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# Phosphate-based treatments for consolidation of salt-bearing Globigerina limestone

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**Abstract.** Phosphate-based treatments have proven to be effective for consolidation of porous limestone. However, application on salt-laden stone must be evaluated, as salt-weathering is among the main deterioration phenomena for this lithotype and salts present in the stone can interfere with the outcome of consolidation. For this reason, here, the phosphate-based consolidant was tested on a salt-bearing porous limestone (Globigerina limestone). To achieve salt contamination and to induce weathering, stone samples were subjected to crystallization cycles in sodium sulfate, which is among the most common and damaging salts that affect limestone on site. Phase formation and distribution of the consolidant were evaluated in the presence of salts. The treatment efficacy was investigated in comparison with ethyl silicate, which is currently the most used consolidant for porous limestone. Promising results were obtained, indicating that the presence of sodium sulfate does not hamper penetration of the phosphate-based consolidant. By penetrating deeply into the stone and sealing cracks caused by weathering, the consolidant enhances strength and stiffness. Moreover, the presence of salts does not interfere with the formation of calcium phosphates, hydroxyapatite being the only phase to be detected. These results indicate that the phosphate-based treatment is suitable for consolidation of limestone, even when contaminated with salt.

## 1. Introduction

Consolidation of porous limestone and other carbonate substrates by phosphate-based treatments has yielded promising results in terms of efficacy, compatibility and durability [1-12]. These treatments aim at forming insoluble hydroxyapatite (HAP,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) inside the stone, by reaction of a water-based solution of diammonium hydrogen phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ , DAP) with calcium ions (deriving from the stone itself or externally added). Notably, because the precursor is applied in solution and no particles are present, even at the nanoscale, the consolidant exhibits remarkable penetration depth [3]. In addition, it is capable of successfully binding cracks formed by weathering, hence guaranteeing efficacy while maintaining good compatibility [3].

The efficacy of the treatments depends on the formation of hydroxyapatite, or, at least, calcium phosphates having low solubility, such as octacalcium phosphate ( $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ , OCP). However,



different outcomes in terms of amount, morphology and composition of phases that form as a result of the treatment could be experienced, depending on the substrate, the treating solution and procedure and on the presence of substrate contaminants, such as soluble salts [6,13].

In particular, salts in the stone might affect the outcome of consolidation by two main mechanisms:

- by blocking pores, thereby inhibiting penetration and homogeneous distribution of the consolidant in the substrate;
  - by interfering with HAP-formation reactions. This can be detrimental if soluble calcium phosphates, or other phosphate compounds (not including calcium) form instead of HAP [14-16].
- On the other hand, increased phase formation in the presence of salts has also been reported [6,13], indicating that the substrate lithotype, weathering level and surface roughness, as well as the salt type and its amount, can all have an impact on phase formation.

Salt contamination of porous limestone is very common in the field, as salt weathering is among the most frequent and severe deterioration phenomena for this lithotype [17-22]. In addition, it is rarely possible to completely remove salts from the stone, even when desalination procedures are carried out.

For these reasons, here, application of phosphate-based treatments is tested on *Globigerina* limestone, purposely contaminated by sodium sulfate crystallization cycles. The effects of the treatments on mechanical properties are investigated and the impact of the presence of sodium sulfate on phase formation is evaluated in terms of their nature, morphology and distribution.

## 2. Materials and Methods

### 2.1. Materials

Tests were carried out on *Globigerina* limestone, an organogenic limestone, mainly composed of calcite with fractions of silicates (kaolinite) and quartz [23]. Cores (5 cm in height and 2 cm in diameter) were used for all the tests, all cut from one single quarry slab.

### 2.2. Contamination by sodium sulfate crystallization cycles

Samples were contaminated by 3 cycles of sodium sulfate crystallization, 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 sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) in deionized water as recommended in the European Standard EN12370;
- 2) Drying phase (22 h): samples were dried in a ventilated oven with forced convection at 50°C;
- 3) Cooling (1 h) and measuring of weight and dynamic elastic modulus (total: 2 h).

