	3.0 (±0.3)	0.19 (±0.01)
GL-DAP 1.0 M	15.3(±0.2)	3.0 (±0.3)	0.07 (±0.01)
GL-400	11.4 (±0.6)	2.5 (±0.4)	0.21 (±0.00)
GL-400-DAP 1.0 M	15.7 (±0.2)	2.7 (±0.2)	0.02 (±0.01)

Table 1. Dynamic elastic modulus (E_d), tensile strength (σ_t) and weight loss after abrasion (W_a) of GL samples unweathered, artificially weathered and artificially weathered and treated in various conditions. E_d and σ_t are averaged for 4 samples, W_a for 2 samples (standard deviations in brackets)

	E_d [GPa]	σ_t [MPa]	CA [kg/m^2·s$^{1/2}$]	WA$_{24}$ [%]	μ
GL-400	11.4 (±0.6)	2.5 (±0.4)	0.178	16.1	4.9
GL-400-DAP 1.0 M	15.7 (±0.2)	2.7 (±0.2)	0.131	15.2	5.6
GL-400-TEOS	18.5 (±0.2)	5.2 (±0.6)	0.001	0.6	5.7

Table 2. Physical-mechanical parameters of GL samples unweathered, artificially weathered and artificially weathered and treated in various conditions. E_d and σ_t values are averages for 6 samples (standard deviations in brackets)

3.3.2   Evaluation of the treatment effects and comparison with TEOS

The 1.0 M DAP solution proved to have significant effects on mechanical properties of heated GL samples, particularly in terms of dynamic modulus and resistance to abrasion (Tables 1 and 2). Such improvement is owing to the formation of calcium phosphate phases on the surface of stone pores, as confirmed by SEM/EDS spectrum and FT-IR spectra, where bands at 566 and 602 cm^{-1}, owing to P-O bonds of HAP (Maravelaki-Kalaitzaki 2005, Mròz et al. 2010), arise after the treatment, as shown

in Figure 3. As EDS and FT-IR spectra were taken at a depth of 1 cm from the surface, the penetration depth of the DAP treatment can be assessed as at least equal to 1 cm.
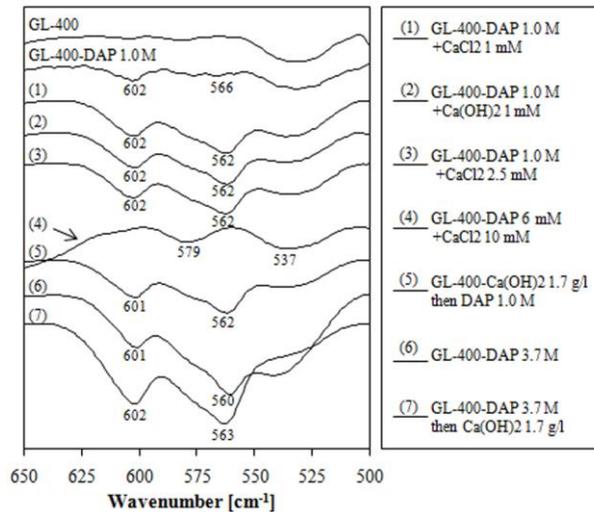

Figure 3. FT-IR spectra of GL samples untreated and treated in various conditions

Remarkably, the improvement in mechanical properties is not owing to pore occlusion, as the pore size distribution is substantially unaltered after the treatment with 1.0 M DAP (Figure 1). The binding action of HAP is in fact limited to re-sealing nano-cracks at grain boundaries, without occluding the pores, so that also transport properties of DAP-treated stone are almost unchanged (Figure 2). The fact that stone sorptivity is not altered after the treatment can be an advantage when later restoration works involving water (e.g. cleaning, use of grouts, etc.) are to be carried out. Moreover, the good permeability of treated stone to water vapor (Table 2) allows water to easily exit the stone as water vapor.

If one compares the effects of the 1.0 M DAP treatment with those of a commercial TEOS-based consolidant, the following observations can be derived. Notwithstanding the calcareous nature of the stone, the TEOS treatment proved to be highly effective in improving stone mechanical properties (Table 2). Such an improvement can be explained considering, on the one hand, the partial micropores occlusion and, on the other hand, the fact that GL contains small amounts of quartz, which might allow some chemical bonding between the consolidant and the stone.

