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ARTICLE

Protecting white Carrara marble with organophosphorus salts: case study of ammonium hydrogen phenylphosphonate

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Ammonium hydrogen phenylphosphonate (**1**) was investigated as a novel agent for the protection and consolidation of carbonate stone substrates. Compound **1** quantitatively reacted with calcium carbonate to give calcium phenylphosphonate dihydrate (**2**), which was characterized by spectroscopic and microanalytic means and whose structure was solved using 3D electron diffraction. Compound **1** was applied to artificially weathered Statuario white Carrara marble mock-ups through immersion, brushing, and spraying techniques, and its effect on structural, hygric, and mechanical properties was evaluated by means of a comprehensive set of techniques including X-ray diffraction, ultrasonic velocity measurements, colorimetry, porosimetry, and contact angle determinations. While the application of well-known diammonium hydrogen phosphate (DAP) on carbonate stones results in the deposition of non-stoichiometric hydroxyapatite (HAP), the treatment with compound **1** results in the formation of a thin, homogeneous coating of stoichiometric compound **2** that enhances cohesion, reduces porosity, and improves mechanical resistance, restoring the marble properties to near-pristine conditions. The treatment induces only minimal chromatic changes, making it a promising solution for the conservation of stone cultural heritage.

Introduction

Marbles and limestones are among the most fascinating materials due to their historical use in sculpture and architecture. However, these natural calcareous stones are prone to deterioration caused by both natural and human-induced factors, such as climate conditions and exposure to pollutants.[1–6] A major cause of degradation is represented by the dissolution of calcite in water[7] ($K_{sp} = 3.27 \cdot 10^{-9}$ at 25 °C).[8] Acid rain in polluted urban environments increases the stone dissolution as well as the process of sulfation, while salt crystallization and particulate deposition further harm the carbonate structure, particularly in outdoor archaeologic and heritage sites. Several organic[9–12] and inorganic compounds[13–17] have been studied for their ability to protect and/or consolidate carbonate matrices. Organic molecular compounds are generally easy to apply and provide immediate beneficial effects, but they are difficult to remove, have limited durability, and can cause irreversible changes to the original colour of marble.[13] In contrast, inorganic and organic salts are more compatible with the carbonate matrix of the stone, offering several advantages, including better solubility, environmental friendliness, low cost, and ease of preparation. For instance, the reinforcement of the carbonate microstructure can be achieved by applying $CaCO_3$, which can be deposited on the stone under appropriate conditions.[18] *In situ* carbonation can be facilitated by using suitable precursors such as barium and calcium hydroxides, as well as nanolime.[1,19–22] Biomineralization represents a further approach for the deposition of a neo-formed calcium carbonate layer.[18,23–25] Since the mid-1980s, a promising approach involving the artificial coating of calcium oxalate (CaOx) using an appropriate precursor has been developed.[26] Ammonium oxalate, $(NH_4)_2(C_2O_4)$ (AmOx) reacts with calcium carbonate to afford calcium oxalate crystalline phases $CaC_2O_4{\cdot}nH_2O$ (reaction 1), in their monohydrate (whewellite; n = 1) and dihydrate (weddellite; n = 2) forms (solubility product $K_{sp} = 2.0{\cdot}10^{-9}$ and $3.8{\cdot}10^{-9}$ at 25 °C, respectively).[27,28]

$$CaCO_3 + (NH_4)_2(C_2O_4) + (n\text{–}1)\ H_2O \longrightarrow CaC_2O_4{\cdot}nH_2O + 2\ NH_3 + CO_2 \qquad (1)$$

However, the resulting CaOx layer on treated marble samples is typically not thicker than a few tens of micrometres, also depending on the application method.[26,29] This limited thickness

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is due to several factors, including the low concentration of AmOx in aqueous solutions (maximum 0.4 mol·L^{-1}, 5% w/w)[30] and the limited ability of water to penetrate deeply into the carbonate matrix, especially for poorly permeable stones, such as marble (generally showing a total porosity < 0.5%). During the past decade, in an effort to overcome these intrinsic limitations of AmOx, several derivatives have been tested, including ammonium monoesters and monoamides (oxamates) of oxalic acid, which can form alternative insoluble calcium salts, such as in the case of ammonium oxamate[31] and *N*-phenyloxamate,[32] or behave as precursors of the oxalate anion,[33] as observed in the case of the treatments with ammonium methyl- and ethyl-oxalate,[31,34] and *N*-(pyridin-2-yl)oxamate.[35]

Among inorganic salts, promising results have been obtained using diammonium hydrogen phosphate [DAP, $(NH_4)_2HPO_4$], a precursor of hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$], as a consolidating agent for carbonate stones.[36,37] However, the treatment of calcium carbonate substrates with DAP results in the formation of non-stoichiometric products $Ca_{10}(PO_4,CO_3)_6(OH,CO_3)$, since carbonate ions can replace both OH^- and PO_4^{3-} anions.[38] Along with the main insoluble reaction products, other calcium phosphates, such as $Ca_8(HPO_4)_2(PO_4)_4{\cdot}5H_2O$[39] and $CaHPO_4{\cdot}2H_2O$ (brushite),[40,41] have been observed, the latter being particularly undesirable[42] due to its higher solubility compared to calcite ($K_{sp} = 2.5{\cdot}10^{-7}$).[43,44] In addition, the formation of the pyrophosphate anion has been reported in systems with free Ca^{2+} ions.[45] The variability in the stoichiometry of the deposition on the surface can be related to the similar size of the anions, which are easily interchanged in the crystal lattice of the neo-formed depositions. In order to minimise the presence of byproducts, the tuning of a variety of parameters have been tested including the concentration of the DAP solution, the acidity of the solution,[46] the duration of the treatment,[36,47,48] the addition of external ions,[47,49] including exogenic Ca^{2+},[50] and the modulation of the polarity of the solution by using solvent mixtures.[51] Notably, different treatment methods, regardless of the nature of the adopted consolidant, can lead to different results and help modulate the effect of the deposition on the stone surface.[52,53]

The synthetic functionalization of the phosphate anion offers a potential strategy to reduce the anion interchange, hence obtaining stoichiometric reproducible deposition, provided that the starting ammonium salt is soluble in water and the calcium salt is less soluble than calcite. Substituted organophosphorus anions include organophosphates, phosphonates, and phosphinates (Chart 1).[54]

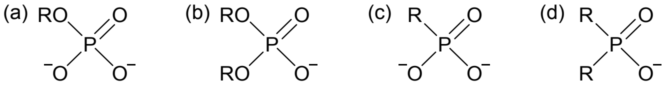

Chart 1. Organophosphorus anions: substituted phosphate (a, b), phosphonate (c), and phosphinate (d). R = alkyl or aryl substituents.

In this work, the ammonium salt of the bulky hydrogen phenylphosphonate anion has been tested as a potential agent for the conservative treatment of carbonate stones, starting with the case study of Statuario white Carrara marble.

Results and discussion

Synthesis and characterization

Inorganic salts suitable for the treatment of calcium carbonate substrates must satisfy several criteria, including (i) a large solubility in water, allowing for a variety of treatment methods, ranging from immersion to spraying;[52,53,55] (ii) the resulting calcium derivative, acting as surface protective and/or consolidating agent, must be poorly soluble, featuring a solubility product ideally comparable to that of calcite ($K_{sp} < 3.27{\cdot}10^{-9}$);[8] (iii) the reaction byproducts must be water-soluble or volatile. In this context, ammonium is a suitable cation in salts containing substituted oxalate, oxamate and phosphate anions, since it releases ammonia and carbon dioxide when reacted with the carbonate anion (see reaction 1 for AmOx).

With the purpose of improving the performance and overcoming the limitations of DAP as an inorganic salt for the treatment of calcium carbonate substrates, we have turned to increase the hindrance of the anion, preserving the solubility of its ammonium salt, by passing from the phosphate to the phenylphosphonate anion (R = Ph in Chart 1c).