The number and duration of the cycles were selected based on preliminary tests, with the aim of contaminating the stone with salts and cause weathering, while not causing rupture and conserving a morphology suitable for mechanical testing. To reproduce the conditions on site, where treatment of stone exhibiting abundant efflorescence is uncommon and the substrate is normally desalinated by poulticing before the application of the consolidant, the cores were desalinated after contamination, purposely leaving a fraction of the salts in the stone ("samples DESALT"). This allows evaluation of the effects of salt contamination and simulates the conditions on site, where it is often impossible to completely remove salts from the substrate, even when desalination is performed. Desalination was achieved 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.

### 2.3. Treating procedure

Two HAP-based treatments were tested that were previously developed for the consolidation and protection of limestone and marble [2,8]:

1) Treatment “3M”: a 3 M DAP solution is applied by brushing (10 strokes) followed by the application of a limewater poultice (1.7 g/L  $\text{Ca}(\text{OH})_2$ , limewater:poultice ratio 1:6). Limewater poultice is applied with the aim of providing further calcium ions to boost HAP formation and to remove possible residual DAP from the stone after treatment;

2) Treatment “0.1M”: a 0.1 M DAP solution also containing 0.1 mM  $\text{CaCl}_2$  and 10 vol% ethanol is applied, followed by the application of a 0.1 M DAP + 0.1 mM  $\text{CaCl}_2$  solution without the addition of ethanol. Both solutions are applied by brushing (10 strokes). This procedure was developed for the consolidation of marble, for which it was found that ethanol promotes HAP formation (and thus efficacy), while using lower amounts of precursors [16,24].

Ethyl silicate (ES) was also tested for comparison's sake, as it is currently the most widely used product for consolidation of Globigerina limestone. 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.

For all the procedures, stone cores were treated on the whole external surface.

#### 2.4. Post-treatment characterization

All characterizations were performed on partially desalinated (“DESALT”) cores, before and after treatment.

Mechanical properties after treatments were evaluated in terms of dynamic elastic modulus ( $E_d$ , measured by ultrasonic tests) and tensile strength ( $\sigma_T$ , measured by tensile splitting tests). Ultrasonic tests were carried out by a Matest instrument with 55KH transducers. Rubber couplants and vaseline were used to ensure proper contact between the samples and the transducers, while avoiding contamination of the sample. Briefly, an ultrasonic pulse is transmitted across the sample by piezoelectric transducers. The time required by the wave to cross the sample is recorded, that is linked to dynamic elastic modulus by the equation:  $E_d = \rho v^2$ ,  $v$  being the ultrasonic pulse velocity. Tensile splitting test consists in subjecting cylindrical specimens to compression along two lines parallel to the axis.  $\sigma_T$  is calculated with the equation  $\sigma_T = 2P/(\pi DL)$ ,  $P$  being the maximum load,  $D$  the diameter and  $L$  the length of the cylindrical specimens, respectively. Three samples were taken for each consolidation treatment (3M, 0.1M and ES) and for the untreated reference (UT). Variations in dynamic elastic modulus and tensile strength caused by the treatments were also calculated, according to the formulas:

$$\Delta E_d = (E_{d,\text{after treatment}} - E_{d,\text{before treatment}}) / E_{d,\text{after treatment}}; \Delta \sigma_T = (\sigma_{T,\text{after treatment}} - \sigma_{T,\text{before treatment}}) / \sigma_{T,\text{after treatment}}$$

Salt content after salt contamination, desalination and consolidation treatment was evaluated by ion chromatography (IC), performed on the ground stone after salt extraction and filtering. Salt extraction was performed by grinding the samples and boiling the obtained powder in deionized water, to favor solubilization of the salts. Samples ( $\sim 5 \times 5 \times 5 \text{ mm}^3$ ) were collected from the tops of the cores (i.e. the area opposite to that immersed in the sodium sulfate solution), where salt concentration is expected to be maximal.

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

Phase formation after 3M and 0.1M treatments was examined by FT-IR to verify which phases form in the presence of salt contamination. FT-IR (Perkin Elmer Spectrum 2, ATR mode, resolution  $2 \text{ cm}^{-1}$ , 32 scans) was performed on ground samples, to maximize the intensity of the bands. Powder was collected from the surface of the samples (0-2 mm depth). FT-IR was also performed on ES-treated samples to verify whether the presence of salts interferes with ES curing, according to the very same procedure.

