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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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## **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.

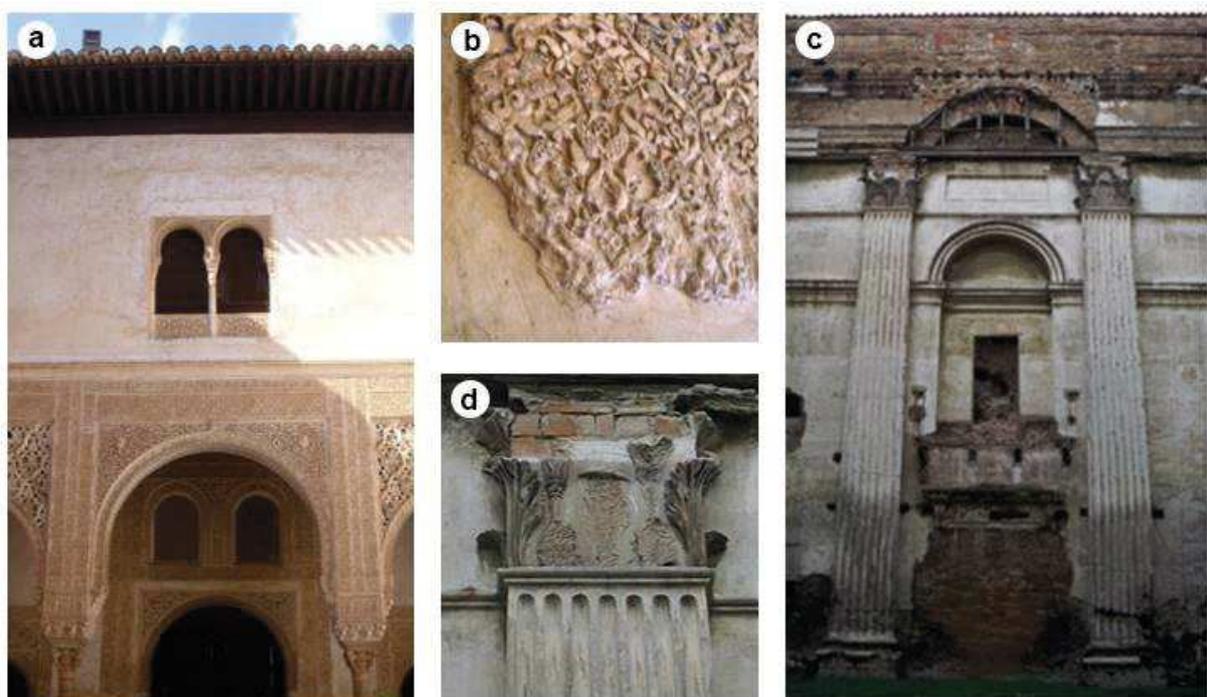
### **KEYWORDS**

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 ( $\sim 2.5 \text{ g/l}$ ), 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.



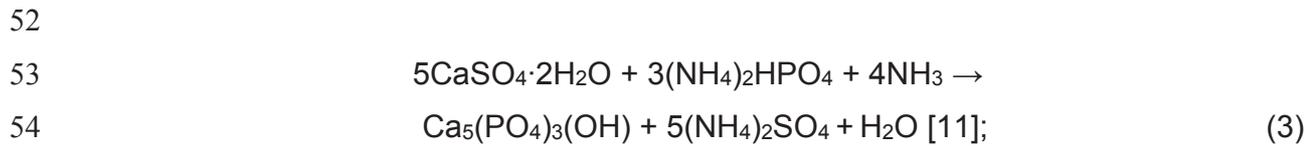
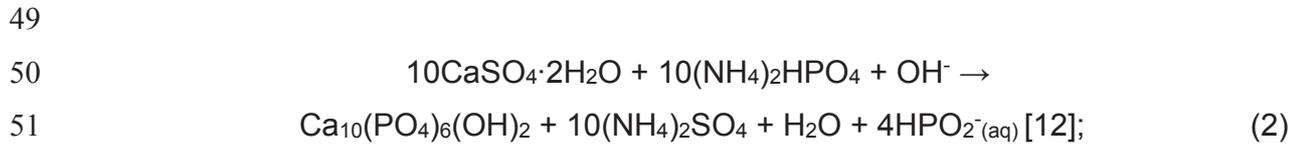
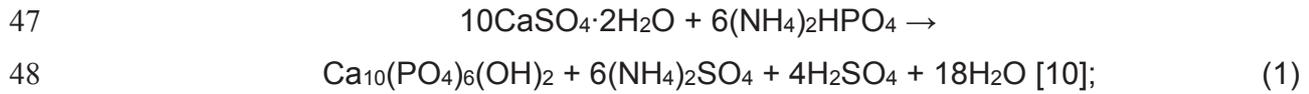
13  
14 **Figure 1.** Examples of weathered gypsum decorations: (a,b) decorations in the Alhambra Palace in  
15 Granada (Spain, XIV century) exposed to rain; (c,d) stuccoes in the church of San Francesco in Fano  
16 (Italy, XIX cent.) exposed to rising damp from the ground and rain (because of the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