The reaction of phenylphosphonic acid with ammonium carbonate in water quantitatively affords ammonium hydrogen phenylphosphonate (AmHPP, **1**), according to reaction 2:

$$2H_2PhPO_3 + (NH_4)_2CO_3 \rightarrow 2(NH_4)(HPhPO_3) + CO_2 + H_2O \qquad (2)$$

Compound **1**, isolated as white crystals, was characterised by microanalytical means (melting point determination and elemental analysis), spectroscopic (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}-NMR; FT-IR; UV-Vis), and diffractometric techniques (Table S1, Figures S1–S6 in ESI). A DMSO-d$_6$ solution of compound **1** displays a single signal in the ^{31}P{^{1}H}-NMR spectrum at 8.40 ppm (10.97 ppm in the solid-state CP-MAS ^{13}P{^{1}H}-NMR spectrum), and the expected two multiplets, centred at 7.28 and 7.62 ppm (Figure S2 in ESI), slightly downfield-shifted compared to the starting acid, in the ^{1}H-NMR spectrum (Figure S1 in ESI). The powder X-ray diffractogram (PXRD) is in good agreement with the calculated PXRD pattern from the single-crystal X-ray diffraction (SC-XRD) data reported previously (Figure S5 in ESI).[56,57] The lack of diffraction peaks of the starting acid in the PXRD diffractogram recorded for compound **1**, is consistent with a complete conversion of the starting acid. The solubility of compound **1** in water was determined spectrophotometrically to be 0.93 mol·L^{-1}, corresponding to 16% w/w. Thus, despite the functionalization of the phosphonate anion with a bulky phenyl group, the solubility of compound **1** remains sufficiently high to obtain relatively concentrated solutions (∼0.9 mol·L^{-1}).

Reactivity towards $CaCO_3$ powder

As mentioned above, one of the main drawbacks of using DAP as a consolidant is the formation of HAP and other secondary phases on stone surfaces. This strongly depends on pH and can lead to metastable phases such as brushite and other soluble crystalline phases.[40,41] To assess the reactivity of ammonium phenylphosphonate towards carbonate-based stone surfaces, compound **1** and $CaCO_3$ powder were made to react in water in 2:1 molar ratio under continuous stirring at ambient temperature (23 ± 2°C) for 24 hours. The powder diffractograms collected on the filtered microcrystalline insoluble fraction (**2**) did not show the peaks of compound **1** (Figure S5 in ESI). The

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CP-MAS $^{31}P\{^1H\}$-NMR spectrum recorded on compound **2** displayed a single signal at 13.28 ppm, being slightly upfield shifted compared to that of compound **1** (Figure S6 in ESI). The CP-MAS $^{13}C\{^1H\}$ shows the signals of the phenyl substituents in compound **2** slightly upfield-shifted with respect to those of compound **1**. Thermogravimetric analysis (TGA) under nitrogen flow revealed a weight loss of humidity in the range 30–90 °C (7.8%), a loss of crystallization water (7.4%) in the range 90.5–193.8 °C, followed by a weight loss attributed to the organic fraction in the range 193–769 °C (30.3%; Figure S7 in ESI). The analysis of the differential scanning calorimetry (DSC) curve demonstrated all the processes to be endothermic (Figure S8 in ESI). The elemental analysis carried out on the same solid excluded the presence of the ammonium cation and was consistent with compound **2** being calcium phenylphosphonate dihydrate, formed according to reaction 3:

$$(NH_4)(HPhPO_3) + CaCO_3 + H_2O \rightarrow Ca(PhPO_3)\cdot 2H_2O + NH_3 + CO_2 \qquad (3)$$

3D electron diffraction (3D ED)

3D Electron Diffraction (3D ED) has emerged as a powerful technique for the structural elucidation of small molecules, providing atomic resolution from crystals that are too small for conventional Single-Crystal X-Ray Diffraction (SC-XRD) analysis.[58,59] This is particularly relevant for materials where crystal growth is the main bottleneck due to the significant challenge of obtaining crystals of sufficient size for traditional X-ray crystallography. 3D ED demonstrated its potential in fields such as drug discovery, metal-organic frameworks, and materials science.[60] In this context, materials with extremely low solubility product values pose a significant challenge for crystallization, and 3D ED offers a valuable alternative for their structural characterization.

The very low solubility of compound **2** prevented the growth of single-crystals suitable for SC-XRD analysis. However, the solid directly isolated from the reaction of compound **1** and $CaCO_3$ powder (see above) proved to be suitable for crystal structure determination using 3D ED. This is, to the best of our knowledge, the first example of a structural characterization carried out by 3D ED in the context of cultural heritage conservation, highlighting the application of this sough-after technique for the study of materials relevant to this field.[61] According to 3D ED analysis, compound **2**, formulated as $Ca(PhPO_3)\cdot 2H_2O$, in perfect agreement with elemental analysis and TGA measurements (see above), crystallizes in the orthorhombic space group *Pbca*. The asymmetric unit comprises a single calcium(II) ion, a phenylphosphonato dianion, and two independent water molecules, one of which is coordinated to the calcium ion (Figure S9 and Table S2 in ESI). The Ca^{2+} ion exhibits a coordination number 7, with five positions occupied by symmetry-related phenylphosphonate oxygen atoms (O1–O3) and the remaining two by water molecules (O4; Figure 1). The crystal packing consists of a 2D-layered network in which calcium nodes are interconnected by phenylphosphonate moieties and water molecules, with the phenyl rings protruding out of the layers, which extend parallel to the *bc* plane (Figure 2).

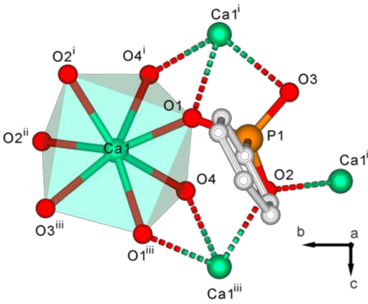

Figure 1. View of the crystal structure of compound **2** along the a-axis. Symmetry codes: ^{i} = +x, 3/2−y, −1/2+z; ^{ii} = 1−x, 1/2+y, 3/2−z; ^{iii} = +x, 3/2−y, 1/2+z; ^{iv} = 1−x, −1/2+y, 3/2−z.

Water molecules (O5, Figure S9 in ESI) fill the interlayer spaces left by the partially interdigitated phenyl rings (Figure 2a). In Figure 2b, the predicted crystal morphology obtained using the Bravais Friedel Donnay Harker (BFDH) method implemented in Mercury is depicted.[62] Finally, the structure model was refined against 3D ED data using the Rietveld method, (Figure S10 in ESI), confirming that compound **2** was the only crystalline phase present.

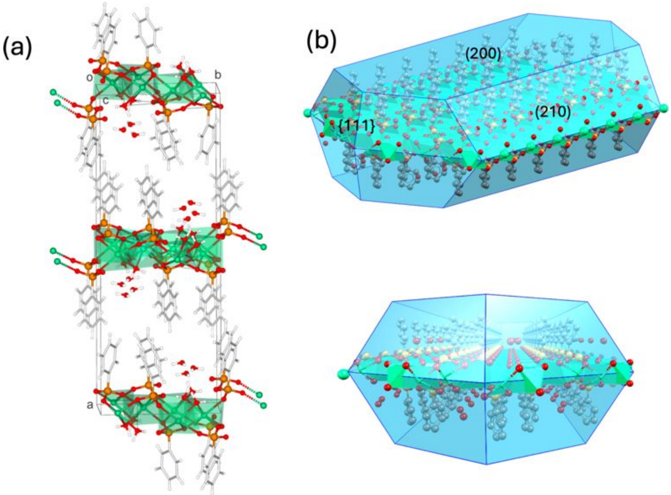

Figure 2. (a) Crystal packing seen along the c-axis; (b) predicted crystal morphology for compound **2**.

Assays with Statuario white Carrara marble fragments

White marble specimens (prisms 2.0 × 2.0 × 8.0 cm: cubes 2.0 × 2.0 × 2.0 cm; fragments ~1 cm^3) were artificially weathered by a slow heating process (from r.t. to 300 °C, 2.3 °C min^{-1}), followed by a static heating (300 °C, 5 h), and subsequent cooling to r.t. (4.6 °C·min^{-1}; Figure S11 in ESI). Due to the intrinsic anisotropy of the structure of marble, the treatment was applied twice, by turning over the stone mock-ups before the second application. The degree of weathering was evaluated by measuring the ultrasonic speed within the stone sample, which was found to decrease from 2.8 km·s^{-1} in the pristine specimens to 1.2 km·s^{-1} in the weathered specimens. The weathering process therefore led the samples to a condition of severe risk of structural breakdown (class IV

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according to Köhler classification),[63,64] without altering the mineralogic composition of the samples. Overall, the thermal cycle induced a general degradation of the dynamic and structural bulk and surface features as compared to the intact sample reminiscent of that displayed by naturally weathered marble (Table 1).[65] Accordingly, the Scanning Electron Microscopy (SEM) analysis on the weathered marble samples revealed microcracks around the edges of the specimens and a detachment of boundary calcite grains (Figure S12 in ESI).

