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Conversion of calcium sulfate dihydrate into calcium phosphates as a route for conservation of gypsum stuccoes and sulfated marble

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ABSTRACT

To increase the water resistance of gypsum-based stuccoes (i.e., pastes and mortars), the possible conversion of gypsum into less soluble calcium phosphates (CaP), by reaction with an aqueous solution of diammonium hydrogen phosphate (DAP), was investigated. The effect of several reaction parameters (DAP concentration, ethanol addition to the DAP solution, pH) on nature and morphology of the new CaP was explored. For the most promising formulation, the ability to improve mechanical properties and reduce solubility in water of treated stuccoes was investigated. The treatment provided better results than ammonium oxalate (an inorganic treatment frequently used for consolidation, protection and de-sulphation of carbonate stones), but the high reaction speed limited the penetration depth and the performance of the DAP-treatment.

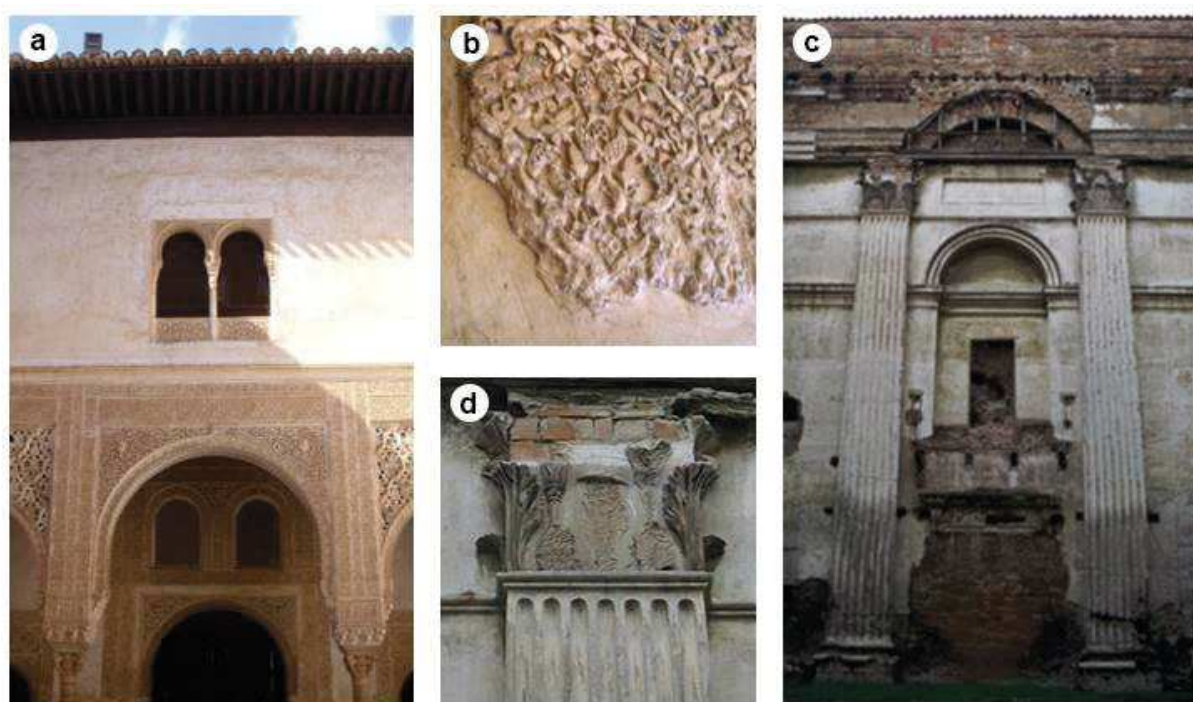
KEYWORDS

Hydroxyapatite; Brushite; Gypsum; Marble; Solubility; Consolidation; Protection; Acid rain; Cultural Heritage; Stucco

1 1. INTRODUCTION

2 Pastes and mortars based on gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), formed from the reaction
3 between the binder bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) and water, have been used since
4 ancient times to create plasters, renders and bedding mortars. The so-called stuccoes
5 (i.e. pastes and mortars molded to create decorative elements) have been used to
6 imitate white and colored marbles, when the supply of real stones from distant quarries
7 was too costly [1].

8 Because of the high solubility of gypsum in water (~ 2.5 g/l), decorative elements
9 exposed to rain, rising damp or water vapor condensation may undergo progressive
10 dissolution, leading to surface recession and pulverization [2]. Figure 1 illustrates some
11 examples of gypsum decorations severely weathered because of their exposure to rain
12 and/or rising damp.



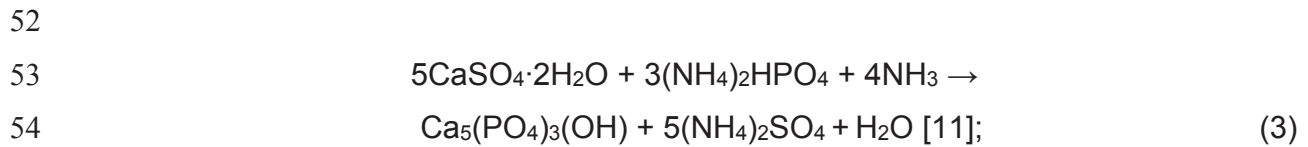
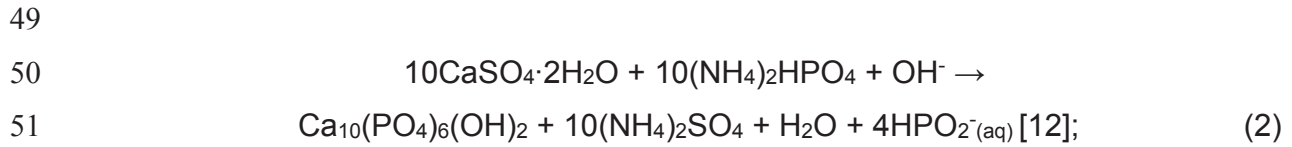
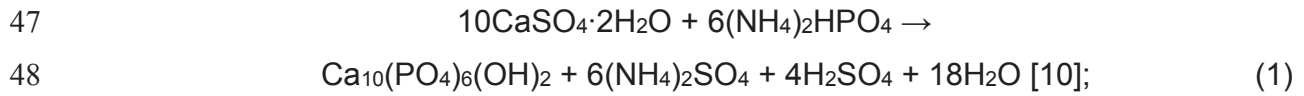
13
14 **Figure 1.** Examples of weathered gypsum decorations: (a,b) decorations in the Alhambra Palace in
15 Granada (Spain, XIV century) exposed to rain; (c,d) stuccoes in the church of San Francesco in Fano
16 (Italy, XIX cent.) exposed to rising damp from the ground and rain (because of the collapse of the church
17 roof).

18 At the time of gypsum stucco creation, it was common practice to add several types of
19 organic additives to the stucco recipes, with the aim of increasing their durability.
20 Sugars, glycerin and citric acid were added to reduce solubility in water [3], while animal
21 blood, egg whites and casein were added to achieve water-repellency [4-6]. Currently,
22 protectives and consolidants are often used. However, commercial treatments (such as
23 ethyl silicate and organic polymers) have exhibited serious limitations when applied to
24 gypsum stuccoes [7]. Ethyl silicate provides little mechanical strengthening, because of
25 the poor bonding between the substrate and the amorphous silica coating, which is
26 affected by diffused cracking; organic polymers exhibit low penetration depth, thus
27 creating a surface layer blocking the pores and negatively altering the water
28 permeability [7]. For these reasons, innovative solutions are needed.