Contrary to HAP, the TEOS-based treatment causes a significant occlusion of pores (Figure 1), particularly in the case of pores with radius < 2 μm. Such occlusion might represent a risk in case it is limited to the most superficial part of the treated stone, under which an unaltered, more porous part with different physical-mechanical characteristics is present. Moreover, TEOS-treated GL exhibits a marked reduction in sorptivity (Figure 2) 1 month after the treatment. Such hydrophobic behavior may represent a drawback, in case of water-based restoration treatments planned after consolidation and/or in case of water trapped behind the consolidated layer (Scherer and Wheeler 2010). However, in the latter case, the risk is mitigated by the fact that, after prolonged

contact with water (7 days), water absorption almost reaches that of the untreated stone (Figure 2) and by the fact that water vapor permeability is not substantially inhibited by the treatment (Table 2). This is presumably due to the microstructure of GL, whose high open porosity and large amounts of coarse pores allow water vapor, as well as liquid water, to be exchanged with the environment.

3.3.3 Investigation of novel improving treatments

The first five treatments described in § 2.4.3 were aimed at promoting the formation of HAP by adding calcium salts, at a constant 1.0 M DAP concentration (except treatment (4), involving a 6 mM DAP concentration). Apart from treatment (4), for which no bands ascribable to HAP were found, treatments (1-3) and (5) caused a definite increase in the amount of formed HAP. Indeed, as shown in Figure 3, for treatments (1-3) and (5) the bands at 562 and 602 cm^{-1}, owing to P-O bonds of HAP, are markedly more defined, which suggests that the formation of HAP was promoted. Nonetheless, no significant improvement in E_d and σ_t, compared to the 1.0 M DAP treatment with no calcium addition, was found. This could be due to the fact that not all the formed HAP is actually chemically bonded to the calcitic surface, but rather simply deposited on it. The investigation of this issue is currently in progress.

In the case of GL treated with more concentrated DAP solutions (3.7 M and 3.7 M followed by impregnation with a solution of calcium hydroxide) good results were obtained. By increasing the DAP concentration to 3.7 M, very significant increases in mechanical properties are achieved (ΔE_d = +71% and $\Delta\sigma_t$ = +40%), compared to the artificially weathered, untreated stone (Table 3). Notably, also compared to the 1.0 M DAP-treated stone, a marked increase in the mechanical benefit can be observed (Table 3). This can be attributed to the larger amounts of phosphate ions available to form HAP, as confirmed by the higher weight increase of treated samples (Table 3) and by the FT-IR spectra, where a marked increase in the P-O bands can be observed when DAP concentration is increased from 1.0 M to 3.7 M (Figure 3). The possible presence of unreacted DAP inside the stone, when the 3.7 M DAP solution is used, was investigated by measuring the amount of soluble PO_4^{3-} in the stone after the treatment. As shown in Table 3, small amounts of soluble PO_4^{3-} are present. Consequently, with the double aim of making the unreacted DAP partly react and partly be removed, the effect of treating the 3.7 M DAP-treated stone with two applications of a saturated solution of Ca(OH)$_2$ was investigated. As reported in Table 3, an increase in tensile strength ($\Delta\sigma_t$ = +52%, compared to the untreated stone) was registered, while the weight gain decreased from Δw = 1.1 g (after the treatment with 3.7 M DAP) to Δw = 0.5 g (after the treatment with 3.7 M DAP followed by treatment with the Ca(OH)$_2$ solution). Therefore, the calcium hydroxide treatment allowed the unreacted DAP (as well as possible soluble calcium phosphate phases that may form alongside HAP) to either exit the stone (hence the weight decrease) or react with Ca^{2+} ions contained in the calcium hydroxide solution (hence the tensile strength increase). Consistently, the amount of soluble PO_4^{3-} that remain in the stone after the treatment with Ca(OH)$_2$ is significantly reduced (Table 3), while the height of the P-O bands in the FT-IR spectra is slightly increased (Figure 3).

4. Conclusions

In the reference conditions (1.0 M DAP solution), the treatment is able to significantly improve stone mechanical properties, particularly the resistance to abrasion, without occluding stone porosity and substantially altering water transport properties. Even though a commercial TEOS-based consolidant proved to be more effective in improving dynamic modulus and tensile strength of GL, the TEOS-treated stone exhibited a definite reduction in stone porosity and sorptivity, particularly for short periods of exposure to water, which sometimes might give rise to problems in performing further restoration works and/or in durability.