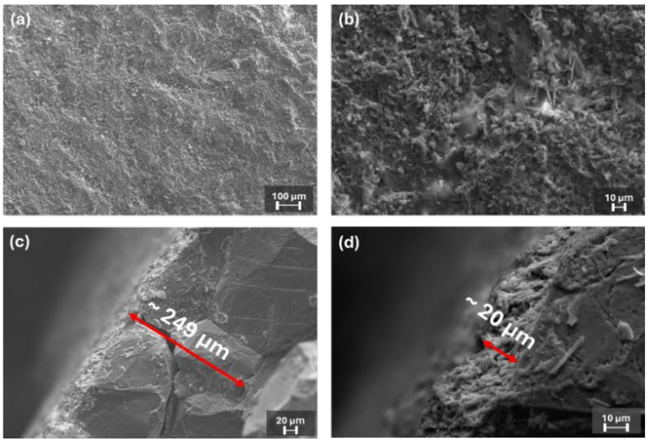

Figure 3. SEM images of weathered Carrara marble immersion treated with a 5% w/w solution of compound **1**. (a-b) mock-up surface, (c) cross-section, penetration width, (d) cross-section, film width.

The thermally weathered samples were treated with a 5.0% w/w (0.30 mol·L^{-1}) aqueous solution of compound **1** (pH = 5.0 at r.t.; conductivity 15.3 ± 0.1 mS·cm^{-1}) using different application techniques: (i) 24 h immersion in a static bath, following the protocol previously adopted for oxalate and oxamate derivatives;[31–35] (ii) brushing (10 brushstrokes); and (iii) spraying by a pressure nebulizer up to rejection (from a controlled distance of 20 cm; flow rate of 16.4(8) mL·min^{-1}). The amount of deposited compound **2** was evaluated on three of the largest mock-ups (4.5 × 4.5 × 2.0 cm), weighed before and after the application of each consolidating treatment. The spraying and brushing technique proved to be the most effective (3.1(5) and 3(1) mg·cm^{-2}, respectively), followed by the immersion treatment (1.3(4) mg·cm^{-2}).

The marble specimens were analysed before and after the treatments (Table 1, Table S1, Figures S12–S18 in ESI) by means of a comprehensive set of techniques, namely Powder X-ray Diffraction (PXRD), colorimetry, surface roughness determination, ultrasonic propagation, water saturation measurements (including under pressure), Helium pycnometry, mercury intrusion porosimetry (MIP), shore scale hardness (C and D), pull-of test, liquid and vapour water permeability, capillary uptake, determination of drying properties, optical microscopy (OM) and SEM. Helium pycnometry and MIP require small irregular fragments (∼1 cm^3, ∼3 g), samples that were not suitable for the brushing and spraying treatments.

SEM images of the marble samples treated by immersion revealed a uniform coating of small crystals a few µm in size, distributed across the surfaces and localized along the fractures and grain boundaries (Figure 3). SEM and OM images of sections of the treated samples clearly showed a coating 10–15 µm thick (Figures 3 and S13 in ESI). The fine coating acts as a cement between disjointed grains with an efficient consolidation, reaching a penetration depth of a few hundred of µm. PXRD analyses carried out directly on the treated surfaces confirmed that compound **2** is the only crystalline component of the coating (Figure S14 in ESI).

Since the mass of compound **2** penetrated in the marble texture is small (lower than 0.1% with respect to calcite), SEM-EDS measurements for determining the phosphorus content could not be used to evaluate the penetration depth, which was estimated visually by OM. Visual analysis of the surfaces and cross-section of the mock-ups treated by brushing and spraying showed a coating thickness of about 20 and 15 µm, and a penetration depth as large as about 150 and 270 µm, respectively (Figure S15 in ESI).

Since thermal weathering did not induce a complex internal porous structure, these results suggest that all the treatment protocols led to the deposition of consolidating phases, even with the reduced porosity of the marble mock-ups used in this study. Therefore, better results can be expected for the treatments of stone featuring a higher porosity, such as real marble artifacts from authentic restoration sites, or different lithotypes, for example biomicrites[31–34] and carbonate sandstones.

A comparison of the surface roughness measured on the same samples before and after the weathering, and after the consolidation treatments shown that the mean roughness depth Rz increased by up to +36% as a result of the weathering thermal cycle. However, Rz decreased sensibly after all the treatments, restoring the roughness approximately to the value of the pristine samples (Table 1). In addition, the treated samples exhibited an improved cohesion, as evidenced by a marked increase in the ultrasonic velocity v_{uts} and the dynamic elastic index E_d, partially restoring, and in the case of the brush application, even improving the properties of the pristine marble samples (Table 1). Accordingly, in the case of the immersion treatment, the average pore size of treated marble, determined by MIP,[66,67] was reduced as compared to both untreated specimens (Figure S16 in ESI). Notably, the increased porosity determined by MIP after the treatments can be tentatively attributed to a novel secondary porosity, as previously observed in the case of the treatment with ammonium *N*-phenyloxamate.[32] This can be ascribed to the neo-deposited layers, resulting in a new unimodal pore distribution, with an average size of approximately 1.5 µm. This addition does not significantly modify the average pore size of the treated mock-ups with respect to the pristine marble, ensuring the preservation of the natural porosity of the stone.

Contact angle measurements clearly shown the effects of surface degradation caused by weathering and subsequent restoration following treatment with compound **1**.

Untreated marble displayed average contact angle of water ϑ_C^{2s} = 44(12)° measured 2 s after the droplet deposition (Table 1 and Figure 4). This angle was remarkably lower after a longer delay. Weathered samples exhibited minimal contact angles ϑ_C^{2s} (about 10°), and a measurement with a delay larger than 2 s was not possible. Samples treated by immersion shown a ϑ_C^{2s} value restored to about 50°. While this value is well below 90°, a conventional threshold between hydrophilic and hydrophobic behaviour, it indicates a lower wettability of the treated marble surface compared to the pristine non-weathered specimens. Worthy of note, these results obtained on specimens treated by immersion are very close to those reported for marble samples treated by brushing with DAP and nanolime (ϑ_C^{5s} = 55±1 and 49±1°, respectively).[68,69]

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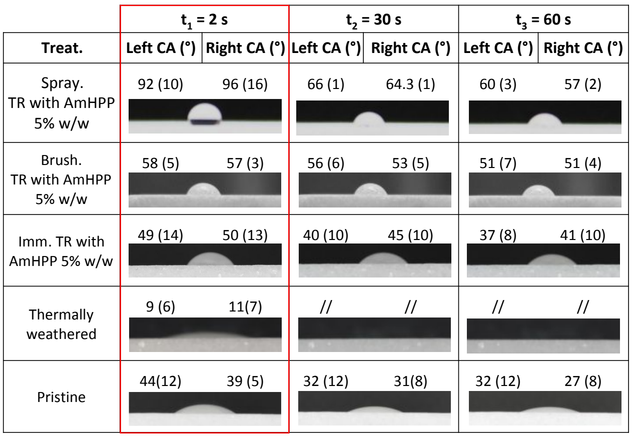

	t_1 = 2 s		t_2 = 30 s		t_3 = 60 s	
Treat.	Left CA (°)	Right CA (°)	Left CA (°)	Right CA (°)	Left CA (°)	Right CA (°)
Spray. TR with AmHPP 5% w/w	92 (10)	96 (16)	66 (1)	64.3 (1)	60 (3)	57 (2)
Brush. TR with AmHPP 5% w/w	58 (5)	57 (3)	56 (6)	53 (5)	51 (7)	51 (4)
Imm. TR with AmHPP 5% w/w	49 (14)	50 (13)	40 (10)	45 (10)	37 (8)	41 (10)
Thermally weathered	9 (6)	11(7)	//	//	//	//
Pristine	44(12)	39 (5)	32 (12)	31(8)	32 (12)	27 (8)

Figure 4. Contact angle measurements performed on both untreated and treated stone mock-ups. For each treatment, three analyses are shown at 2, 30 and 60 s after the deposition of the water drop.