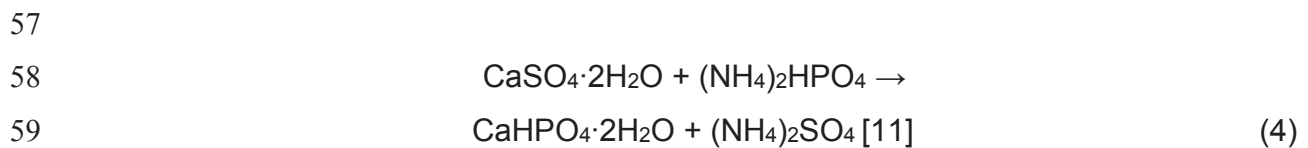
29 A novel route to preserve gypsum-based elements is converting gypsum into less
30 soluble calcium phosphates (CaP), by treatment with an aqueous solution of
31 diammonium hydrogen phosphate (DAP, $(\text{NH}_4)_2\text{HPO}_4$). Transforming gypsum into a
32 different mineral might raise concerns in the field of cultural heritage conservation,
33 where very strict requirements about authenticity apply [8]. However, because
34 preserving an artifact by using the same type of mineral is not always feasible and/or
35 effective, conservation of architectural heritage by formation of minerals possibly
36 different from the original ones is commonly accepted and performed in practice. For
37 instance, amorphous silica and polymers (formed by silicate and organic consolidants,
38 respectively) are currently used for conservation of gypsum stuccoes in spite of the
39 above-mentioned limitations of these treatments. Therefore, the compatibility
40 requirement is often interpreted as allowing a treatment that does not have negative
41 consequences on the original substrate [9], which is expected to be the case of
42 phosphate treatment aimed at transforming gypsum into calcium phosphates.

43 The reaction between gypsum and DAP solutions has been explored in different fields
44 (e.g., biomaterials [10] and building materials [11,12]) and different chemical reactions
45 have been proposed to describe the gypsum transformation:

46



55
 56 or



60
 61 According to reactions 1-3, hydroxyapatite (HAP, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) should form. HAP is
 62 usually written as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, to denote that the crystal unit cell comprises two
 63 formula units. Having a dissolution rate in water about 4 orders of magnitude lower than
 64 gypsum and being the most stable calcium phosphate [13-15], HAP is the most
 65 desirable phase to form. However, in several studies, formation of HAP starting from
 66 gypsum was reported to be associated with diffused cracking [10,11], most probably
 67 caused by shrinkage during drying [11]. Cracking is undesired, as it can reduce the
 68 performance of the HAP layer and even lead to its partial detachment and separation
 69 [12]. Alongside HAP [11,12] or even instead of HAP [16], other CaP phases have been
 70 reported to form, such as brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, predicted by reaction 4) and
 71 octacalcium phosphate ($\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$). A list of CaP phases and their
 72 respective properties is reported in Table 1; for comparison, the solubility of gypsum is
 73 2.5-3.1 g/L [17]. These CaP phases have solubility in water higher than HAP, but still
 74 much lower than gypsum [15], hence their formation is expected to be beneficial, as
 75 long as cracking is prevented. According to reactions 1-3, ammonium sulfate
 76 ($(\text{NH}_4)_2\text{SO}_4$) is also expected to form as a by-product. Being highly soluble in water,

77 ammonium sulfate is expected to be removed by washing with water, as demonstrated
 78 experimentally [11,12].

79

Abbreviation	Name	Formula	Ca/P ratio	Solubility at 25 °C [g/L]
HAP	Hydroxyapatite	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	1.67	~0.0003
CDHA	Calcium-deficient HAP	$\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$ ($0 < x < 1$)	1.5-1.67	~0.0094
ACP	Amorphous calcium phosphate	$\text{Ca}_x\text{H}_y(\text{PO}_4)_z \cdot n\text{H}_2\text{O}$ ($n=3-4.5$, 15-20% H_2O)	1.2-2.2	n.a.
β -TCP	β -Tricalcium phosphate (or calcium phosphate tribasic)	$\beta\text{-Ca}_3(\text{PO}_4)_2$	1.5	~0.0005
OCP	Octacalcium phosphate	$\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$	1.33	~0.0081
DCPD	Dicalcium phosphate dihydrate (or brushite)	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	1.0	~0.088
DCPA	Dicalcium phosphate anhydrous (or monetite)	CaHPO_4	1.0	~0.0048
MCPM	Monocalcium phosphate monohydrate	$\text{Ca}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	0.5	~18
MCPA	Monocalcium phosphate anhydrous (or calcium phosphate monobasic)	$\text{Ca}(\text{HPO}_4)_2$	0.5	~17
-	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-	~2.5

80 **Table 1.** Name, abbreviation, formula, Ca/P, solubility of different CaP phases and gypsum [15].

81

82 In a previous preliminary study, we found that reacting specimens of gypsum pastes
 83 with a 1 M DAP solution led to the formation of brushite, as well as ammonium sulfate
 84 and kokaite ($(\text{NH}_4)_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$) as by-products [16]. A possible reason why only
 85 brushite was formed, and not HAP (as would be expected based on the chemical
 86 reactions reported above), may be the lowering of pH during the reaction (according to
 87 reaction 1, H_2SO_4 should form). If pH decreases below 4, formation of brushite is
 88 expected, as this phase is the most stable at $\text{pH} < 4$ [18,19]. Alongside ammonium
 89 sulfate, the formation of kokaite as a by-product is thought to result from the high
 90 amount of calcium ions in the solution, originating from the high solubility of gypsum in
 91 water [16].

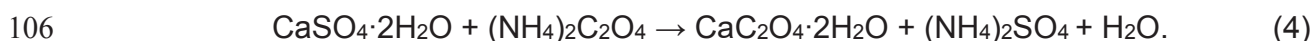
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93 In light of the above reported studies, the aims of the present paper are the following:

94 1) to study the influence of several reaction parameters (viz., concentration of the DAP
95 solution, addition of ethanol, pH of the DAP solution) on the nature and the
96 morphology of the new CaP phases, and to optimize the treatment by promoting
97 formation of phases with low solubility and preventing cracking;

98 2) for the most promising formulation, to test the improvement in mechanical properties
99 and the reduction in solubility of gypsum stuccoes resulting from the formation of the
100 new CaP phases;

101 3) to compare the performance of the most promising formulation of the phosphate
102 treatment with that of ammonium oxalate. The ammonium oxalate treatment was
103 proposed in the 90s for protection of carbonate stones and wall paintings and for
104 desulfation of sulfated substrates [11,20,21]. This latter action can be achieved by
105 transforming gypsum into less soluble calcium oxalate, according to the reaction:



107 The consolidating ability of the oxalate treatment on gypsum stuccoes was here
108 investigated because a good mechanical improvement has been reported in the
109 case of sugaring marble [21], even if a poor performance has been found in other
110 studies [15] (so that new routes for improving the treatment based on calcium
111 oxalate are currently being investigated [22]).

112 Moreover, based on the results obtained on gypsum stuccoes, the suitability of using
113 the same formulation of the phosphate treatment also for conservation of sulfated
114 marble was preliminarily investigated. The use of DAP solutions for marble protection
115 [23-26] and consolidation [15,27-29] has been studied in the last few years with very
116 encouraging results. However, the cited studies have been carried out on
117 uncontaminated marble samples, whereas marble in the field is often covered with a
118 layer of gypsum. This gypsum layer is the result of the reaction between marble and
119 sulfur dioxide, which was present in the atmosphere in high concentrations in the past
120 decades, before traffic regulation policies led to the current low values [30], and which is
121 still present in places where such regulations have not been established yet. Some pilot

122 applications of the DAP-based treatment onto naturally decayed stones (exhibiting
123 gypsum contamination) have shown that the presence of gypsum can significantly alter
124 the composition of the CaP phases formed after treatment [15,31]. Therefore, in the
125 present study, a preliminary evaluation of the treatment effect on sulfated marble was
126 carried out, in terms of morphology and composition of the new CaP phases formed
127 after treatment. It is noteworthy that, in the case of sulfated marble, the possible pH
128 decrease during the reaction (where, according to reaction 1, H₂SO₄ may form) is
129 potentially a major issue, because it might cause severe aggression to marble
130 underlying the gypsum layer. Therefore, the variation in pH during treatment of sulfated
131 marble with the DAP solution was carefully monitored.

132

133 **2. MATERIALS AND METHODS**

134 **2.1. Materials**

135 *2.1.1. Gypsum stuccoes*

136 To simulate ancient stuccoes, specimens of gypsum pastes (with no aggregates) were
137 prepared starting from bassanite (the so-called “*scagliola*”), supplied by Gessificio Prioli
138 srl, Italy (purity ~95%). Bassanite was mixed with water (water/bassanite weight ratio of
139 0.5) and prismatic specimens (4×4×16 cm³) were cast. After hardening, the specimens
140 were sawn to obtain cubic (1 cm edge length), cylindrical (2 cm diameter, 4 cm height)
141 and prismatic samples (1×1×16 cm³).

