Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Calcium phosphate coatings for marble conservation: Influence of ethanol and isopropanol addition to the precipitation medium on the coating microstructure and performance

This is the final peer-reviewed accepted manuscript of:

Sassoni E., Graziani G., Franzoni E., Scherer G.W., Calcium phosphate coatings for marble conservation: influence of ethanol and isopropanol addition to the precipitation medium on the coating microstructure and performance, Corrosion Science 136 (2018) 255–267

The final published version is available online at: DOI: 10.1016/j.corsci.2018.03.019

Calcium phosphate coatings for marble conservation: influence of ethanol and isopropanol addition to the precipitation medium on the coating microstructure and performance

Enrico Sassoni[1,*], Gabriela Graziani[1], Elisa Franzoni[1], George W. Scherer[2]

[1] Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Via Terracini 28, 40131, Bologna, Italy

[2] Department of Civil and Environmental Engineering (CEE), Princeton University, 69 Olden Street, 08542, Princeton (NJ), U.S.A.

* corresponding author: enrico.sassoni2@unibo.it

ABSTRACT

The effect of adding ethanol and isopropanol to aqueous solutions of diammonium hydrogen phosphate, used to create a passivating layer of calcium phosphates over marble, was investigated. Thanks to its weakening effect on the hydration sphere of ions in solution, ethanol allowed complete coverage of marble surface by a crack-free and pore-free layer of octacalcium phosphate. Even better results were obtained using isopropanol, because it has lower adsorption affinity to calcite than ethanol. Treatments involving alcohols provided good acid protection and also restored cohesion among calcite grains in weathered marble.

KEYWORDS

1. INTRODUCTION

Dissolution in rain is one of the major causes of deterioration of marble artworks exposed outdoors. Corrosion of marble is a consequence of the aqueous solubility of its constituent mineral, calcite, whose solubility product at 25°C is $K_{sp} = 5 \cdot 10^{-9}$ [1]. The dissolution rate of calcite is a function of pH, amounting to ~10^{-10} mol/(cm^2·s) at pH 5.6 [2] and sensibly increasing for lower pH [1].

In the past decades, when high SO_x concentrations were present in the atmosphere in Europe and USA, with consequent low rain pH, recession rates of carbonate stone surface up to 130 µm/year were reached [4]. Nowadays, after traffic regulations policies in Europe and USA led to a significant decrease in SO_x concentrations, so that rain generally has pH~5 [5,6], the average surface recession rate is estimated to be ~10 µm/year and is expected to remain substantially stable until the end of the century [6]. Such a dissolution rate, although less dramatic than in the past, is still sufficient to cause the loss of carved elements and inscriptions over a period of one century. Moreover, in countries where regulation of atmospheric pollutants has started only recently, high surface recession rates are still experienced, because of low rain pH (e.g., pH values as low as 3.4 are still experienced in China [7]). To assess the rates of marble surface recession, to investigate its dependence on climatic factors and pollutant concentrations and to predict future recession rates in a changing climate, several research projects have been funded by the European Union and the US [8-12].

To arrest surface recession of marble artworks exposed to rain, materials science has been researching protective coatings to inhibit calcite dissolution. Two main routes have been pursued: (i) developing organic protectives that modify the wettability of marble surface and (ii) developing inorganic protectives that form a superficial layer with reduced solubility. Although effective, organic protectives (such as acrylic resins and fluorinated polymers) exhibit several limitations in terms of compatibility with the substrate and durability [13]. In turn, inorganic protectives generally exhibit a limited effectiveness [14]. The most widely used inorganic treatment is formation of a passivating layer of calcium oxalate monohydrate (whewellite) over marble surface, by reaction with an aqueous solution of ammonium oxalate [15]. Even if the so-formed layer of whewellite generally exhibits a good ability to completely cover marble surfaces, still the solubility of whewellite is only slightly lower than that of calcite (Table 1), so that only limited protecting efficacy is achieved [16]. To improve the performance of the oxalate treatment, several innovative approaches are being explored [17,18].

As an alternative to calcium oxalate, in 2010 we started investigating the use of calcium phosphates (CaP) to form a passivating layer over marble. The idea is forming hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$, the most stable CaP at pH > 4 [19]) by reacting marble with an aqueous solution of diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$) [20,21], according to the reaction:

$$10CaCO_3 + 5(NH_4)_2HPO_4 \rightarrow$$
$$Ca_{10}(PO_4,CO_3)_6(OH,CO_3)_2 + 5(NH_4)_2CO_3 + 3CO_2 + 2H_2O.$$
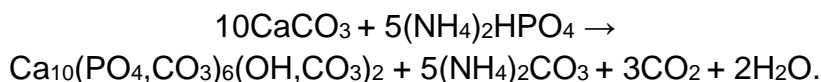
HAP has much lower solubility and slower dissolution rate than calcite, but still very close lattice parameters (Table 1). Therefore, formation of a well-adhering layer of HAP over marble is expected to provide significant protection from dissolution in rain.