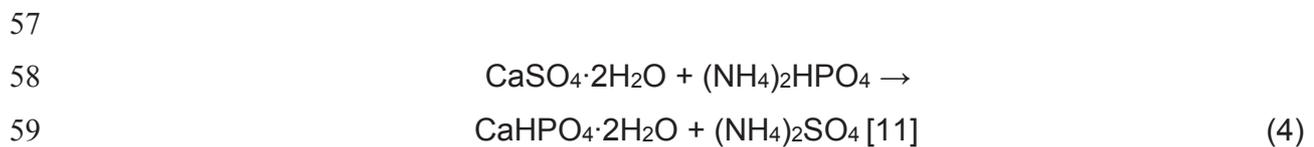
29 A novel route to preserve gypsum-based elements is converting gypsum into less  
30 soluble calcium phosphates (CaP), by treatment with an aqueous solution of  
31 diammonium hydrogen phosphate (DAP,  $(\text{NH}_4)_2\text{HPO}_4$ ). Transforming gypsum into a  
32 different mineral might raise concerns 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% $\text{H}_2\text{O}$ )	1.2-2.2	n.a.
$\beta$ -TCP	$\beta$ -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)	$\text{CaHPO}_4$	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,  $\text{H}_2\text{SO}_4$  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].

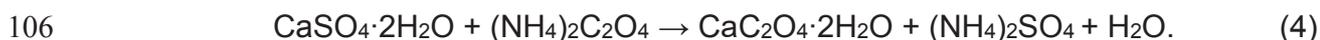
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93 In light of the above reported studies, the aims of the present paper are the following:

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, H<sub>2</sub>SO<sub>4</sub> 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 cm<sup>3</sup>) 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 cm<sup>3</sup>).

#### 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 H<sub>2</sub>SO<sub>4</sub>  
145 (Sigma Aldrich) at pH 2 for 24 hours. In this way, a surface layer of gypsum was formed  
146 over the marble substrate.