142 *2.1.2. Sulfated marble*

143 To simulate sulfated marble, cubic specimens (1 cm edge length) of Carrara marble
144 (BasketweaveMosaics.com, USA) were immersed in an aqueous solution of H₂SO₄
145 (Sigma Aldrich) at pH 2 for 24 hours. In this way, a surface layer of gypsum was formed
146 over the marble substrate.

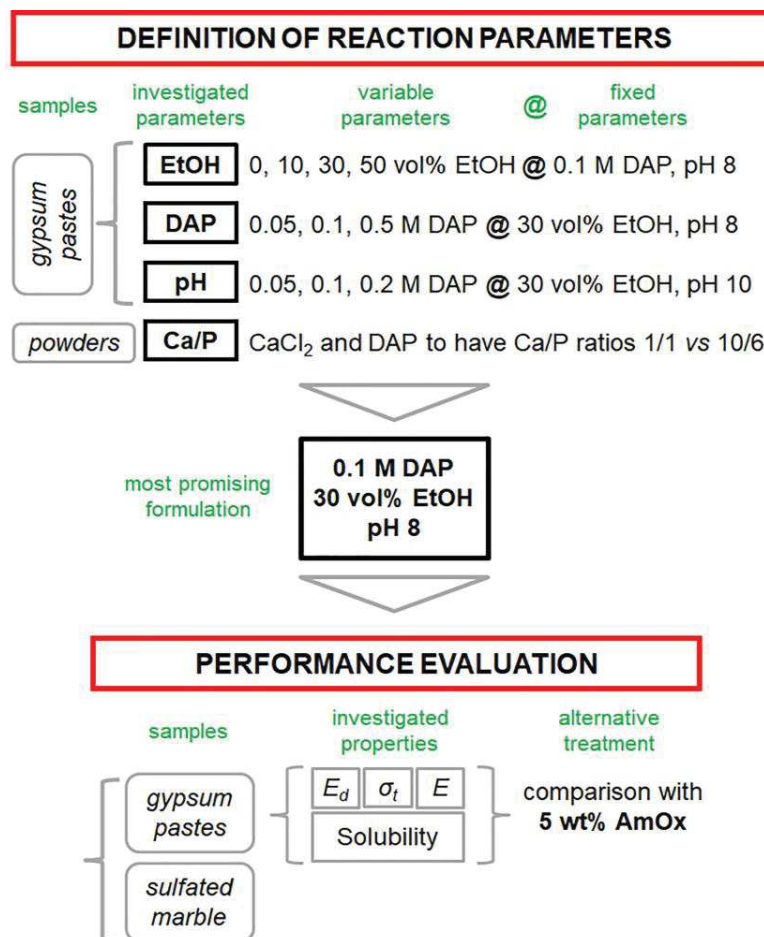
147 **2.1.3. Chemicals**

148 Diammonium hydrogen phosphate (DAP, $(\text{NH}_4)_2\text{HPO}_4$, assay > 99%, Sigma Aldrich),
 149 ammonium oxalate $((\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, assay > 99%, Sigma Aldrich), calcium chloride
 150 $(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, assay > 99%, Sigma Aldrich), ammonium hydroxide (ACS Grade),
 151 ethanol (Fisher-Scientific) and deionized water were used.

152 **2.2. Treatments**

153 A scheme summarizing the various treatment conditions and the respective specimens
 154 is reported in Figure 2.

155



156

157 **Figure 2.** Scheme illustrating the various treatment conditions and specimens.

158 2.2.1. Phosphate treatment

159 Apart from the role of the Ca/P ratio (investigated as described in the following), the
160 influence of all the other parameters was tested by immersing specimens of gypsum
161 stuccoes (1 cm cubes) in 200 ml of DAP solution for 24 hours. The variation in pH of the
162 DAP solution was monitored during the 24-hour reaction. At the end of the treatment,
163 samples were abundantly rinsed with water and then dried at room temperature. The
164 following parameters were considered:

165 ➤ ethanol concentration. A previous study had shown that the undesired, soluble
166 phase kokaite was formed when samples of gypsum stuccoes were reacted with a 1
167 M DAP solution [16]. The formation of this phase was ascribed to an excess of
168 calcium ions available in the DAP solution, as a result of the high solubility of
169 gypsum in water. Consequently, a reduction in the solubility of gypsum in the DAP
170 solution (and hence a reduction in the free calcium ions) appears as a promising
171 route to prevent the formation of kokaite. According to the literature, a reduction in
172 gypsum solubility in aqueous solutions can be achieved by adding ethanol to water:
173 a 30 wt% addition of ethanol to water was found to reduce gypsum solubility by
174 about 30% [32]. Consequently, ethanol additions of 0, 10, 30 and 50 vol% to a 0.1 M
175 aqueous DAP solution were here investigated. A DAP concentration of 0.1 M was
176 selected (instead of the higher concentrations previously tested in the literature,
177 namely 1 M [16], 3 M [12] and 3.8 M [11]) because studies on marble showed that
178 the addition of ethanol to the DAP solution provides a continuous, crack-free and
179 pore-free film, using only millimolar concentrations of DAP. This is possible thanks to
180 the boosting effect that ethanol has on the reactivity of phosphate ions in the solution
181 [25,29].

182 ➤ DAP concentration. For the ethanol concentration that showed the best results (30
183 vol%, cf. § 3.1), the effects of higher and lower DAP concentrations were
184 investigated. Samples were reacted in 0.05, 0.1 and 0.5 M DAP solutions, in all
185 cases containing 30 vol% ethanol.

186 ➤ pH of the DAP solution. Without any pH modification, a 0.1 M DAP solution has pH
187 8. However, at higher pH a higher amount of PO_4^{3-} ions (necessary to form HAP) is

188 expected to form from DAP dissociation [24,33]. Therefore, the effect of increasing
189 the pH of the DAP solution from 8 to 10 was investigated. Solutions with increasing
190 DAP concentration (0.05, 0.1 and 0.2 M, the latter being the maximum concentration
191 not leading to immediate precipitation at pH 10) were explored, at a constant ethanol
192 concentration of 30 vol% and pH 10. The pH was adjusted using ammonium
193 hydroxide, which was selected among possible bases because it leaves no
194 undesired cations in the solution.

195 ➤ Ca/P ratio. To study the influence of the starting Ca/P ratio on the composition of the
196 new CaP phases, a simplified system was considered. Two aqueous solutions with
197 different Ca/P ratios were prepared. DAP was added to a 10 mM aqueous solution
198 of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in such an amount to obtain (i) a Ca/P ratio of 10/6 (corresponding to
199 that of HAP) and (ii) a Ca/P ratio of 1/1 (corresponding to that of brushite). In both
200 cases, the precipitate was filtered, dried at room temperature and then analyzed by
201 powder X-ray diffraction (XRD), using a Rigaku MiniFlex diffractometer (detector
202 scan range $2\theta=3-60^\circ$, step size = 0.04 θ , step time = 0.8 s, kV = 40, mA = 40).

203 2.2.2. Oxalate treatment

204 For comparison's sake, specimens of gypsum stuccoes were also treated by immersion
205 in a 5 wt% aqueous solution of ammonium oxalate for 24 hours. At the end of the
206 treatment, samples were abundantly rinsed with water and then dried at room
207 temperature.

208 2.3. Characterization

209 2.3.1. Nature and morphology of the new CaP phases

210 The mineralogical composition of the new CaP phases formed on the surface of treated
211 samples (1 cm cubes) was determined by grazing incidence diffractometry (GID), using
212 a Bruker D8 Discover X-Ray Diffractometer (incidence radiation $\theta=0.5^\circ$, detector scan
213 range $2\theta=3-37^\circ$, step size = 0.02 θ , step time = 0.4 s, kV = 40, mA = 40). Thanks to the
214 low penetration depth of the incoming radiation (a few hundreds of nanometers from the

215 surface), by GID it is possible to determine the composition of the surface layers without
216 interference from the substrate. The same technique was used also for checking the
217 formation of gypsum after the preliminary accelerated sulfation procedure carried out on
218 marble samples (cf. § 2.1.2).