When the solution of compound **1** was applied by brushing and spraying, larger values of contact angle were obtained (Table 1 and Figure 4), reaching, in the case of the latter, the hydrophobization of the surface, thus potentially increasing the resistance towards chemical and biological agents. These results suggest that the brushing and spraying application methods produce a more homogeneous covering layer as compared to immersion.

The effects induced by the consolidation treatment were further elucidated by investigating the variation in the water-transport properties. The increased rugosity and microfractures between the calcite grains induced by the thermal weathering (Figure S12 in ESI) are reflected in an increase both in speed and amount of water sorbed during the capillary uptake. On the other hand, after the treatments, a slight decrease in the water capillary uptake speed was observed, as shown by the capillary absorption coefficient CA. The drying curves shown no significant difference after the application of the consolidant (Table 1 and Figure S17 in ESI). This can be tentatively attributed to the new micrometric secondary porosity obtained with the deposition of calcium phenylphosphonate dihydrate, evidenced by MIP measurements (see above). The indices derived from the sorption curves were compared with the results of a water saturation test performed under pressure (Table 1). The increase in the material porosity after the weathering process confirms the results obtained with from MIP measurements, while the recovery of the skeletal density to a value comparable with to that of the pristine marble ensures the preservation of the normal density of calcite (2.71 g·cm^{-3}).[70]

To better understand the effect of the new deposited phases on the material permeability, liquid water permeability index and vapour water permeability resistance were determined for all the mock-ups, before and after the artificial weathering and after the consolidating treatments (Table 1). The indices show an increase in water permeability after the weathering, which was reduced following the application of the compound **1**, resulting in the formation of a coating of compound **2**.

The variations in the chromatic indices $\Delta E_{CIELAB1976}$ and $\Delta E_{CIELAB2000}$ between the treated and the original untreated samples were evaluated, obtaining values well below the threshold value of 3 (Table 1). This indicates that the treatment did not produce significant colour changes perceptible to the naked eye (Figure S18 in ESI).[40,71,72]

Finally, the mechanical resistance of the deposited layer of compound **2** was tested by means of surface durimetry (shore C and D scale), followed by a measure of the cohesion of Carrara marble with a pull-off test (determination of the tensile strength, f_h; Table 1). The results indicated a substantial improvement in the mechanical resistance of the material following the consolidation treatment, with immersion treatment almost restoring the property of the pristine marble, while the brushing and spraying applications ensure even better consolidating effects, as confirmed by the higher values of hardness and tensile strength.

Accelerated aging

Mock–ups treated with a 5.0% w/w (0.3 mol·L^{-1}) solution of compound **2** were subjected to different accelerated aging tests. Thermal shock (T–S) tests were carried out according to the EN 140666:2014 standard method (Figure S19 and Table S3 in ESI).[73] Subsequently, freeze–thaw (F–T) resistance experiments were carried out (Figure S19 and Table S3 in ESI), on another set of mock–ups, as specified in EN 12371:2010.[74] Both methodologies involve a consequent temporary change in the grain size dimension, but in the case of F–T tests the formation of ice inside the fractures or pores of the material can be observed. The outcome of the two thermal shock experiments was monitored with a preliminary visual inspection and determination of the Young elastic module by means of ultrasonic propagation speed. For both treatments only very minor damages of the mock–ups was detected (score 1 according to the F–T standard),[74] which did not compromise the integrity of the specimens (Figure S19 in ESI). The loss in elastic module (Table S3 in ESI) in the case of the T–S tests was significative only for the pristine and thermally weathered specimens. On the contrary, in the case of F–T a significative decrease in the elastic modulus was observed only for the pristine material, suggesting that the fractures of the thermally weathered specimens were already wide enough not to induce an internal compression of the material during the formation of ice. In general, whatever the treatment method, the mock–ups consolidated with compound **1** showed a Young elastic modulus always higher than the that of thermally weathered specimens, and in most cases even higher than pristine specimens, after both T–S and F–T tests.

Moreover, the resistance to acid rains was tested following the same methodology reported in literature for mock–ups treated with DAP.[7,49,75] While both HNO_3 and HCl can be used for this test, the former was preferred, as the latter causes the lowest ion exchange with calcium phosphates/phosphonate salts (e.g. HAP).[76] The mock–ups (Figure S20 in ESI) were visually inspected by SEM before and after the treatments (Figures S21 and S22 in ESI, respectively), consisting in keeping the samples immersed for 24 h in a solution at pH = 5 (average harsher condition of pH in European rains).[49] The effect of the acid treatment was also evaluated by ultrasonic propagation speed measurement, colourimetry, rugosimetry, and superficial hardness (Table S4 in ESI). In the case of the pristine and the thermally weathered mock–ups SEM imaging showed the effect of acid washing on carbonate rocks, with the clear dissolution of the material (Figure S23a and S23b in ESI). Accordingly, the acid treatment had a flattening effect on the surface of pristine specimens, as denoted by average rugosity.

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Table 1. *Macroscopic properties of pristine (PR), weathered (TW), and treated (TR) marble samples and relative variations (%) of TR samples with respect to PR ($\Delta\%_{Improve}$) and TW ($\Delta\%_{Restore}$) samples. Characterizations: ultrasonic propagation time, t_{uts}; ultrasonic propagation speed, v_{uts}; Young elastic module, E_d; skeletal density from water saturation, $\rho_{skeletal\,H2O}$; skeletal density from water saturation under pressure, $\rho_{skeletal\,H2O\,vac.}$; bulk density from water saturation, $\rho_{bulk\,H2O}$; bulk density from water saturation under pressure, $\rho_{bulk\,H2O\,vac.}$; compact index, I_c%; water open porosity, Φ_{H_2O} %; water open porosity under pressure, $\Phi_{H_2O\,vac}$ %; Shore scale hardness C, HC; Shore scale hardness D, HD; tensile strength, f_h; CIELAB colour space coordinates, L*, a* and b*; chromatic index, C; white index, WI; colour difference ΔE; arithmetical mean roughness value, Ra; mean roughness depth, Rz; root mean square roughness, Rq; contact angle, ϑ_c, measured after 2, 30, or 60 s; drying index, DI; capillary uptake coefficient, CA; liquid water permeability, w; vapor water resistance, μ*