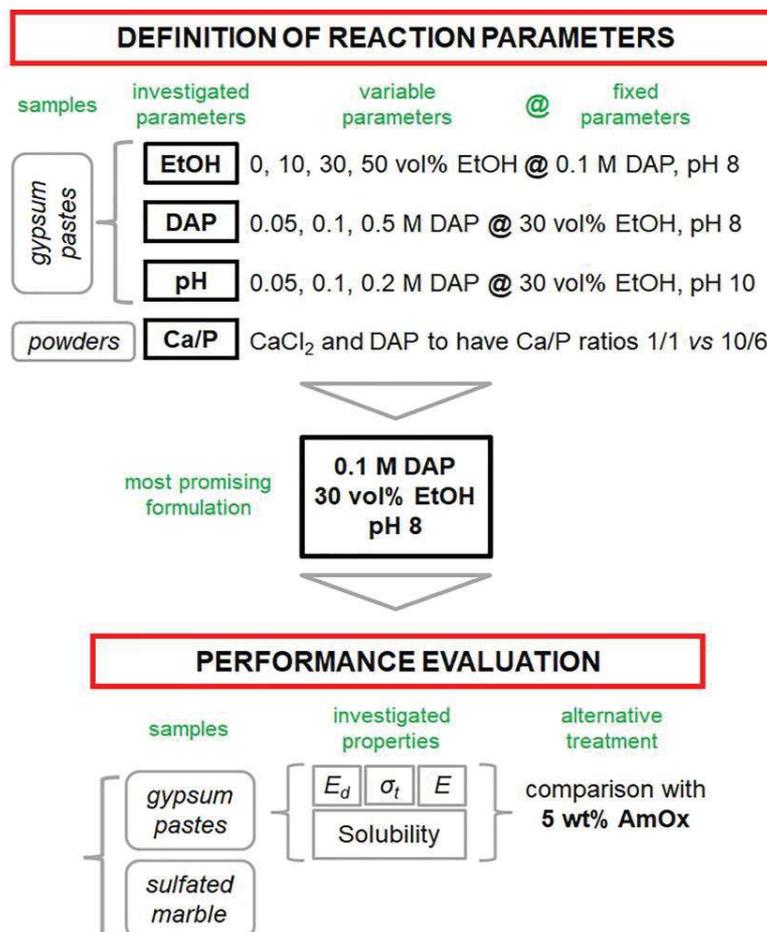
147 **2.1.3. Chemicals**

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  $\text{PO}_4^{3-}$  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  $\theta$ , 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  $\theta$ , 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  $\rho$  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  $1 \times 1 \times 16$  cm<sup>3</sup> 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 ( $\sigma_t$ ).  $\sigma_t$  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.

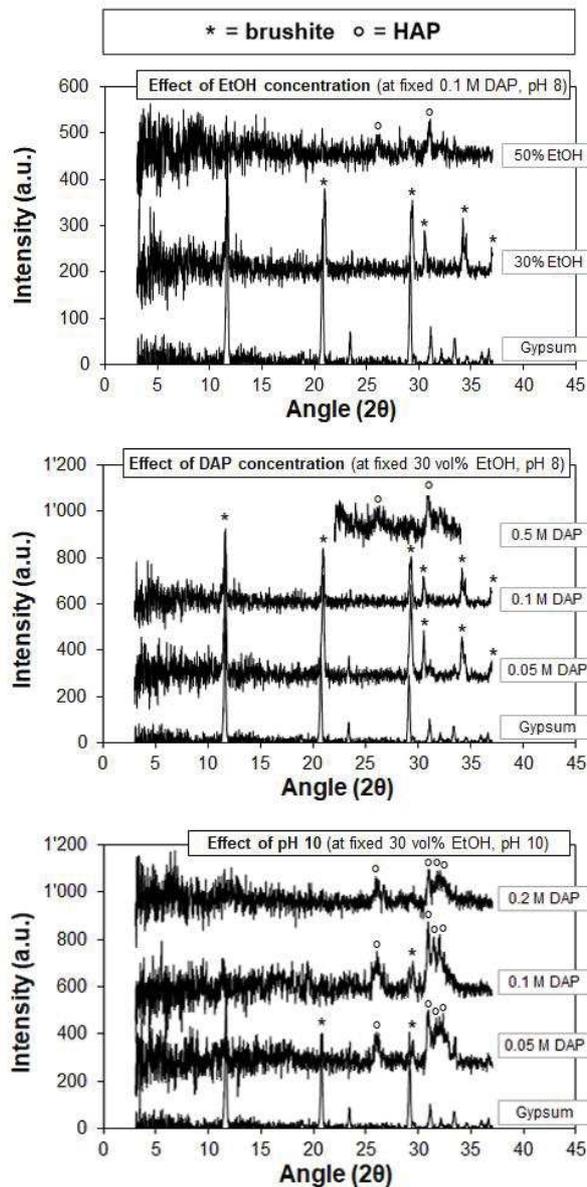
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## 269 3. RESULTS AND DISCUSSION