219 The morphology and the possible presence of cracks in the new CaP phases formed
220 after treatment was assessed by observation with an environmental scanning electron
221 microscope (FEI Quanta 200 FEG ESEM) equipped with an energy dispersive x-ray
222 spectroscopy device (Oxford Instruments EDS probe). Before ESEM observation,
223 samples were made conductive by coating with carbon. The same instrument was used
224 also for observing the gypsum layer formed after accelerated sulfation of marble
225 samples (cf. § 2.1.2).

226 2.3.2. Mechanical properties

227 The improvement in mechanical properties of the gypsum stuccoes after consolidation
228 was evaluated for (i) the phosphate treatment based on 0.1 M DAP with 30 vol%
229 ethanol at pH 8 (labeled “DAP”) and (ii) for the ammonium oxalate treatment (labeled
230 “AmOx”). The mechanical improvement was evaluated in terms of:

231 ➤ dynamic elastic modulus (E_d). E_d can be determined non-destructively by measuring
232 the time required by an ultrasonic pulse to cross the sample. Being a non-destructive
233 test, it can be repeated on the same sample before and after consolidation. E_d was
234 determined according to the formula $E_d = \rho v^2$, where ρ is the density and v is the
235 ultrasonic pulse velocity. v was measured across the 4 cm height of the cylindrical
236 samples by a PUNDIT instrument with 54 kHz transducers, using a rubber couplant
237 to improve the contact. For each condition, 5 samples were tested.

238 ➤ static elastic modulus (E). E was tested because, unlike E_d , it is not affected by the
239 pore-clogging effect that consolidants might have, which could lead to an increase in
240 E_d without necessarily implying an increase in the actual stiffness. E was determined
241 by three-point beam bending, from the slope of the stress-strain curve obtained by
242 loading the $1 \times 1 \times 16$ cm³ samples. Samples were placed on two supports at a
243 distance of 120 mm and then loaded in the center by a pushrod, activated by a

244 stepping motor. The load was measured by a 1 kg load cell, while the deflection was
245 measured by a linear variable displacement transducer (LVDT). E was calculated
246 from the slope of the stress-strain curve, determined by linear regression of five
247 stress-strain coordinates. For each condition, 5 samples were tested.

248 ➤ tensile strength (σ_t). σ_t was determined because the tendency of grains to detach
249 from the substrate depends on the material cohesion, which can be evaluated by the
250 splitting test. The same cylindrical samples as for the E_d measurement were used.
251 Samples were loaded along two diametric lines until failure, using an Instron testing
252 machine (loading rate 2 mm/min). This method generates tension in a narrow band
253 between the lines of contact, so it is not much affected by treatments that produce
254 only superficial hardening of the cylinder.

255 2.3.3. Solubility

256 The reduction in solubility after treatment was determined by a simplified test. After
257 drying to constant weight, untreated and treated cylindrical samples were immersed in
258 600 ml of deionized water at initial pH 5 (each sample in a different container), water
259 being kept stirring by a magnetic stirrer. After 24 hours, the samples were extracted
260 from water and dried at room temperature until constant weight. The weight loss after
261 prolonged exposure to water was then determined by comparing the initial and the final
262 weights.

263 2.3.4. Penetration depth

264 The penetration depth of the phosphate and oxalate treatments was assessed by SEM
265 observation of cross sections obtained by chisel from the cylindrical samples used for
266 the splitting tensile test. After coating with aluminum to make them conductive, the
267 samples were observed using a Philips XL20 SEM equipped with an EDAX EDS probe.

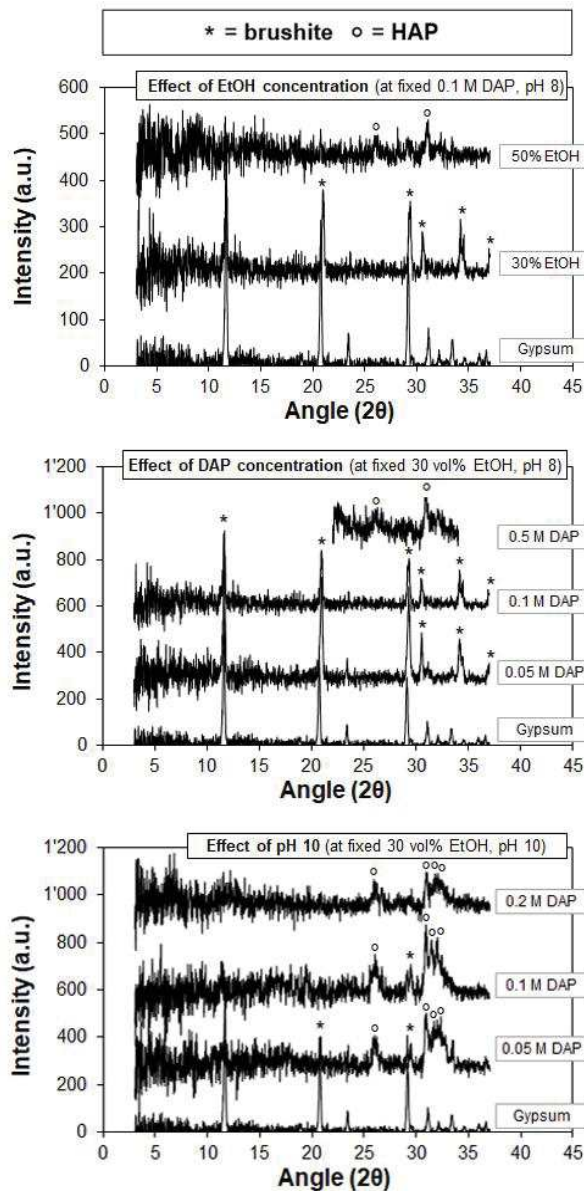
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269 3. RESULTS AND DISCUSSION