Property	PR	TW	$\Delta\%_{Weather}$	Immersion	$\Delta\%_{Improve}$	$\Delta\%_{Restore}$	Brushing	$\Delta\%_{Improve}$	$\Delta\%_{Restore}$	Spraying	$\Delta\%_{Improve}$	$\Delta\%_{Restore}$
Dynamics												
t_{uts} (μs)	29.0 ± 0.1	68.9 ± 0.1	+138	38.2 ± 0.1	+31.7	−44.6	26.0 ± 0.1	−10.3	−62.3	37.0 ± 0.1	+27.6	−46.3
v_{uts} (km·s^{-1})	2.8 ± 0.2	1.2 ± 0.1	−60	2.1 ± 0.1	−25	+75	3.1 ± 0.2	−11	+160	2.2 ± 0.2	−21	+83
E_d (MN·m^{-2})	14.1 ± 0.5	2.41 ± 0.04	−82.9	7.7 ± 0.2	−45.4	+219	16.5 ± 0.6	−17.0	+585	8.2 ± 0.2	−41.8	+240
Structure												
$\rho_{skeletal\,H_2O}$ (g·cm^{-3})	2.724(2)	2.729(6)	+0.18	2.719(2)	−0.18	−0.37	2.70(2)	−0.88	−1.1	2.708(4)	−0.59	−0.77
$\rho_{skeletal\,H_2O\,vac.}$ (g·cm^{-3})	2.70(1)	2.689(2)	−0.41	2.70(1)	0	+0.41	2.70(1)	0.00	+0.41	2.70(1)	0.00	+0.41
$\rho_{bulk\,H_2O}$ (g·cm^{-3})	2.705(3)	2.724(2)	+0.70	2.677(3)	−1.04	−1.73	2.68(2)	−0.92	−1.62	2.664(1)	−1.52	−2.20
$\rho_{bulk\,H_2O\,vac.}$ (g·cm^{-3})	2.67(1)	2.637(3)	−1.24	2.639(6)	−1.16	+0.08	2.637(5)	−1.24	0.00	2.64(1)	−1.12	+0.11
I_c %	99.3	98.2	−1.07	98.5	−0.85	+0.22	99.4	+0.08	+1.16	98.4	−0.92	+0.15
Φ_{H_2O}%	0.54(4)	1.6(1)	+200	1.4(2)	+160	−12	0.6(1)	+11	−62	0.9(1)	+70	−44
$\Phi_{H_2O\,vac}$%	1.2(1)	2.0(1)	+67	2.3(2)	+92	+15	2.2(1)	+83	+10	2.4(1)	+100	+20
HC	93.7(8)	85(2)	−9.28	92(1)	−1.8	+8.2	94(2)	+0.32	+11	95(2)	+1.4	+12
HD	87(1)	75(1)	−14	86(2)	−1.1	+15	90(2)	+3.5	+20	92.3(8)	+6.09	+23.1
f_h (N·mm^{-2})	0.76 ± 0.02	0.46 ± 0.02	−39	0.66 ± 0.02	−13	+44	0.85 ± 0.02	+12	+85	0.80 ± 0.02	+5.3	+74
Colorimetry												
L*	92.72	94.50	–	94.53	–	–	93.51	–	–	94.40	–	–
a*	−0.31	−0.13	–	−0.18	–	–	0.06	–	–	−0.28	–	–
b*	−0.59	0.60	–	0.28	–	–	2.46	–	–	0.46	–	–
C	0.67	1.04	–	0.33	–	–	2.50	–	–	0.54	–	–
$WI_{CIELAB76}$	85.05	79.41	–	85.23	–	–	72.75	–	–	84.12	–	–
$\Delta E_{CIE1976}$	–	–	2.15	–	2.01	0.32	–	3.17	2.15	–	2.15	1.06
$\Delta E_{CIE2000}$	–	–	1.62	–	1.41	0.32	–	3.01	1.87	–	1.62	1.07
Roughness												
Ra (μm)	5.0(3)	6.4(5)	+28	5.7(6)	+14	−11	5.5(3)	+10.00	−14.06	6.0(5)	+20	−6.3
Rz (μm)	45(5)	61(6)	+36	48(3)	+6.7	−21	47(4)	+4.44	−22.95	40(5)	−11	−34
Rq (μm)	6.3(7)	8.6(6)	+36	8(1)	+30	−7	7.0(3)	+11.11	−18.60	7.7(7)	+20	−10
Contact Angle												
ϑ_c 2 s$_{left}$ (°)	44(12)	9(6)	–	49(14)	–	–	58(5)	–	–	92(10)	–	–
ϑ_c 2 s$_{right}$ (°)	39(5)	11(7)	–	50(13)	–	–	57(3)	–	–	96(16)	–	–
ϑ_c 30 s$_{left}$ (°)	32(12)	–	–	40(10)	–	–	56(6)	–	–	66(1)	–	–
ϑ_c 30 s$_{right}$ (°)	31(8)	–	–	45(10)	–	–	53(5)	–	–	64.3(1)	–	–
ϑ_c 60 s$_{left}$ (°)	32(12)	–	–	37(8)	–	–	51(7)	–	–	60(3)	–	–
ϑ_c 60 s$_{right}$ (°)	27(8)	–	–	41(10)	–	–	51(4)	–	–	57(2)	–	–
Hydric												
DI (%h^{-1})	297(32)	66(1)	−78	66(2)	−77.78	0	65(2)	−78.11	−1.5	64.9(4)	−78.1	−1.67
CA (kg·m^{-2}·h$^{-1/2}$)	0.14(1)	2.81(4)	+1900	1.41(1)	+907.14	−50.0	0.96(7)	+585.71	−66	0.92(4)	+560	−67
w (kg·m^{-2}·h$^{-1/2}$)	0.03(1)	0.10(2)	+200	0.05(1)	+66.67	−50	0.09(2)	+200.00	−10	0.06(1)	+100	−40
μ	69(4)	27(4)	−61	68(2)	−1.45	+150	70(3)	+1.45	+160	105(5)	+52.1	+300

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In the case of the materials treated with compound **1**, the deposition of compound **2** acted as a passivating/sacrificial layer and was partially removed instead of calcite, showing a similar behaviour to the what it was reported for stone samples treated with DAP.[75] When the covering layer is locally removed with the detachment of a crystallite, the material is protected by penetrated compound **2** (Figure S23c in ESI), unless the acid attacks directly the exposed calcite (Figure S23d in ESI). Since no fractures were formed during the treatment, the physical effect of the acidic attack was concentrated only on the surface (Table S4 in ESI), and no significant changes in ultrasonic propagation speed, Young elastic module, and superficial hardness were detected. Oppositely, the colour was generally slightly affected by the acidic treatment, with a decrease in the white index for all the specimens, visually detectable ($\Delta E_{CIELAB2000} > 3$) only for untreated thermally weathered mock–ups. Worthy of note, the colour change determined for all treated samples is negligible ($\Delta E_{CIELAB2000} < 2.5$, Table S4 in ESI).

Materials and Methods

Reagents and solvents were purchased from Carlo Erba, Fluorochem, TCL and used without further purification. The white marble variety “Statuario Michelangelo” from the Apuan Alps was obtained from Cava Franchi (Carrara, Italy). Prism-shaped specimens of different size (4.5 × 4.5 × 2.0 cm, 2.0 × 2.0 × 8.0 cm, and 2.0 × 2.0 × 2.0 cm) were sliced stone. Small irregular fragments (∼1 cm^3, weight = 3 g) were additionally used for the immersion treatment to perform the He pycnometry and Hg porosity determination. Carrara marble samples were partly naturally degraded, hence only a mild thermal weathering was applied using a Carbolite CWF 1200 muffle furnace, where the temperature was ramped to 300 °C (2 h), held for 7 h, and cooled down to 25 °C in 2 h (Figure S11).

Synthesis of ammonium hydrogen phenylphosphonate (1)

A phenylphosphonic acid aqueous solution (20.0 g, 0.127 mol, in 80 mL of distilled water) was slowly added to an ammonium carbonate solution (12.32 g, 0.127 mol, in 160 mL of the same solvent). The resulting solution was stirred for 3 h, then rotary evaporated to dryness to give a white solid. Yield: 21.33 g, 0.121 mol, (96.3%). M.p. = 260 °C. ^{1}H-NMR (DMSO-d_6): δ = 7.62 (m, 2H, Ar), 7.28 (m, 3H, Ar) ppm. ^{31}P-NMR (DMSO-d_6): δ = 8.40 (s, 1P, phosphonate) ppm. CP-MAS $^{13}C\{^1H\}$-NMR: δ = 127.46 (s, Ar), 130.60 (s, Ar), 136.59 (d,Ar) ppm. CP-MAS $^{31}P\{^1H\}$-NMR δ = 10.97 ppm. Elemental Analysis (calcd. for $C_6H_{10}PO_3N$): C 41.43 (41.15), H 5.18 (5.76), N 8.04 (8.00)%. FT-IR (KBr Pellet): $\tilde{\nu}$ = 3238 (m), 3047 (vw), 2783 (w), 2347 (w), 1970 (vw), 1911 (m), 1711 (m), 1439 (s), 1244 (s), 1144 (vs), 1036 (s), 920 (s), 748 (m), 700 (s), 571 (s), 526 (s), 498 (s), 440 (w) cm^{-1}.