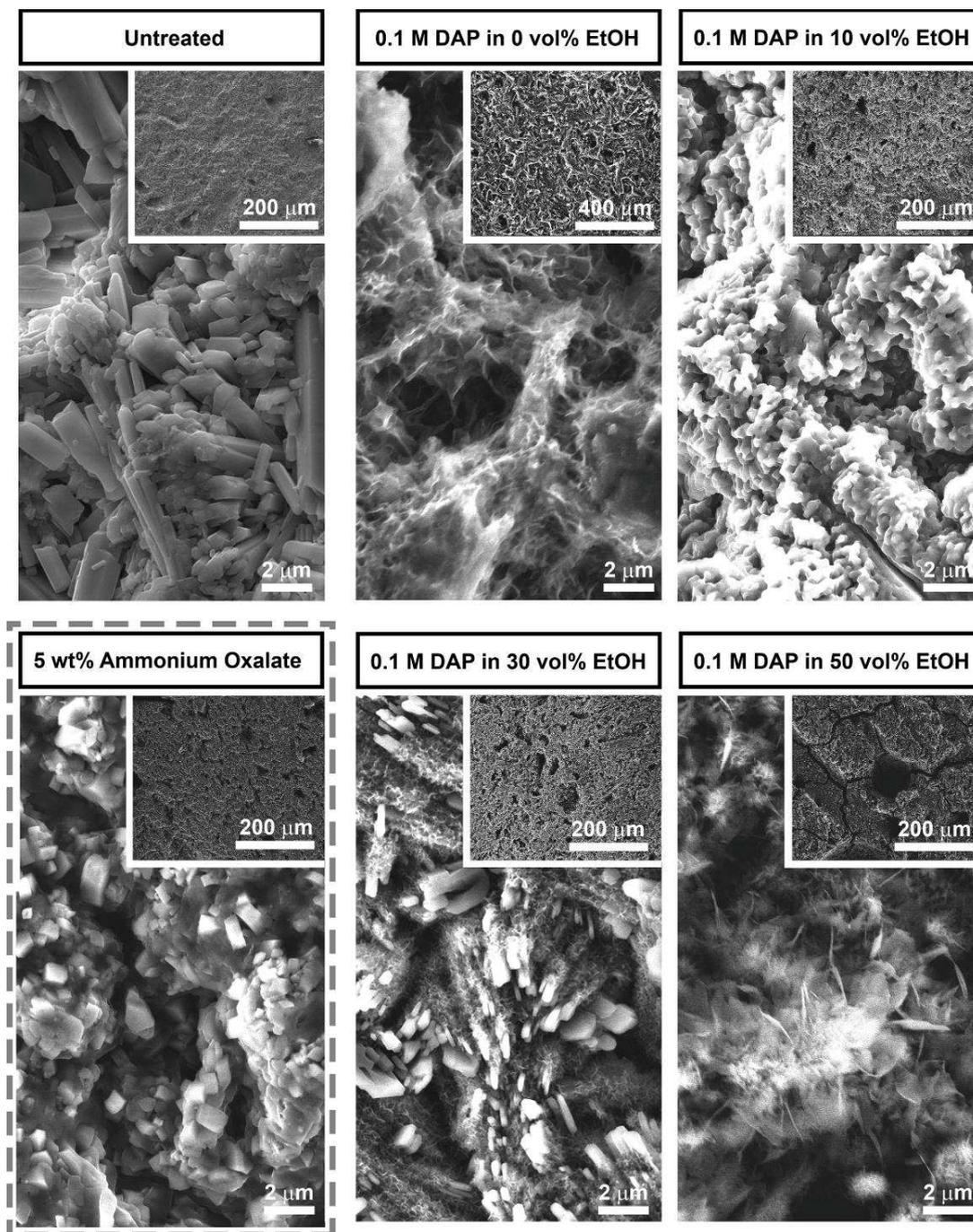
### 270 3.1. Gypsum stuccoes

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.