### 3. Results

As a result of salt contamination and desalination, sulfate concentrations of 1.4 wt% and 0.3 wt% are achieved, respectively.

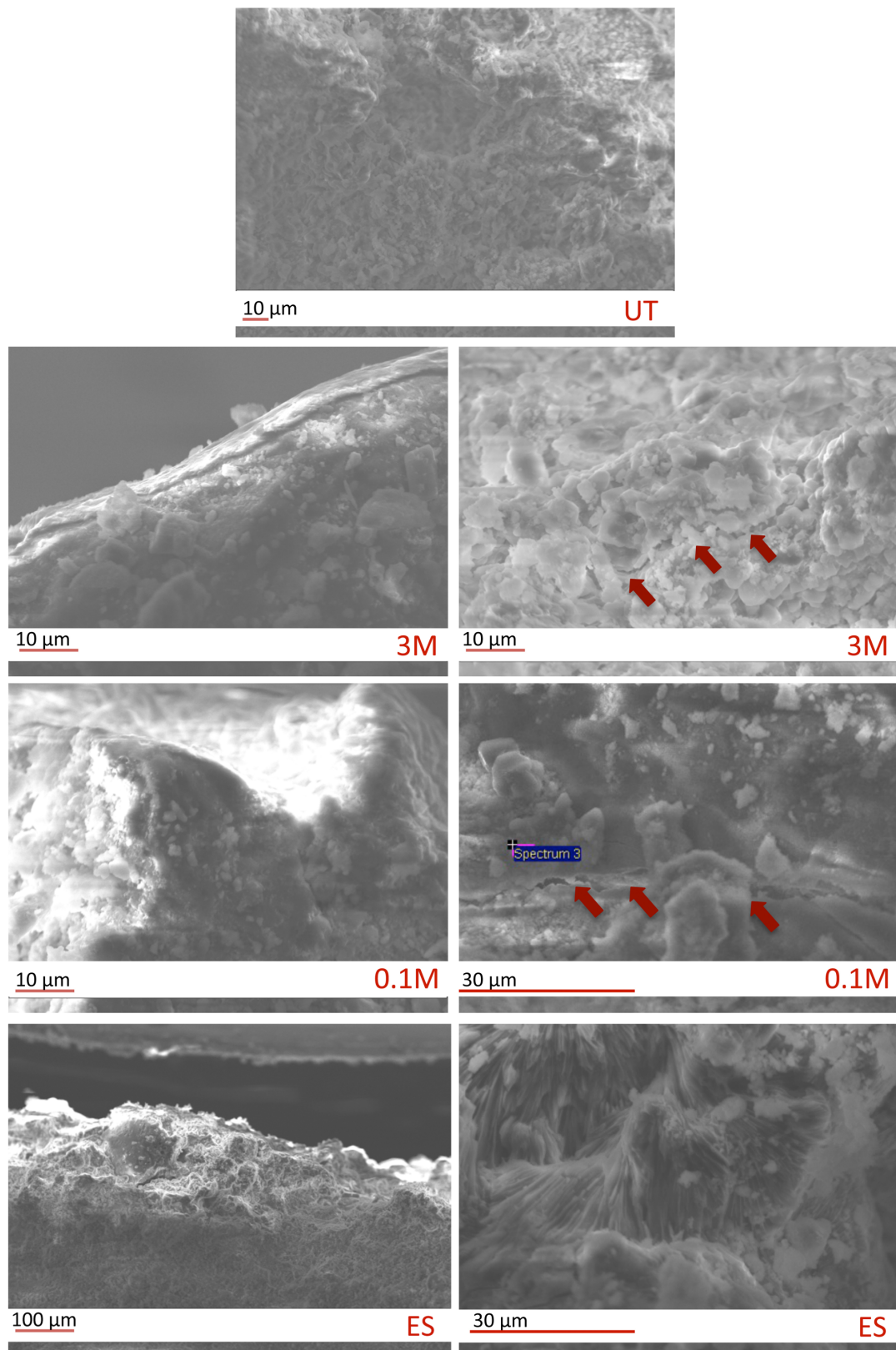
Dynamic elastic modulus and tensile strength after salt contamination, desalination and consolidation are reported in Table 1. HAP-based treatments cause a minor change in dynamic elastic modulus, but a significant increase in tensile strength, indicating good efficacy for both treatments. The different behavior in terms of  $E_d$  and  $\sigma_T$  can be explained as follows.  $\sigma_T$  is essentially determined by the capability of the consolidant to increase stone cohesion by bridging cracks caused by weathering. For the consolidant to be effective, it must seal at least the tip of the cracks caused by weathering, so as to bind the surfaces together and prevent them from propagating through the boundary. However, some porosity in the binder can be beneficial, because it allows volume variations in calcite grains from temperature changes to be accommodated without causing stress [25].  $E_d$ , on the other hand, is raised by pore occlusion and by large amounts of precipitates, even if they don't bind strongly to the substrate. As a consequence, if the consolidant bridges cracks without significantly filling them, the effect can be much more visible in terms of  $\sigma_T$  than it is in terms of  $E_d$ . ES, in contrast, causes a significant increase in terms of  $E_d$  and, especially,  $\sigma_T$ . Such a large increase in tensile strength can cause over-strengthening, as it is generally believed that increases lower than +50% are to be preferred [26,27]. In fact, the final dynamic elastic modulus and tensile strength are significantly higher than those of unweathered stone ( $E_d = 14.2$  GPa,  $\sigma_T = 3.1$  MPa). Both treatments with DAP exhibit similar increases in both dynamic elastic modulus and tensile strength, indicating that the treatments have similar performance despite significant differences in the amount of DAP used as a precursor, pointing out the efficacy of the addition of ethanol to the treating solution.