Synthesis of calcium phenylphosphonate dihydrate (2)

A weighed amount of compound **1** (5.00 g, 0.028 mol) was dissolved in 300 mL of distilled water under stirring. A stoichiometric amount (1.4 g, 0.014 mol) of calcium carbonate was added, and the suspension was stirred for 24 h. The resulting grainy white solid was separated by filtration and air dried. Yield: 2.90 g, 0.0148 mol, (89.3%). CP-MAS $^{13}C\{^1H\}$-NMR δ = 129.00 (s, Ar), 131.68 (s, Ar), 139.12 (d, Ar) ppm. CP-MAS $^{31}P\{^1H\}$-NMR δ = 13.27 ppm. Elemental Analysis (Calcd. for $C_6H_9O_5PCa$): C 30.63 (31.04), H 3.32 (3.91) %. FT-IR (KBr Pellets): $\tilde{\nu}$ =3576 (m), 3410 (m), 3190 (m), 3074 (m), 3055 (m), 1962 (vw), 1899 (vw), 1633 (w), 1484 (vw), 1437 (m), 1387 (vw), 1383 (vw), 1309 (vw), 1142 (s), 1122 (s), 1095 (s), 1082 (s), 1068 (s), 1030 (s), 993 (s), 926 (w), 841 (w), 748 (m), 723 (s), 698 (s), 598 (s), 555 (m), 538 (s), 468 (w) cm^{-1}.

Application of compound 1 *via* immersion treatment

The mock-ups mass was stabilized in a thermostatic heater at 60 ± 2 °C. The specimens were then immersed in a 5.0% w/w solution of compound **1** (0.30 $mol \cdot L^{-1}$) and left in a static bath for 24 h, following a previous applied technique[31–35] At the end of the treatment, the pH of the solution was measured (5.92) and the unreacted salts were washed with distilled water, monitoring pH and conductivity of the washing solutions. Once the washing was completed, the specimens were air dried and subsequently kept in a thermostatic heather (60 °C) for 24 h.

Application of compound 1 *via* brushing treatment

The mock-ups mass was stabilized in a thermostatic heather at 60 ± 2 °C. A 5.0% w/w solution of compound **1** (0.30 $mol \cdot L^{-1}$) was then applied using a brush with synthetic (polypropylene) bristles appropriately sized for the dimensions of the treated specimen. Each surface was treated with 10 brushstrokes, rotating the specimen by 90° between each stroke and allowing a one-minute pause between each application, to enable the solution to absorb. Before repeating this process for the next surface, the mock-up was allowed to rest under ambient conditions, until the treated surface appeared dry. At the end of the treatment, the specimens were wrapped with a layer of parafilm and left to rest for 24 h. Any unreacted salts were subsequently washed off with distilled water, while the pH and conductivity of the washing solutions were monitored. The specimens were air-dried, then placed into a thermostatic heather at 60 °C for 24 h.

Application of compound 1 *via* spraying treatment

The mock-ups mass was stabilized in a thermostatic heater at 60 ± 2 °C. A 5.0% w/w solution of compound **1** (0.30 $mol \cdot L^{-1}$) was then applied until surface rejection using a pressure nebulizer, at a controlled distance of 20 cm and a total flow rate of 16.4(8) $mL \cdot min^{-1}$. This process was repeated 6 times for each surface of the test specimen, rotating it by 180° between each spray and giving allowing 5 minutes interval between applications, to allow enable the solution to be absorbed.

Before proceeding to treat the next surface, the mock-up was allowed to rest under ambient conditions, until it appeared dry. At the end of the treatment, specimens were wrapped within in a layer of parafilm and left for 24 h. On the following day, any unreacted salts were washed off with distilled water, taking note of the pH and conductivity of the washing solutions. The specimens were then left to air dry, before being put placed into a thermostatic heather at (60 °C) for 24 h.

Physico-chemical characterization

Elemental analyses were carried out with a 2400 series II CHNS/O elemental analyser (T = 925 °C). Melting points were recorded on a FALC melting point apparatus, mod. C (25–300 °C). FT-IR spectra (KBr beam-splitter, KBr windows, 4000–400 cm^{-1}, resolution 4 cm^{-1}) were recorded on a Thermo-Nicolet 5700 spectrometer at room temperature on KBr pellets of the analysed samples. Electronic absorption spectra were recorded at 25 °C in a quartz cell (10.00 mm optical path) on a Thermo Evolution 300 (190–600 nm) spectrophotometer. ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR measurements were carried out in DMSO-d$_6$ at 25 °C, using a Bruker Avance III HD 600 MHz (14.1 T) spectrometer at the operating frequency of 600.15 MHz. Chemical shifts are reported in ppm (δ) and are calibrated to the solvent residue. Solid-state NMR spectra were acquired with the same instrument (Bruker Avance III HD 600 MHz spectrometer) operating at frequencies of 242.94 MHz for ^{31}P-NMR and 150.15 MHz for ^{13}C-NMR. The instrument was equipped with a 2.5 mm CPMAS H/X VTN solid-state sample probe. The magic angle (54.74°) was calibrated on the ^{79}Br signal of a standard KBr sample, while field calibration and probe shimming were performed using a standard adamantane sample. The samples, in the form of finely ground powder, were packed in zirconia rotors with an inner diameter of 2.5 mm and an inner volume of approximately 14 µL. Spectra were acquired with rotation frequency at the magic angle of 15 kHz. Cross-polarization (CP) technique was used for the measurements, which conditions were determined for the two nuclei, using an adamantane standard (^{13}C) and an ammonium dihydrogen phosphate (^{31}P) standard. Solubility and K_{sp} values were evaluated spectrophotometrically at 25 °C on filtered saturated aqueous solutions, after recording a calibration curve. The pH of the solutions was determined using a Hanna 112 pH-meter. Conductivity measurements were carried out with a Crison GLP instrument, after calibration with standards solution of KCl.

3D Electron Diffraction (3D-ED)

3D ED measurements were conducted using a Rigaku Synergy-ED electron diffractometer (LaB$_6$ 200 kV), equipped with a Rigaku HyPix hybrid pixel area array detector. Grid (lacey carbon coated copper TEM grids; Agar Scientific, UK) loading was achieved by first gently grinding compound **2** between glass slides, then lightly dabbing the grid into these solids. The loaded grid was then mounted within a Gatan Elsa cryogenic holder (model 698) and introduced into the instrument *via* cryo-transfer at 175(5) K. Prior to exposing the grid to the column, the holder was held within the airlock (for approx. 15 min) to sublime any ice crystals which may have formed on the grid during transfer. Data collections were performed in continuous rotation mode with selected area aperture (diameter of approximately 2 µm in the image plane) using CrysAlisPRO (v1.171.44.66a)[77] at 175(5) K. Several particles were surveyed and one data collection chosen for structure determination and refinement. The dataset was indexed, reduced, integrated, and scaled using CrysAlisPRO (v1.171.44.90a)[77] and SCALE3 ABSPACK implemented therein. Where necessary, frames were rejected during the processing stage due to holder shadowing and similar effects. The structure was solved using ShelXT[78] and refined kinematically using ShelXL[79] within the Olex2 GUI (v1.5)[80,81] using published scattering factors for electrons.[82]

Refinements were performed in the presence of an extinction correction parameter to broadly account for dynamical effects. Hydrogen atoms were placed and refined geometrically constrained, their distances fixed to published X—H bond lengths for neutron diffraction,[83] and their ADPs refined isotropically using a riding model.

Crystal Data: *$C_6H_9CaO_5P$, M_r = 232.18, orthorhombic, Pbca (No. 61), a = 29.55 Å, b = 10.95 Å, c = 5.65 Å, α = β = γ = 90°, V = 1829.4 Å^3, T = 175(2) K, Z = 8, Z' = 1.*

Table S2 reports experimental parameters from the used dataset. Complete experimental and refinement information are contained in the deposited CIFs along with structure factors and embedded .RES files. These are deposited in the CSD with CCDC reference codes CCDC 2473954.

Powder X-ray Diffraction (PXRD)

PXRD analyses were carried out at room temperature on a Bruker D8 Advance diffractometer equipped with a CuKα radiation source, operating at 40 kV and 40 mA, and a LynxEyE XE-T position-sensitive detector (PSD). Marble stone mock-ups were examined by placing the bulk samples onto a UMC xyz motorized stage, allowing for direct measurements on the stone surface. Proper alignment with the diffractometer geometry was ensured before data collection, which was carried out over a 2θ range of 3–60° with a fixed sample illumination length of 18 mm by means of motorized slits. For compounds **1** and **2**, PXRD data were collected using a conventional PTFE specimen holder over a 2θ range of 3–50°, with a step size of 0.03° and a counting time of 2 s per step. Rietveld refinement of the experimental diffraction pattern for 2 was performed using TOPAS v6,[84,85] based on the structural model obtained from 3D ED analysis.[86] In particular, Rietveld refinement was carried out with absorption correction and preferred orientation modelling, which notably affected the (200) reflection at ~6°. The final values were: Rwp = 5.65%, Rexp = 1.56%, and GOF = 3.62. Visual inspection of the fit confirms that the model adequately reproduces the experimental pattern, with no significant unindexed peaks or evidence of secondary phases. The elevated value of the Goodness of Fit (GOF) is likely due to residual effects of preferred orientation.