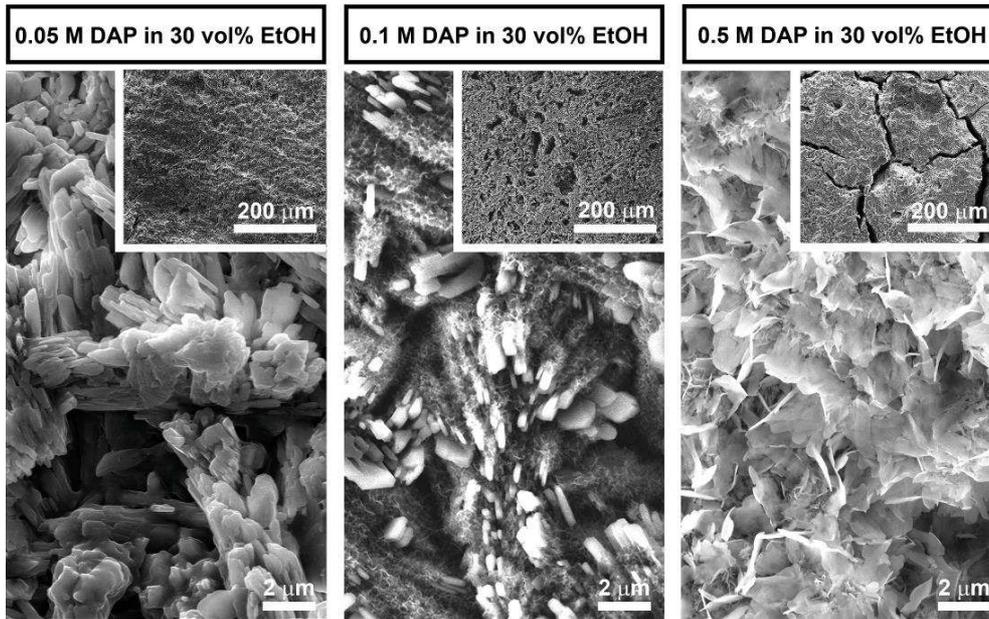


275  
276 **Figure 3.** Mineralogical composition of the new CaP phases formed by treating gypsum  
277 samples with different formulations of the phosphate treatment, to investigate the effect of  
278 ethanol concentration (top), DAP concentration (medium) and pH increase to 10 at various DAP  
279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



280

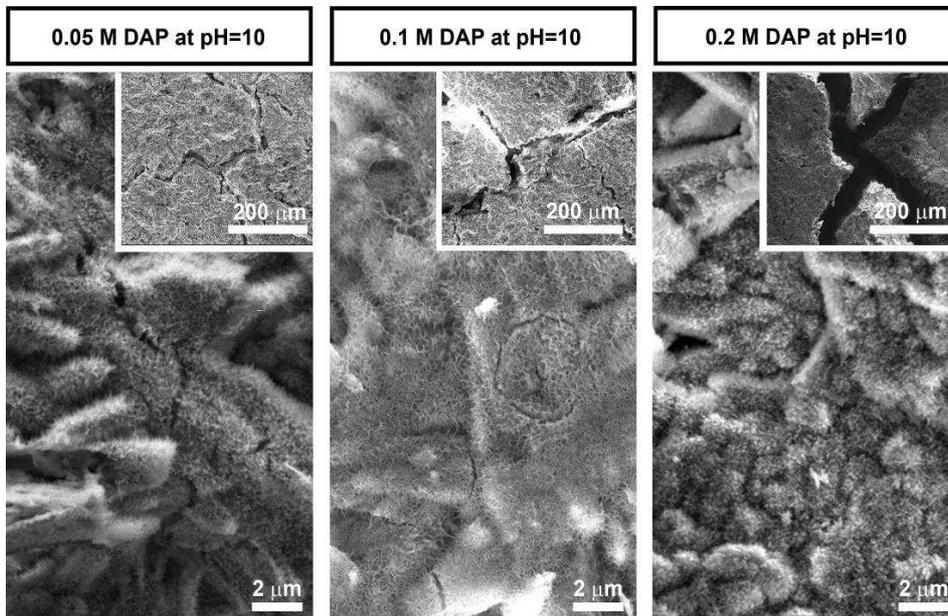
281 **Figure 4.** Morphology of the new CaP phases formed by reacting gypsum with different  
282 formulations of the phosphate treatment, to investigate the effect of ethanol concentration. For  
283 comparison's sake, also the untreated reference and whewellite formed after treatment with  
284 ammonium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

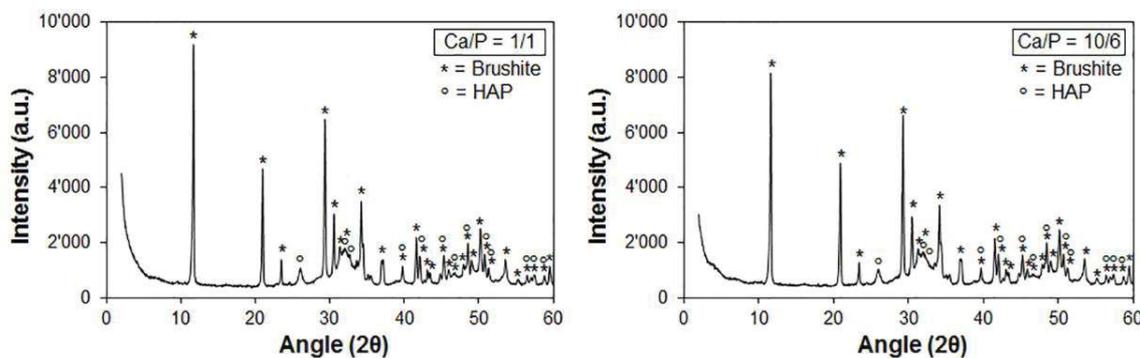
304 When the effect of increasing the DAP concentration was investigated, the modification  
305 in phase composition and morphology reported in Figure 3 and Figure 5, respectively,  
306 was obtained. Whereas brushite was the main phase formed at 0.05 and 0.1 M DAP,  
307 HAP (exhibiting a clearly different 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  $\text{HPO}_4^{2-}$  ions) is kinetically  
320 favored over HAP (requiring  $\text{PO}_4^{3-}$  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  $\text{HPO}_4^{2-}$  ions, 0.0039 M  $\text{H}_2\text{PO}_4^-$  ions and only  $3.3 \times 10^{-5}$  M  
325  $\text{PO}_4^{3-}$  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  $\text{CaCl}_2$  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  $\text{HPO}_4^{2-}$  ions needed to form brushite are more easily available than  $\text{PO}_4^{3-}$  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  $\text{PO}_4^{3-}$  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 ( $\text{CaHPO}_4$ , 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.