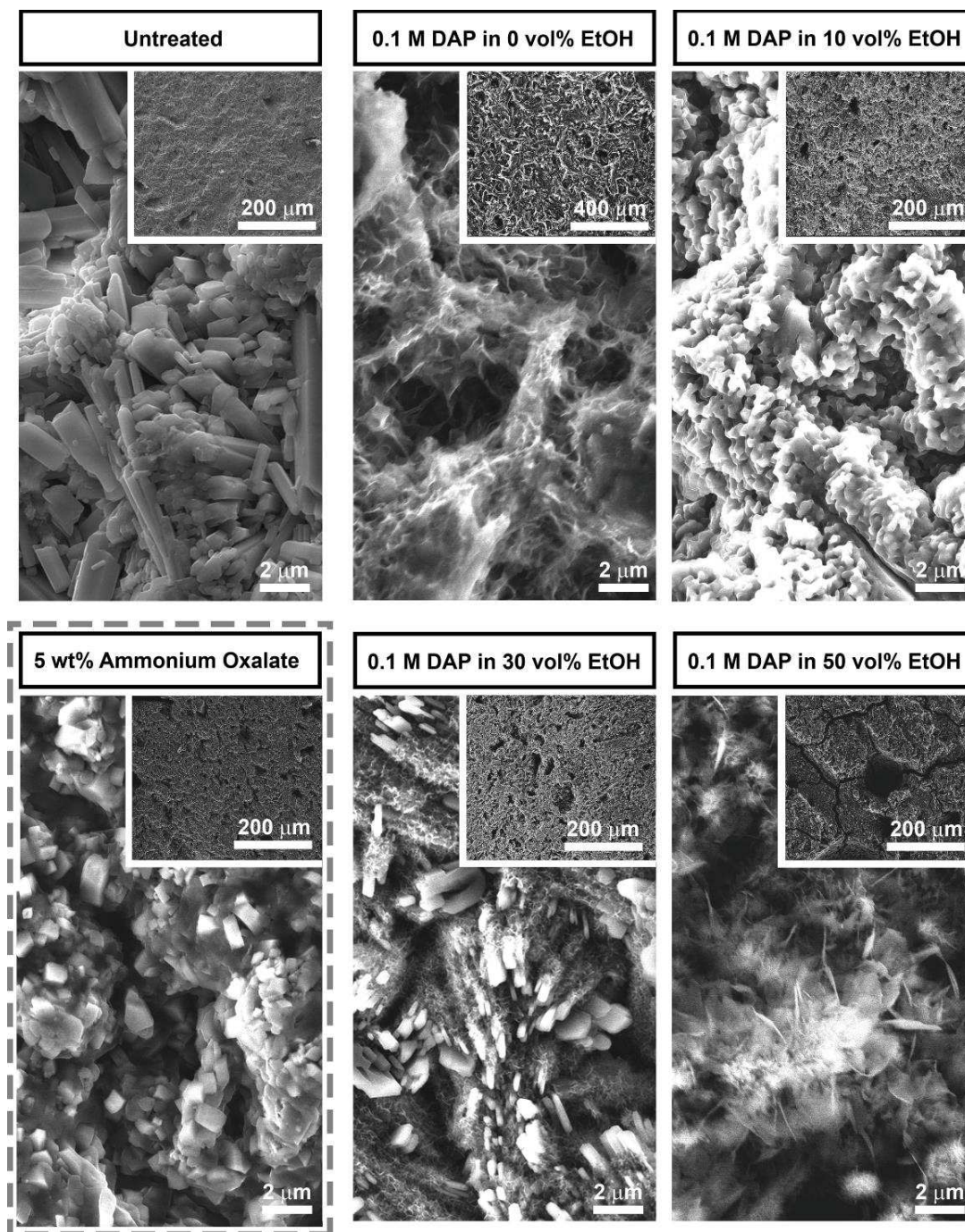
270 3.1. Gypsum stuccoes

271 **3.1.1. Formation of new CaP phases**

272 The effect of the investigated parameters on the mineralogical composition of the new
273 CaP phases is reported in Figure 3, while the morphology of the new phases is
274 illustrated in Figure 4, Figure 5 and Figure 6.

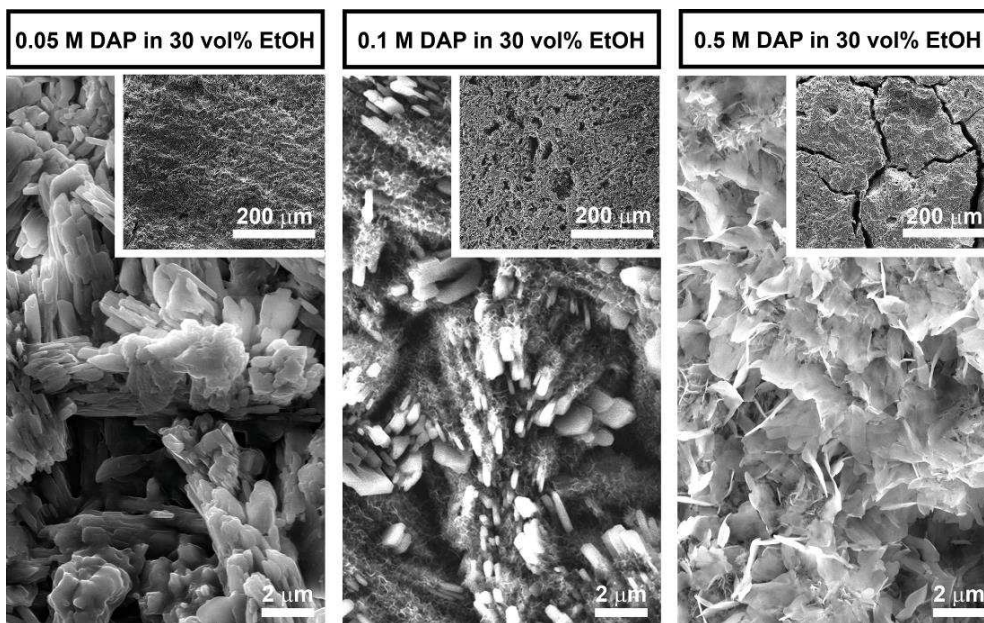


275
276 **Figure 3.** Mineralogical composition of the new CaP phases formed by treating gypsum
277 samples with different formulations of the phosphate treatment, to investigate the effect of
278 ethanol concentration (top), DAP concentration (medium) and pH increase to 10 at various DAP
279 concentrations (bottom).



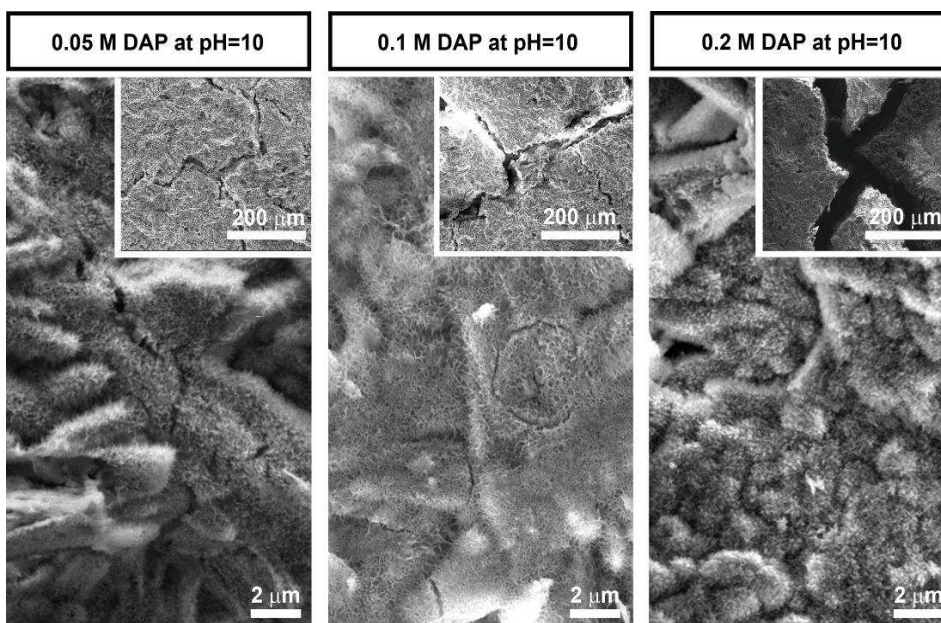
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281 **Figure 4.** Morphology of the new CaP phases formed by reacting gypsum with different
282 formulations of the phosphate treatment, to investigate the effect of ethanol concentration. For
283 comparison's sake, also the untreated reference and whewellite formed after treatment with
284 ammonium oxalate (dashed box) are reported.



285
286 **Figure 5.** Morphology of the new CaP phases formed by reacting gypsum with different
287 formulations of the phosphate treatment, to investigate the effect of DAP concentration.

288



289
290 **Figure 6.** Morphology of the new CaP phases formed by reacting gypsum with different
291 formulations of the phosphate treatment, to investigate the effect of increasing pH to 10, at
292 various DAP concentrations.

293 After reaction with a 0.1 M DAP solution containing no or 10 vol% ethanol addition,
294 some new CaP phases were formed (Figure 4). They could not be identified by GID,
295 likely because of the very small amount produced. The limited formation of CaP phases
296 when such a low DAP concentration was used is consistent with previous results
297 obtained on fresh marble, where no new phases were observed if no ethanol was
298 added to the 0.1 M DAP solution [29]. In the case of gypsum, when the ethanol
299 concentration was increased to 30 and 50 vol%, abundant new phases were formed,
300 having a clearly different morphology (Figure 4). As reported in Figure 3, the new
301 phases were identified as brushite (30 vol% ethanol) and HAP (50 vol% ethanol). In this
302 latter case, the treated sample exhibited diffused cracking (Figure 4), which is
303 undesirable for achieving protection from dissolution in water.

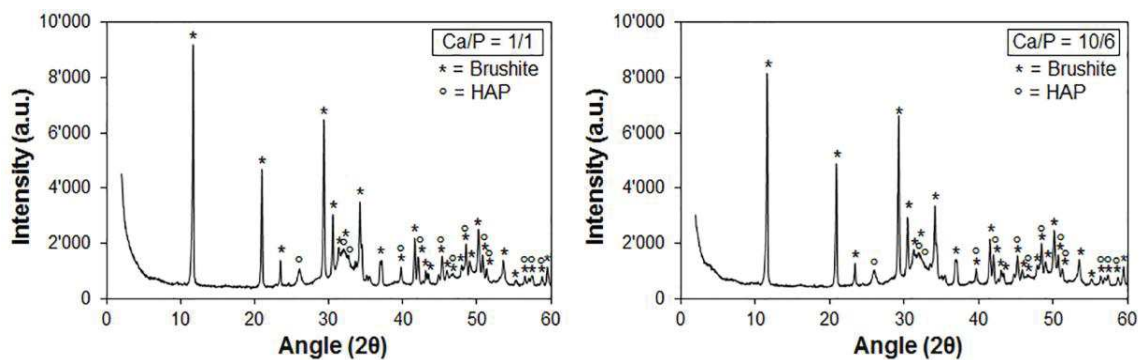
304 When the effect of increasing the DAP concentration was investigated, the modification
305 in phase composition and morphology reported in Figure 3 and Figure 5, respectively,
306 was obtained. Whereas brushite was the main phase formed at 0.05 and 0.1 M DAP,
307 HAP (exhibiting a clearly different morphology, Figure 5) was formed at 0.5 M DAP.
308 However, also in this case, formation of HAP was associated with heavy cracking of the
309 sample surface, while no cracking was observed in samples where brushite formed
310 (Figure 5).