The effectiveness of the HAP-based treatment was found to be significantly improved by increasing the DAP concentration to 3.7 M and by treating the 3.7 M DAP-treated stone with a saturated solution of $Ca(OH)_2$. In fact, thanks to the treatment with calcium hydroxide, some unreacted DAP is eliminated and some of it reacts with the calcium ions supplied in the $Ca(OH)_2$ solution, thus allowing an improvement in both mechanical properties and treatment stability.

	E_d [GPa]	σ_t [MPa]	Δw [g]	PO_4^{3-} [%]
GL-400	11.4 (±0.6)	2.5 (±0.4)	-	0.00
GL-400-DAP 1.0 M	15.7 (±0.2)	2.7 (±0.2)	0.3 (±0.0)	0.01
GL-400-DAP 3.7 M	19.5 (±0.3)	3.5 (±0.4)	1.1 (±0.1)	0.07
GL-400-DAP 3.7 M then Ca(OH)$_2$ 1.7 g/l	17.0 (±0.2)	3.8 (±0.3)	0.5 (±0.0)	0.01

Table 3. E_d, σ_t, Δw and PO_4^{3-} content of GL samples untreated and treated in various conditions. E_d, σ_t and Δw values are averages for at least 4 samples (standard deviations in brackets)

References
Croveri P., Dei L., Giorgi R., Salvadori B. 2004. 'Consolidation of globigerina limestone (Malta) by means of inorganic treatments: preliminary results'. Proceedings of '10th International Congress on the Deterioration and Conservation of Stone', Stockholm (S), vol. 1, 463-470

EN 15801. 2010. Conservation of cultural property - Test methods - Determination of water absorption by capillarity

EN 15803. 2010. Conservation of cultural property - Test methods - Determination of water vapour permeability (δ_p)

Franzoni E., Sassoni E., Scherer G.W., Naidu S. 2013. 'Artificial weathering of stone by heating'. *J Cult Herit* **14S**:85-93

Liu Q., Zhang B. 2011. 'Synthesis and characterization of a novel biomaterial for the conservation of historic stone building and sculptures'. *Mater Sci Forum* **675-677**:317-320

Maravelaki-Kalaitzaki P. 2005. 'Black crusts and patinas on Pentelic marble from the Parthenon and Erecteum (Acropoli, Athens): characterization and origin'. *Anal Chim Acta* **532**:187-198

Misfud T, Cassar J. 2006. 'The treatment of weathered Golobigerina Limestone: the surface conversion of calcium carbonate to calcium oxalate'. Proceedings of 'Heritage, weathering and conservation', Madrid (E) 21-24 June 2006, 727-734

Mròz W., Bombalska A., Budner B., Burdyńska S., Jedyński M., Prokopiuk A., Menaszek E., Ścislowska-Czarnecka A., Niedzielska A., Niedzielski K. 2010. 'Comparative study of hydroxyapatite and octacalcium phosphate coatings on metallic implants by PLD method'. *Appl Phys A* **101**:713-716

Naidu S., Sassoni E., Scherer G.W. 'New treatment for corrosion-resistant coatings for marble and consolidation of limestone'. Proceedings of 'Jardins de Pierres – Conservation of stone in Parks, Gardens and Cemeteries', Paris (F) 22-24 June 2011, 289-294

Rothert E., Eggers T., Cassar J., Ruedrich J., Fitzner B., Siegesmund S. 2007. 'Stone properties and weathering induced by salt crystallization of Maltese Globigerina Limestone'. Prykril R., Smith B.J. (eds) 'Building stone decay: from diagnosis to conservation', Geological Society, London, Specials Publications **271**, 189-198

Sandrolini F., Franzoni E., Cuppini G. 2000. 'Predictive diagnostics for decayed ashlars substitution in architectural restoration in Malta'. *Mater Eng* **11**(3):323-337

Sassoni E., Naidu S., Scherer G.W. 2011. 'The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones'. *J Cult Herit* **12**:346-355

Sassoni E., Franzoni E., Pigino B., Scherer G.W., Naidu S. 2013. 'Consolidation of calcareous and siliceous sandstones by hydroxyapatite: comparison with a TEOS-based consolidant'. *J Cult Herit* **14S**:103-108

Scherer G.W., Wheeler G.S. 2009. 'Silicate consolidants for stone'. *Key Eng Mat* **391**:1-25