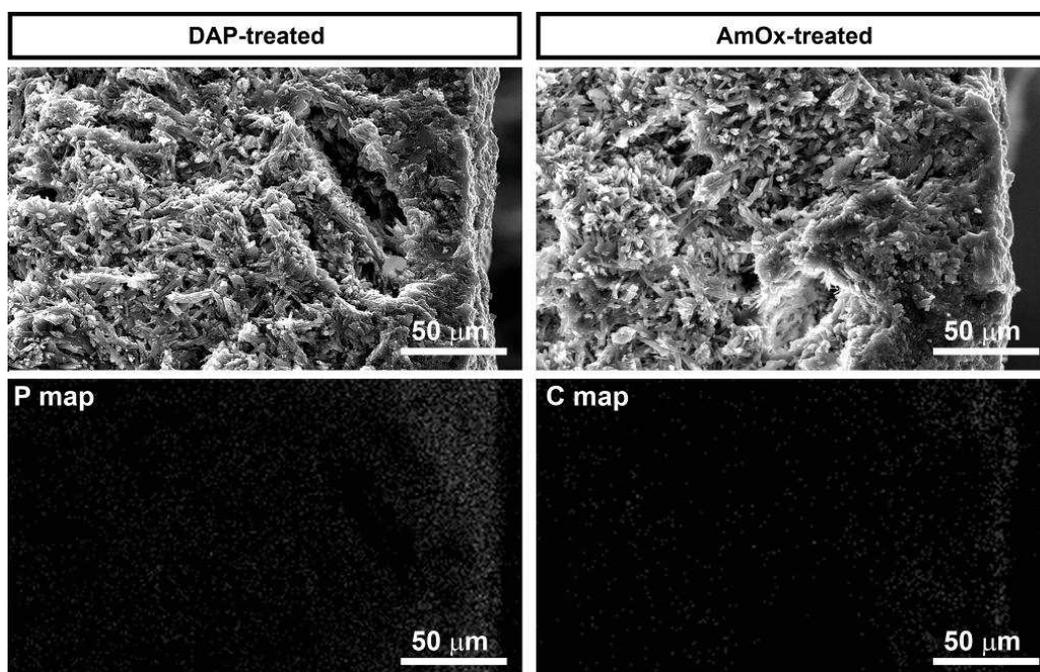
393

	Untreated	DAP	Variation	AmOx	Variation
$E_d$ (GPa)	9.9 ( $\pm 0.4$ )	10.3 ( $\pm 0.1$ )	+3%	11.1 ( $\pm 0.6$ )	+12%
$E$ (GPa)	4.0 ( $\pm 0.5$ )	4.2 ( $\pm 0.2$ )	+5%	4.0 ( $\pm 0.2$ )	0%
$\sigma_t$ (MPa)	3.4 ( $\pm 0.7$ )	3.8 ( $\pm 0.2$ )	+13%	3.3 ( $\pm 0.6$ )	-3%
$\Delta w$ (%)	9.5	7.9	-17%	9.5	0%