311 Formation of HAP is expected from reactions 1-3, but in some of the investigated
312 conditions brushite was formed instead of HAP. A possible explanation for this might be
313 the lowering of pH during the reaction as predicted by reaction 1. If pH decreases below
314 4, then brushite would be the most stable CaP phase and hence its formation would be
315 expected [19]. To verify whether this was the case, in all the experiments the pH was
316 monitored. The pH was found to change only slightly during the reaction (from 8.1 to
317 8.0), hence never getting below 4. Therefore, pH variation was excluded as the possible
318 reason why brushite was formed instead of HAP.

319 Another possible explanation could be that brushite (requiring HPO_4^{2-} ions) is kinetically
320 favored over HAP (requiring PO_4^{3-} ions), as DAP speciation leads to a much higher
321 amount of the former ions with respect to the latter. For instance, in the case of a 0.1 M

322 DAP solution (with no ethanol addition), calculations performed with Mathematica®
323 (following the method described in [24]) predict the following concentrations of
324 phosphate ions: 0.0959 M HPO_4^{2-} ions, 0.0039 M H_2PO_4^- ions and only 3.3×10^{-5} M
325 PO_4^{3-} ions, hence a ratio of $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ of about 2900. The ratio becomes even higher
326 (about 5850) if an amount of CaCl_2 sufficient to match gypsum solubility limit (15.1 mM
327 [34]) is also considered in the solution. The hypothesis that brushite is kinetically
328 favored over HAP would also explain the change in phase composition detected for
329 increasing ethanol concentration or increasing DAP concentration. In fact, in either
330 case, the Ca/P ratio is decreasing (because fewer Ca ions are available and more P
331 ions are available, respectively). Because HAP has a higher Ca/P ratio than brushite
332 (1.67 vs 1, respectively), formation of HAP would be expected to be favored at higher
333 Ca concentrations (i.e., lower ethanol concentrations) or at lower DAP concentrations.

334 To verify whether formation of brushite occurs because the kinetics predominates over
335 the effect of the Ca/P ratio, solutions were prepared with different Ca/P ratios, namely
336 10/6 (corresponding to that of HAP) and 1/1 (corresponding to that of brushite) (cf. §
337 2.2.1). As illustrated in Figure 7, in both cases brushite was the main phase that formed,
338 with only minor amounts of HAP. This suggests that, independently of the starting Ca/P
339 ratio, formation of more soluble brushite is favored over less soluble HAP, likely
340 because HPO_4^{2-} ions needed to form brushite are more easily available than PO_4^{3-} ions
341 needed to form HAP. Accordingly, in a recent paper [12] it was proposed that formation
342 of CaP phases follows the Ostwald's rule, i.e. the phase with the fastest precipitation
343 rate is preferentially formed, even if it is not the most stable one [12].



344
345 **Figure 7.** Composition of the new CaP phases precipitated from solutions with Ca/P ratio of 1/1
346 (left) and Ca/P ratio of 10/6 (right).

347 To promote formation of HAP, we increased the pH of the starting DAP solution from 8
348 to 10, because more PO_4^{3-} ions (required to form HAP) are available at higher pH [33].
349 As expected, a significant change in phase composition was achieved by increasing the
350 pH (Figure 3). At low DAP concentrations (0.05 and 0.1 M), brushite was still present,
351 but also HAP was formed. At higher DAP concentration (0.2 M, the highest
352 concentration not leading to direct precipitation at pH 10), only HAP was detected.
353 However, in all cases the new CaP phases exhibited diffused cracking (Figure 6), which
354 presumably occurred during drying because the porous films exceeded the critical
355 thickness for cracking (below the critical thickness, cracking is thermodynamically
356 inhibited [35]). In addition to altering the aesthetic appearance of the treated stuccoes
357 (as they are visible even by naked eye), cracks are expected to be detrimental to
358 protection from dissolution in water. Therefore, formulations at pH 10, leading to
359 diffused cracking, were regarded as not promising for providing satisfactory protection.

360 It is noteworthy that in no case was formation of undesired kokaite [16] detected, which
361 was the aim of adding ethanol to the DAP solution (because ethanol reduces the
362 solubility of gypsum in water [32] and hence the amount of free calcium ions in the DAP
363 solution). Moreover, neither was formation of ammonium sulfate detected by GID, which
364 is the positive result of abundantly washing samples with deionized water at the end of
365 the 24 hour reaction. However, this washing procedure was sufficient to entirely remove
366 ammonium sulfate in the samples used for GID (1 cm cubes), but not in bigger samples
367 used for mechanical tests (e.g. cylinders with 2 cm diameter and 4 cm height). After
368 treatment, washing and drying, the latter samples exhibited some color change towards
369 grey, owing to formation of ammonium sulfate, detected also by GID. However, by
370 further saturating the samples with deionized water by capillary rise and then
371 submerging the samples, ammonium sulphate was almost completely removed, as
372 indicated by GID and by the color change back to the initial one. Accordingly, no traces
373 of nitrogen were detected by SEM/EDS on cross sections obtained from the cylindrical
374 samples used for the tensile strength test.

375 In light of these results, the formulation of the phosphate treatment based on a 0.1 M
376 DAP solution also containing 30 vol% ethanol at pH 8 was considered as the most

377 promising one, as it leads to formation of brushite (significantly less soluble than
 378 gypsum, although more soluble than HAP), without cracking. In terms of long term
 379 stability, brushite (as well as other metastable CaP phases) are expected to undergo
 380 dissolution and reprecipitation processes, finally leading to formation of the most stable
 381 CaP phase, i.e. HAP. In the case of a CaP layer formed by reacting gypsum with DAP
 382 solutions, progressive densification of the layer with time, thanks to formation of
 383 additional CaP phases, was found experimentally [12]. On the contrary, dehydration of
 384 brushite to monetite (CaHPO_4 , having much higher water solubility than brushite, Table
 385 1) was not found to occur in practical conditions [11]. Therefore, the long term stability
 386 of the so-formed brushite is expected to be satisfactory.

387 The consolidating and protecting ability of the above-reported formulation (labeled
 388 “DAP”) was hence investigated and compared to that of commercial ammonium oxalate
 389 (labeled “AmOx”).

390 3.1.2. Mechanical consolidation

391 The variations in mechanical properties after application of the phosphate and oxalate
 392 treatments are reported in Table 2.