**Table 1. Mechanical properties after treatment.**

	$E_d$ (GPa)	$\Delta E_d$ (GPa)	$\sigma_T$ (MPa)	$\Delta \sigma_T$ (MPa)
UT	$12.8 \pm 0.2$	/	$2.3 \pm 0.4$	/
3M	$13.1 \pm 0.1$	+2%	$3.3 \pm 0.2$	+ 39%
0.1M	$13.1 \pm 0.2$	+2%	$3.3 \pm 0.3$	+ 40%
ES	$15.7 \pm 0.1$	+23%	$5.5 \pm 0.9$	+ 134%

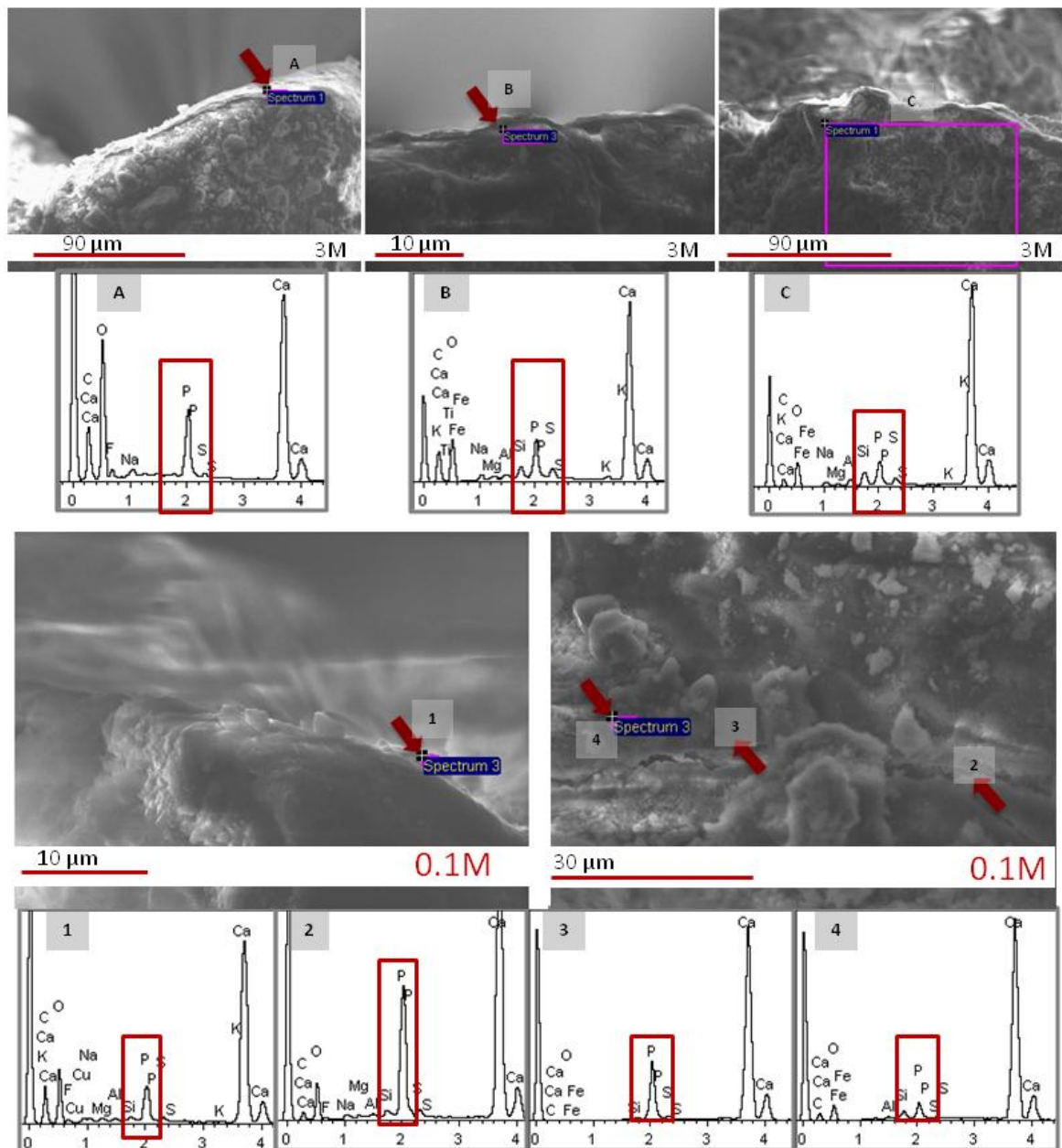
SEM images of samples 3M and 0.1M (Figure 1) show that phosphate phases formed both on the exterior surface in the form of a coating (~1-2  $\mu\text{m}$  thick) and in the interior of the samples. This indicates that the presence of the salt did not prevent the penetration and curing of the consolidant due to pore blocking.

Phase formation (Figures 1 and 2) is more abundant for samples treated by 3M compared with 0.1M, which is consistent with the much higher amount of precursor used. However, for both treatments, the phosphate phases that form are capable of bridging cracks caused by weathering, including in the areas far from the surfaces (see red arrows in Figure 1). This explains the similar increase in the mechanical properties caused by the two treatments, in spite of the different amount of phases formed. In ES-treated samples, agglomerates of salts, probably incorporated in the glass network constituted by cured ethyl silicate, are visible across the whole sample. This indicates that significant pore clogging occurs, which can be responsible for the large increase in mechanical properties. For this reason, evaluation of compatibility and durability of the treatments is in progress.



**Figure 1.** SEM images of cross sections of treated samples, at the surface (left column) and at a depth  $\sim 1$  cm from the treated surface (right column). Red arrows indicate cracks bridged by HAP.