Optical Microscopy (OM) and Scanning Electron Microscopy (SEM)

Examinations of the surfaces were carried out by OM using a Zeiss Axioskop 40 optical microscope equipped with a Zeiss camera AxioCam HR, while SEM investigations were performed with a Zeiss Evo LS15 microscopy equipped with a LaB$_6$ filament as electron source (operating at 20.00 kV) and a solid-state detector with a window of 50 mm^2. Prior to examination, the samples were homogenously gold coated using a Leica EM SCD005 sputter coater, operating for 80 s, with a current of 50 mA, working distance of 50 mm, and a pressure of 0.05 mbar.

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Ultrasonic measurements

Ultrasonic pulse velocity (v_{uts}) measurements were carried out before and after each treatment on a CNS Electronics Pundit tester (accuracy ± 0.1 ms). 150 MHz (1), 11.82 mm⌀ transducers were attached to the stone surface with Henkel Sichozell Kleister (carboxymethyl cellulose) paste to enhance the transducer-stone coupling. Three v_{uts} measurements were made directly and consecutively along the horizontal axis and then averaged. The results were used to calculate the Young elastic module (E_d) with the following equation:

$$E_d = \rho \cdot V_p{}^2 \frac{(1+\delta)(1-2\delta)}{(1-\delta)}$$

where ρ is the sample skeletal density, determined by He pycnometry; δ is the Poisson coefficient ($\delta_{marble} = 0.29$).[87]

Colorimetric measurements

Colorimetric measurements were carried out by using a Konica Minolta CM-700d spectrophotometer (illuminant D65), setup to carry out 6 measurements on each point. The results were evaluated as L* (brightness), a* (redness colour), and b* (yellowness colour) coordinates. The total colour difference ΔE was calculated according to the CIELAB76 and CIELAB2000 colour space standards.[88]

Hygric measurements

Skeletal density ($\rho_{skeletal}$), bulk density (ρ_{bulk}), compactness index (I_c) and water open porosity index ($\phi\%_{H_2O}$) were determined with a water saturation experiment. Before the test, the specimens were brought to constant mass in an oven at T = 60 ± 2 °C. Weighed samples were immersed in distilled H_2O for 24 h. The specimens were subsequently weighed on a hydrostatic balance and an analytical balance after having gently buffered the surfaces with a humid cloth. Based on the three masses measured, it was possible to calculate the following parameters:

$$\boldsymbol{\rho_{skeletal}} = \frac{\boldsymbol{m_i}}{\boldsymbol{m_{idr}} - (\boldsymbol{m_{ps}} - \boldsymbol{m_i})} \cdot \boldsymbol{\rho_{H_2O}}$$

$$\boldsymbol{\rho_{bulk}} = \frac{\boldsymbol{m_i}}{\boldsymbol{m_{hydr}}} \cdot \boldsymbol{\rho_{H_2O}}$$

$$\boldsymbol{I_c} = \frac{\boldsymbol{\rho_{skeletal}}}{\boldsymbol{\rho_{bulk}}} \cdot \mathbf{100} \qquad \boldsymbol{\phi\%} = \frac{(\boldsymbol{m_{ps}} - \boldsymbol{m_i})}{(\boldsymbol{m_{ps}} - \boldsymbol{m_{hydr}})} \cdot \mathbf{100}$$

where m_i is the initial mass of the dry specimen, m_{ps} the specimen mass after saturation with water, m_{hydr} the specimen mass weighed on the hydrostatic balance.

The skeletal density ($\rho_{skeletal}$), used for the calculation of the Young elastic modulus was determined using a Micromeritics AccuPyc II 1340 helium pycnometer, equipped with a 3.5 cm^3 sample holder cell. The measurements were carried out on stone fragments of 1 $cm^3 < V <$ 2 cm^3. For each treatment, three fragments were selected, and five density measurements were performed on each.

Capillary water uptake tests were performed in accordance with the European Standard UNI EN 15801:2010.[89] The samples were dried at 60 °C for 24h. The water absorption curve is expressed as Q ($kg \cdot m^{-2}$) for the y-axis vs the square root of the absorption time ($t^{1/2}$) for the x-axis. The curves shown in Figure 18 in ESI have absorption time reported in the x-axis expressed simply in hours (t), to better understand the span necessary for the desorption. The slope of the curve in the initial steep region is the capillary absorption coefficient CA, calculated as:

$$\boldsymbol{CA} = \frac{\boldsymbol{Q_1} - \boldsymbol{Q_0}}{\boldsymbol{t_1^{\frac{1}{2}}} - \boldsymbol{t_0^{\frac{1}{2}}}}$$

Drying experiments were carried out according to NorMaL 29/88.[90] Soaked samples were weighed at increasing time intervals. The drying index (DI), was calculated by using the following equation:

$$\boldsymbol{DI} = \frac{\int_{t_i}^{t_f} \boldsymbol{f(wt)dt}}{\boldsymbol{wt_{max}} \cdot \boldsymbol{t_f}}$$

on a time interval ranging between t_i and t_f; wt_{max} is the maximum water content at initial testing time.[90] Vacuum water absorption tests were performed on all samples according to UNE EN 1936:2010 (pressure = 0.2 kPa).[91] From this free-water saturation method through Archimedes' principle and buoyancy techniques the open porosity of the stone samples can also be determined by:[92]

$$\Phi\%_{H2O\,vac} = \frac{m_s - m_d}{m_s - m_h} \cdot 100$$

where m_d, m_h, and m_s are the mass values of the dry and saturated specimen in water and air, respectively. From these measurements, the skeletal ($\rho_{skeletal}$) and bulk density (ρ_{bulk}) were determined.[93] Measurements of liquid water permeability were carried out with the Karsten test, according to UNI EN 16302:2013 standard.[94] Measurements were repeated on 3 specimens measuring 4.5 × 4.5 × 2.0 cm for each lithotype under study. Karsten tubes (8 mL of capacity, 3 cm base diameter) were placed on top of the specimens, with a perfect adhesion of the base ensured by a clay plastiform polymer. The tube was filled with distilled water, allowing the water to flow through the material. To ensure constant water head pressure, the water volume was restored after every 0.5 mL permeated. The volumes of water dispensed were recorded at time intervals of 2, 4, 6, 10, 15 and 30 min. The collected data were used to determine the liquid water permeability index (μ, $kg \cdot m^{-2} \cdot h^{-1/2}$) and the water flow speed ($mL \cdot min^{-1}$).

Vapour permeability tests were performed according to UNI EN 15803:2010 standard.[95] Each mock-up (4.5 × 4.5 × 2.0 cm) was inserted inside a sample holder, with an internal chamber half-filled with distilled water. All the measuring systems were kept under stable conditions of humidity (60 ± 5%) and temperature (21 ± 2 °C), and the weight of the system was measured every 24 h over a week. The permeability coefficient (δ_p) was then determined with the following equations:

$$\boldsymbol{W_p} = \frac{\boldsymbol{G}}{\boldsymbol{A\,\Delta p_v}} \qquad \boldsymbol{\delta_p} = \boldsymbol{W_p} \cdot \boldsymbol{D}$$

where G is the vapour flown through the sample ($kg \cdot s^{-1}$); W_p is the water penetration ($kg \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$); Δpv is the pressure difference between the two sides of the material (Pa); A is the test area in m^2; D is the average width of the sample (m). The G value can be graphically determined, by plotting the system mass variation against the square root of time. By simply dividing the value of δ_p by the air vapour water permeability coefficient ($1.93 \cdot 10^{-10}$ $kg \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$) the vapour water resistance factor μ was calculated.