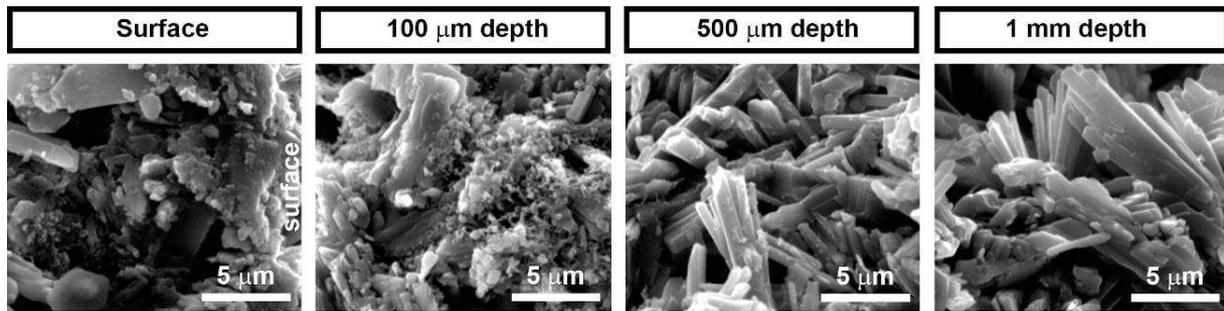
394 **Table 2.** Mechanical properties and weight loss after immersion in water of untreated and  
 395 treated samples ( $E_d$  = dynamic elastic modulus;  $E$  = static modulus;  $\sigma_t$  = tensile strength;  $\Delta w$  =  
 396 weight loss). Values of mechanical properties are averages for 5 samples (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  $\mu\text{m}$   
405 from the surface. Traces of new CaP phases were observed at a depth of 500  $\mu\text{m}$  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  $\mu\text{m}$  depth, only  
421 minor traces of new CaP phases are visible at 500  $\mu\text{m}$  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  $\text{NH}_4^+$  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 kocktaite) 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.

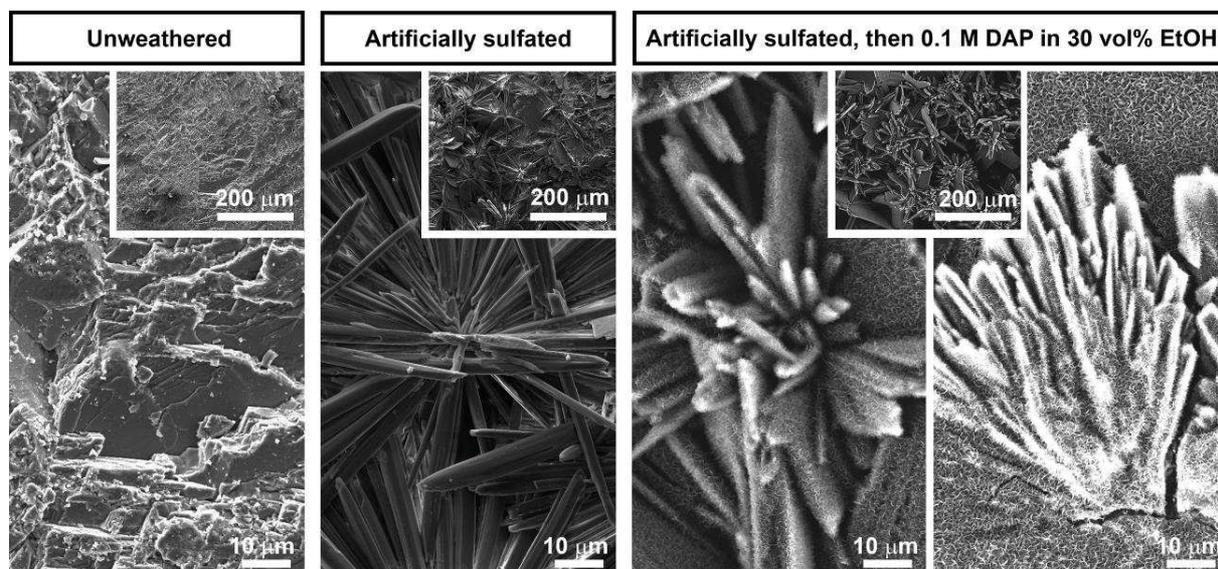
465 In the case of the DAP treatment, thanks to gypsum conversion to brushite, a 17%  
466 reduction in weight loss after prolonged exposure to water was registered. The reason  
467 why the reduction was not higher (in spite of brushite being about 27 times less soluble  
468 than gypsum [15]) is thought 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 H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> 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  $\text{HPO}_4^{2-}$  ions (by far the most abundant species originated from  
529 DAP dissociation) while HAP requires  $\text{PO}_4^{3-}$  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  $\mu\text{m}$  from the surface and present only in traces at a depth of 500  $\mu\text{m}$ .  
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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