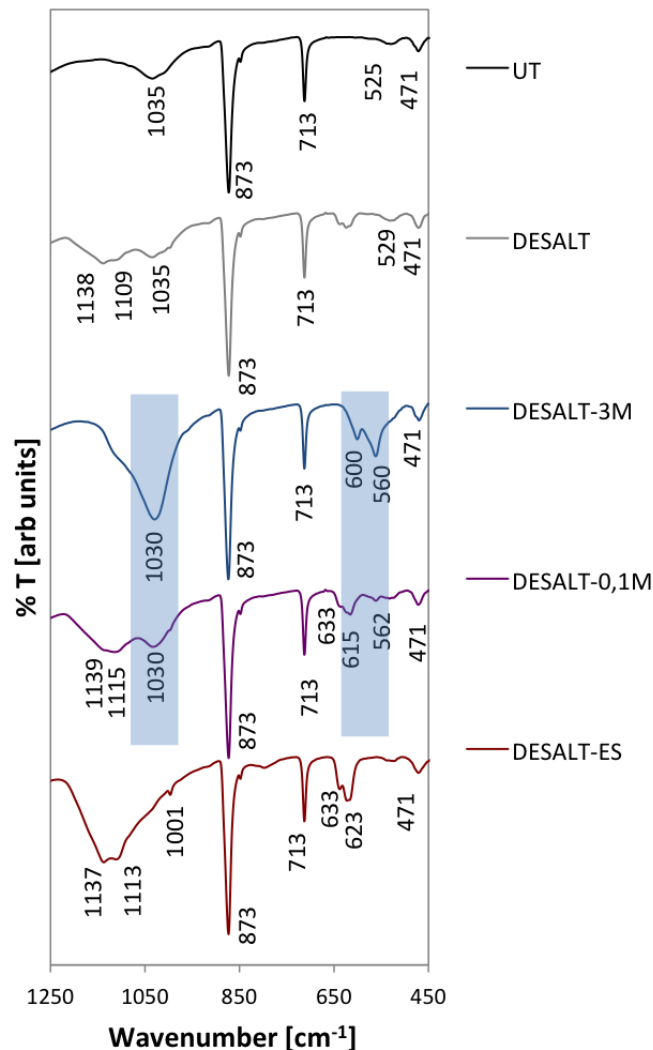




**Figure 2:** EDS spectra of 3M and 0.1M samples. Red arrows indicate points where acquisition was performed. As can be seen by the spectra, abundant formation of phosphate phases can be detected on the exterior surface and around cracks caused by weathering.

FT-IR spectra are reported in Figure 3. Bands detected are characteristic of calcite ( $873, 712, 472 \text{ cm}^{-1}$ ) [28,29] and kaolinite ( $1035, 525, 470 \text{ cm}^{-1}$ ) [29,30] of Globigerina limestone, sodium sulfate ( $1138, 1110 \text{ cm}^{-1}$ ) and either hydroxyapatite ( $1030, 600, 560 \text{ cm}^{-1}$ ) [28,31] or ethyl silicate ( $1080, 1001 \text{ cm}^{-1}$ ) [32-34]. FT-IR data indicate that all phosphate phases, formed as a result of 0.1M and 3M treatments and observed by SEM/EDS, correspond to HAP. No bands characteristic of other calcium phosphates phases or soluble phases are detected. This indicates that the presence of salts did not interfere with HAP nucleation by causing the formation of less stable compounds, which would have been detrimental for the treatment success and could represent an issue for the application of the consolidant on site. This was confirmed by IC results, which indicate that no soluble phosphates were extracted when treated samples were crushed and rinsed with water. Phase formation is more abundant

for treatment 3M compared to 0.1M, as already shown by SEM. Samples 3M also exhibit a negligible content of residual sodium sulfate, which was successfully removed by the limewater poultice, together with unreacted DAP. This is confirmed by ion chromatography, indicating a much lower sulfate concentration for samples 3M (0.07 wt% sulfate vs. 0.31 wt% for ES and 0.1M). The possibility of achieving desalination during consolidation can be regarded as a further advantage of the 3M treatment. Residual salt content is greatest in samples ES, for which the main bands are those of sodium sulfate.



**Figure 3.** FT-IR spectra of salt contaminated samples. Bands characteristic of HAP (1030, 600, 560 cm⁻¹) are highlighted in blue.

#### 4. Conclusions

The application of two HAP-based treatments was tested on *Globigerina* limestone contaminated by sodium sulfate. The following conclusions can be derived:

- The presence of salts in the stone does not prevent penetration of the HAP-based consolidants, nor cause formation of soluble phases. In fact, HAP is the only phase to form.
- Because no formation of soluble phases, nor insufficient or inhomogeneous HAP distribution were found, even for high levels of contamination, it can be concluded that the treatments can be safely applied to sodium sulfate-containing substrates.



- 0.1M and 3M treatments result in a good increase in stone tensile strength as they lead to the formation of HAP that binds cracks caused by weathering. Both treatments have comparable efficacy, even though 3M results in more abundant calcium phosphate formation, as treatment 0.1M still guarantees effective crack-sealing.
- ES provides greater, but possibly excessive, increases in  $E_d$  and  $\sigma_T$ . Durability tests will be carried out to better evaluate the long-term performance of all treatments.

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