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Mercury Intrusion Porosimetry (MIP)

MIP measurements were carried out on small fragments of (< 1 cm^3) of stone using a Micromeritics Autopore IV 9 520 with a maximum pressure of 414 MPa. This technique is based on the Washburn equation:[96]

$$\boldsymbol{P = 2\,\gamma \cdot cos\frac{\theta}{r_c}}$$

where γ is the superficial tension of Hg, θ is the contact angle of Hg,confirms r_c is the radius of the cylinder tube where the sample is inserted during the measurement. This measurement allowed the evaluation of the total open porosity, pore size discriminations of the pore, and cumulative total volume of the samples.

Thermogravimetric analysis

TGA measurements were performed using a Perkin Elmer STA 6000 Simultaneous Thermal Analyser. For all analyses, 5 mg of sample were weighed on an alumina crucible and the simultaneous TGA-DSC thermograms from 25 to 850 °C with a gradient of 10 °C per min using a 40 mL·min^{-1} N_2 flow were recorded.

Mechanical measurements

Pull-off tests were performed according to standard UNI EN 1015-12:2000 and used to evaluate the resistance to tearing of the sample.[97] Steel stubs, 20 mm in diameter, were grit blasted and attached to samples (3 prisms of 8.0 × 8.0 × 2.0 cm) with an epoxy adhesive to form a butt joint for the three lithotypes in study (Carrara marble, biomicritic limestone, carbonate sandstone). After the curing of the adhesive, the joints were then pulled into a universal testing machine fitted with a 5 kN load cell and tested at a rate of 2 mm·min^{-1} at 25 °C. Tensile strength index (f_h, N·mm^{-2}) were then determined using the strength necessary to obtain the pull-off of the attached steel tubes.

Shore Hardness C and D measurements were performed on mock-ups surfaces upon treatment (minimal sampling of three measurements per surface) with Shore durometers (LC Display Meter 0-100HD and 0-100 C), equipped with a standardised indenting foot of hardened steel rod as required by ASTM D2240.[98] Shore scale D: sharp 30° cone, and a 0.1 mm radius tip, force of 44.5 N in a scale ranging between 0 and 100 HD. Shore scale C flat 35° cone, and a 0.79 mm radius tip, force of 44.5 N in a scale ranging between 0 and 100 HC.

Surface properties

Superficial tension measurements were made following standard UNI EN 828:2013 using a Nikon D800 camera equipped with 105 mm macro lens and using white LED lights as illuminating source.[99] A drop of 0.6 µL was released on a regular surface from ∼1 mm distance and pictures were recorded after 2, 30 and 60 s. Using the software BMS.pix3 the collected pictures were then elaborated determining the contact angle for both sides of any drop. For each kind of treated material, the test was applied on a regular surface of three different samples and the results averaged. The surface roughness of the specimens was investigated by means of a Mitutoyo SJ-201 portable surface roughness tester according to the JIS 01 ISO standard. Two faces for each specimen were analysed ten times, with a 1 mm shift after each measurement.

Accelerated aging

All the aging treatments were performed on sets of three 8×2×2 cm mock–ups. Thermal shocks were performed following the international EN 14066:2014 standard.[73] The specimens were dried in a ventilated oven at 40 ± 5 °C for one week and then cooled to ambient temperature before starting the cycles. The dried specimens were subjected to changes of temperature according to the following procedure: 18 ± 1 h inside a ventilated oven at 70 ± 5 °C; immediately followed by 6 ± 0.5 h completely submerged in distilled water (20 ± 5 °C). Both in the oven and in the water container the specimens were placed 50 mm from one another and from the wall. In the water container, specimens were placed on a support located at the bottom, filled with distilled water at a height of 60 ± 10 mm over the height of the submerged specimens. After the 21st cycle the specimens were dried to constant mass at 70 ± 5 °C.

Frost resistance of the mock–ups were determined following the international standard EN 12371:2010.[74] The specimens were dried in a ventilated oven at 70 ± 5 °C to constant mass. The specimens were placed in a container along the vertical axis without coming in contact one with another (50 mm) and with the walls (20 mm). One cycle consists of a 6 h freezing period in air, followed by a 6 h thawing with the specimen immersed in water. After each cycle the mock–ups were rotated by 180° and placed in the same position. After the 21st cycle the specimens were dried to constant mass at 70 ± 5 °C.

Acid attacks were performed following the procedure published by Pasapergio *et al*:[75] before each test, an Hanna 112 pH–meter was calibrated at pH 4, 7 and 10 buffer solutions. Nitric acid (HNO_3) was used to adjust the solution pH to 5. The HNO_3 solution was continuously stirred to allow equilibration before the tests. Untreated and treated small specimens were immersed in separated beakers submerged in such solution of HNO_3 at an initial pH 5 and kept in rotatory motion for 24 h with a magnetic stirrer. Subsequently, the samples were rinsed with distilled water, dried at room temperature until constant weight and observed by SEM as described above. The mock–ups were also characterised by means of superficial hardness determinations, rugosimetry, colourimetry, and ultrasonic speed propagation measurement.

Conclusions

In this paper, we report the synthesis, characterization, and stone treatment tests of the novel salt ammonium hydrogen phenylphosphonate $(NH_4)(HPhPO_3)$ (**1**) as a conservation agent for Statuario Carrara marble. Compound **1** reacts readily with calcium carbonate and calcite to form calcium phenylphosphonate dihydrate $Ca(PhPO_3)\cdot 2H_2O$ (**2**). The crystal structure of compound **2** was elucidated by means of 3D electron diffraction (3D ED). Although this technique has been utilized in the field of cultural heritage in recent years, to the best of our knowledge, this is the first reported application of 3D ED as a structural characterization technique in this context. PXRD measurements shown that the treatment of Carrara marble with compound **1** resulted in the formation of a microcrystalline coating of compound **2**, and no other species could be identified on the surface.

Coating properties strongly depend on the application technique. Brushing and spraying application methods prove more effective in restoring the properties of weathered marble, with treated samples exhibiting dynamic, structural, and hygric properties close to those of the pristine samples. Spraying also increases the surface hydrophobicity, as evidenced by the measured contact angle values. Nevertheless, the deposited patinas, regardless of the treatment method, demonstrated the ability to form a homogeneous phase, with crystals aggregated into a compact layer. This property ensures that subsequent applications of the same treatment can still achieve consolidation, even over a pre-existing coating. These results suggest that both brushing and spraying produce a more homogeneous coating than immersion, allowing in some cases for precise treatment design to achieve surface hydrophobization. The consolidation effect was accompanied by no significant changes in colour or vapour permeability, demonstrating the high compatibility of the treatment with the carbonate substrates. The results of this research prove ammonium hydrogen phenylphosphonate as an innovative, economically affordable, and soluble consolidant for the conservation of carbonate stone materials. It overcomes several of the limitations of currently established consolidants (such diammonium hydrogen phosphate, DAP), whose treatments on carbonate stone lead to the formation of hydroxyapatite (HAP) accompanied by non-stoichiometric products, such as $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$ and $CaHPO_4 \cdot 2H_2O$ (brushite), some of which more soluble than calcite.

A comparison between ammonium hydrogen phenylphosphonate and diammonium hydrogen phosphate exemplifies the subtle role played by the anion size in tailoring the chemical-physical properties and reactivity of the resulting calcium salts.

Future studies may focus on long-term durability assessments and the potential for wider application to other different lithotypes and ancient lime mortars used in historical monuments.

Author contributions

M. A., P. M., M. C. A., D. G., conceptualization; M. A., P. M., D. G., supervision; S. M., G. C., S. C., E. P., A. P., S. J. C., J. B. O. D.N.R, methodology; all authors investigation; S. M., M. A., G. E., E. P., data curation; M. A., S. M., E. P., V. L. writing; all authors, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information. Crystallographic data for compound **2** has been deposited at the CCDC (reference code CCDC 2473954). 3D ED raw data on Zenodo (https://doi.org/10.5281/zenodo.16742748).

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Data availability

The data supporting this article have been included as part of the Supplementary Information. Crystallographic data for compound **2** has been deposited at the CCDC reference codes CCDC 2473954. 3D ED raw data on Zenodo (https://doi.org/10.5281/zenodo.16742748).