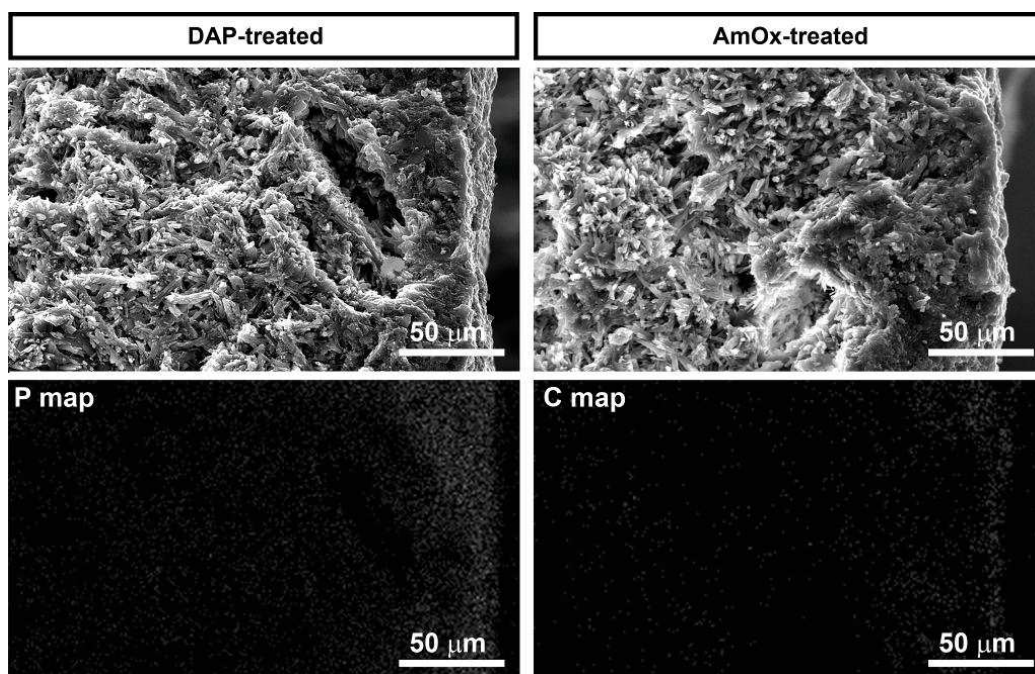
393

	Untreated	DAP	Variation	AmOx	Variation
E_d (GPa)	9.9 (± 0.4)	10.3 (± 0.1)	+3%	11.1 (± 0.6)	+12%
E (GPa)	4.0 (± 0.5)	4.2 (± 0.2)	+5%	4.0 (± 0.2)	0%
σ_t (MPa)	3.4 (± 0.7)	3.8 (± 0.2)	+13%	3.3 (± 0.6)	-3%
Δw (%)	9.5	7.9	-17%	9.5	0%

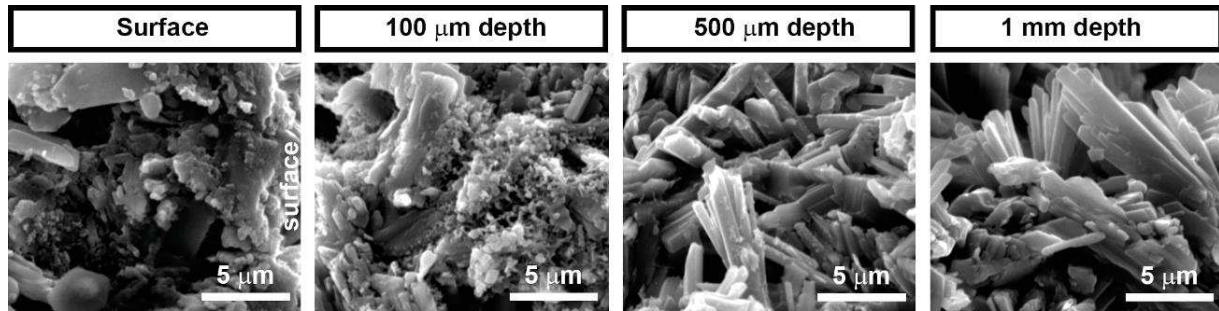
394 **Table 2.** Mechanical properties and weight loss after immersion in water of untreated and
 395 treated samples (E_d = dynamic elastic modulus; E = static modulus; σ_t = tensile strength; Δw =
 396 weight loss). Values of mechanical properties are averages for 5 samples (standard deviations
 397 in brackets).

398

399 The DAP treatment caused modest increases in dynamic elastic modulus E_d and static
400 modulus E (+3% and +5%, respectively) and a slightly higher increase in tensile
401 strength (+13%). This limited mechanical improvement seems to derive from the low
402 depth of formation of new CaP phases, as assessed by SEM/EDS analysis of cross
403 sections. As illustrated in Figure 8 and Figure 9, the formation of new CaP phases and
404 the consequent presence of phosphorus are mainly concentrated in the first 50-100 μm
405 from the surface. Traces of new CaP phases were observed at a depth of 500 μm from
406 the surface, while no new phases were detected at 1 mm (Figure 9). This reduced
407 penetration depth, in spite of the ability of the DAP solution to penetrate deeply into
408 porous substrates (up to 25 mm in porous limestone [36-38]), is thought to be a
409 consequence of the fast reaction between the DAP solution and gypsum.
410 Notwithstanding the addition of ethanol to the DAP solution to reduce gypsum solubility,
411 the presence of a large amount of calcium ions available for reaction is responsible for
412 the consumption of phosphate ions in the DAP solution, so that new CaP phases form
413 mostly near the surface. Possible strategies for reducing the reaction speed and hence
414 favor formation of the new CaP phases also in depth are currently under investigation.



415
416 **Figure 8.** Morphology and elemental maps of cross sections of samples treated by DAP (left)
417 and AmOx (right).



418
419 **Figure 9.** New CaP phases at increasing depth from the surface. Whereas abundant new
420 phases are present near the surface and can still be clearly observed at 100 μm depth, only
421 minor traces of new CaP phases are visible at 500 μm depth (small flakes formed on the
422 surface of the big gypsum crystals) and no trace is found at 1 mm depth.

423

424 In the case of the AmOx treatment, gypsum was transformed into whewellite
425 ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), as indicated by GID and illustrated in Figure 4 (dashed box). In this
426 case, even if a higher increase in E_d was registered (+12%), no significant increase in
427 either the static modulus or the tensile strength was found (Table 2). The lack of any
428 substantial consolidating action is thought to be a consequence of the reduced depth of
429 formation of whewellite, which in turns derives from the kinetics of reaction between the
430 ammonium oxalate solution and the substrate. As recently pointed out in a study on
431 carbonate stones, ammonium oxalate tends to react with calcite more quickly than DAP,
432 which leads to a lower penetration depth of the former treatment compared to the latter
433 [39]. Accordingly, in the case of gypsum (even more soluble than calcite), in the present
434 study a much lower depth of formation of calcium oxalate was found by SEM/EDS,
435 compared to calcium phosphates (Figure 8). The presence of C (assumed as indicative
436 of formation of whewellite) was detected only at a few tens of microns from the surface.
437 This finding is in agreement with previous results reported in the literature on treatment
438 of gypsum with ammonium oxalate and ammonium phosphate solutions [11]. In the
439 cited study, a strong gradient in the formation of calcium oxalate was reported (the
440 highest amount being concentrated near the surface), whereas a more homogenous
441 formation of CaP phases (present also in depth) was found [11]. The apparent increase
442 in E_d registered in the AmOx-treated samples is thought to derive from formation of

443 ammonium sulfate inside the pores of the samples. In the case of the AmOx treatment,
444 traces of ammonium sulfate were detected by GID even in the 1 cm cubes, although
445 washed at the end of the treatment. In the cylindrical samples used for E_d
446 measurements, while saturation and submersion in water were sufficient to remove
447 basically all the ammonium sulfate from the DAP-treated samples, in the case of the
448 AmOx-treated ones, a considerable amount of ammonium sulfate still remained, as
449 suggested by the color change and confirmed by GID. The difference between the DAP-
450 and the AmOx-treatments in the amount of ammonium sulfate formed inside the pores
451 and remaining after washing derives from the fact that NH_4^+ ions were more abundant in
452 the AmOx solution (about 0.4 M) than in the DAP solution (0.1 M).

453 Comparing the performance of the two treatments, the DAP solution was able to
454 penetrate more in depth and provide greater mechanical improvement than the AmOx
455 treatment, but neither is very effective. Compared to ammonium oxalate, the DAP
456 treatment has the advantage of leading to formation of a smaller amount of ammonium
457 sulfate, that can be more easily removed. For the same reason, even if slightly greater
458 mechanical improvements were found in a previous study where a 1 M DAP solution
459 was used ($\Delta E_d = +5\%$ and $\Delta \sigma_t = +16\%$ [16]), still the formulation adopted in this study
460 seems preferable, considering that the small mechanical advantage had been obtained
461 at the cost of a much higher DAP concentration (10 times as much) and formation of
462 much more ammonium sulfate (and koktaite) inside the sample [16].

463 3.1.3. Protection from dissolution in water

464 The results of the simplified dissolution tests are reported in Table 2.

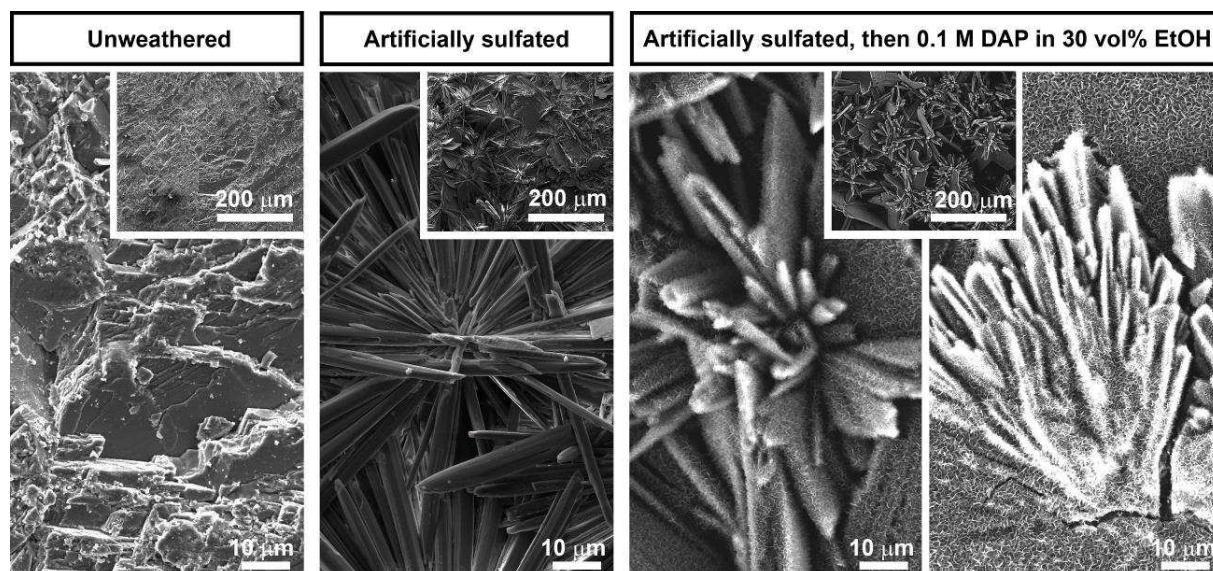
465 In the case of the DAP treatment, thanks to gypsum conversion to brushite, a 17%
466 reduction in weight loss after prolonged exposure to water was registered. The reason
467 why the reduction was not higher (in spite of brushite being about 27 times less soluble
468 than gypsum [15]) is thought to be the porous nature of the brushite layer and of the
469 gypsum substrate, combined with the reduced depth of gypsum conversion to brushite.
470 In fact, porosity allows water to penetrate in depth and reach the inner part of the
471 sample, not completely covered by the newly formed brushite.

472 In the case of the AmOx treatment, no reduction in weight loss was registered,
473 compared to the untreated reference. This is a consequence of the fact that whewellite
474 formed only in the most superficial part of the sample, because of the high speed of the
475 reaction [11]. Combined with the porous nature of the sample, this prevented an
476 effective protecting action from being achieved.

477 3.2. Sulfated marble

478 After immersion in H₂SO₄ at pH 2 for 24 hours, gypsum was formed on the marble
479 surface, as confirmed by GID. The newly formed gypsum exhibited a needle-like
480 morphology, as illustrated in Figure 10.

481



482 **Figure 10.** Morphology of fresh marble (left), artificially sulfated marble (middle) and artificially
483 sulfated marble treated with DAP (right).
484

485
486 During reaction with the formulation that gave the best results on gypsum stuccoes
487 (namely, a 0.1 M DAP solution in 30 vol% ethanol), the pH of the solution was found to
488 change only slightly, from 8.1 to 8.0. Consequently, no risk of marble corrosion owing to
489 the possible formation of H₂SO₄ during reaction of the gypsum layer with the DAP
490 solution (cf. reaction 1 in § 1) was present.

491 After treatment, new CaP phases were formed, as illustrated in Figure 10. These
492 phases exhibit a morphology more similar to that of HAP (Figure 7) than to brushite
493 (Figure 4), but no conclusive phase identification was achieved by GID. This is probably
494 to be ascribed to the reduced thickness of the new CaP phases, as suggested by the
495 fact that these phases closely follow the morphology of the needle-like gypsum crystals
496 originally covering the marble surface. Whatever the nature of the new CaP phases,
497 their solubility is in any case lower than that of gypsum, hence a benefit in terms of
498 resistance to dissolution is expected.

499 However, some micro-cracks were visible in the CaP layer (Figure 10, right), while no
500 similar cracks were observed in the gypsum layer before treatment with the DAP
501 solution. Because the formation of micro-cracks in the CaP layer may negatively affect
502 its durability, further investigation seems opportune to optimize the treatment outcome
503 in the case of sulfated marble, where the morphology of the starting gypsum crystals
504 may affect the phosphate treatment outcome.

505 It is noteworthy that, in the case of marble covered with gypsum layers embedding dust
506 and particulate matter (the so-called “black crusts”), transformation of gypsum into
507 calcium phosphates would encapsulate the dirt in a layer with reduced solubility, which
508 might be counterproductive. Therefore, whenever possible, the dark matter should be
509 removed by cleaning before application of the DAP-based treatment. Nonetheless, in
510 the case of marble covered by black crusts, below which the marble surface is sugaring
511 (so that cleaning the black crust might threaten the conservation of the underlying
512 marble), preliminary tests we have carried out indicate that the DAP treatment, applied
513 over the gypsum crust, is able to pre-consolidate the marble surface, which becomes
514 able to stand the cleaning operations, while the consolidated crust can still be
515 successfully removed by cleaning.

516 **4. CONCLUSIONS**

517 In the present study, the composition and the morphology of new calcium phosphate
518 phases formed by reacting gypsum pastes with different solutions of diammonium

519 hydrogen phosphate was investigated and the consolidating and protecting ability of the
520 most promising formulation were evaluated. The following conclusions can be derived:

521 1) Formation of phases with low solubility (e.g., HAP) can be obtained by increasing
522 the ethanol concentration (added to reduce gypsum solubility and hence the amount
523 of calcium ions in the solution), by increasing the DAP concentration or by increasing
524 the pH. However, HAP formation was found to be associated with diffused and
525 visible cracking, likely because of excessive growth of the new phase. On the
526 contrary, when more soluble brushite was formed, no cracking was observed.

527 2) Formation of brushite was found to be favored over formation of HAP, likely because
528 brushite requires HPO_4^{2-} ions (by far the most abundant species originated from
529 DAP dissociation) while HAP requires PO_4^{3-} ions (which are present only in very
530 minor amounts). This explains why brushite is preferentially formed, even in a pH
531 range and for a starting Ca/P ratio that should favor HAP.

532 3) Samples of gypsum stuccoes treated for 24 hours with a 0.1 M DAP solution
533 containing 30 vol% ethanol at pH 8 exhibited formation of uncracked brushite. As
534 brushite is less soluble than gypsum (although more soluble than HAP), such
535 treatment caused a 17% decrease in weight loss of the gypsum stuccoes after
536 prolonged exposure to water and a 13% increase in their tensile strength. However,
537 the improvement induced by the phosphate treatment was not as high as hoped
538 because of the reduced depth of formation of brushite, mostly concentrated in the
539 first 50-100 μm from the surface and present only in traces at a depth of 500 μm .
540 The phosphate treatment provided better results than the ammonium oxalate
541 treatment, originally proposed for desulfation of calcareous substrates and here
542 investigated for consolidation and protection of gypsum stuccoes. The performance
543 of the oxalate treatment is mainly limited by the high speed of reaction between the
544 oxalate solution and gypsum, so that the depth of formation of calcium oxalate is
545 only a few tens of microns from the surface. Possible routes to reduce the speed of
546 reaction between the phosphate solution and gypsum are currently under
547 investigation. In the case of the oxalate treatment, use of a lower concentration of

548 ammonium oxalate and/or addition of alcohol might improve the performance, but
549 those variations were not explored in the present study.

550 4) With the aim of treating sulfated marble so as to transform gypsum into less soluble
551 calcium phosphate phases, the same formulation of the phosphate treatment
552 reported above was tested also on artificially sulfated samples of Carrara marble.
553 New calcium phosphate phases with the flower-like morphology typical of HAP were
554 observed, but they could not be identified by GID. Because some cracks were
555 observed in the new calcium phosphate layer, some further optimization of the
556 treatment seems necessary for application to sulfated marble, where the morphology
557 of the gypsum crystals may also play a role.

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