However, results obtained so far on the protecting ability of so-formed HAP coatings over marble have been not as good as theoretical considerations would suggest [1,22]. This has been ascribed to the presence of microcracks and pores in the coating, which let acid reach the substrate and trigger its dissolution. Microcracks are likely originated by stress arising in the pores during drying of the film [3]. Drying can cause cracking when the film thickness exceeds a critical value, below which cracking is thermodynamically unfavoured [23]. Pores are suspected to be present in the coating based on its morphology, even if cross sections obtained by encapsulating samples in epoxy resin apparently revealed a dense microstructure [3].

To prevent formation of microcracks in the HAP coating, a possible route is to lower the concentration of DAP in the starting solution. However, previous studies have shown that, if a low DAP concentration (e.g., 0.1 M) is used, a very long treating period (e.g., a few weeks) is needed to obtain complete coverage of the marble surface [20]. To speed up coating formation at low DAP concentration, addition of a calcium source (e.g., 0.1 mM CaCl$_2$) has proven to have a strong impact [20]. Nonetheless, the coating obtained in these conditions is still patchy [22]. In a recent study, we have shown that it is possible to reduce the DAP concentration and still achieve complete coverage of the marble surface with a crack-free coating, by adding small amounts of ethanol to the DAP solution [22]. Starting from this work, the present study has the following goals:

1) To elucidate the influence of ethanol on formation of the CaP coating and systematically investigate how the ethanol concentration, the reaction time, the pH and the DAP concentration, as well as the type of alcohol, influence the surface coverage, the mineralogical composition and the presence of microcracks and pores in the coating. To this end, cross sections of the CaP film were obtained and analysed by a focused ion beam microscope (FIB-ESEM).

2) To evaluate the protective ability of the most promising formulations of the phosphate treatment, in comparison with ammonium oxalate, taken as a reference.

3) For the same formulations, to evaluate the consolidating ability (i.e., the ability to restore mechanical properties of weathered marble), again in comparison with ammonium oxalate.

The latter issue was investigated because the ability to form a crack-free layers may have a positive impact also in the use of DAP solutions as consolidants.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Marble

Carrara marble was selected for the tests, because this lithotype was widely used in historic architecture and sculpture all over Europe, so that it is often adopted in research studies on marble deterioration and conservation [1,24-27]. A slab with $50\times50\times1$ cm^3 size was purchased from BasketweaveMosaics.com (USA) and sawn into cubic and prismatic specimens. Cubes with 1 cm side were used for the tests to define the best treatment parameters (cf. § 2.2) and to evaluate the protection provided by the coating (cf. § 2.3). Prismatic specimens ($5\times5\times1$ cm^3) were used to evaluate the treatment's consolidating ability (cf. § 2.4).

2.1.2. Chemicals

For the phosphate treatments, diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$, assay > 99%, Sigma Aldrich), calcium chloride ($CaCl_2 \cdot 2H_2O$, assay > 99%, Sigma Aldrich), ethanol (EtOH, Fisher-Scientific), isopropanol (IPA, Fisher-Scientific) and ammonium hydroxide (NH_4OH, ACS Grade) were used. For the oxalate treatments, ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$, assay > 99%, Sigma Aldrich) was used. All water was deionized.

2.2. Definition of treatment parameters

The formulation of the phosphate treatment developed in [3] and tested in [1], consisting in a 1 M DAP + 1 mM $CaCl_2$ aqueous solution, was taken as a comparison term (labelled as "1 M DAP"). $CaCl_2$ addition is used to favor the surface coverage and inhibit dissolution of the calcite surface, as indicated by theoretical calculations reported in [3].

The possible improvement of this formulation, in terms of surface coverage and microstructure, was investigated by exploring the influence of the parameters described in § 2.2.1 - § 2.2.5. A summary of the investigated parameters is reported in Figure 1. Treatment by a 5 wt% aqueous solution of ammonium oxalate (labelled as "AmOx") was also taken as a commercial benchmark. All treatments were performed by immersing a cubic specimen in a plastic container with 200 ml of solution and then rotating the containers to ensure stirring of the solutions during treatment. The treatment duration was 24 hours, unless otherwise specified. At the end of the treatment, the specimens were taken out of the solutions, rinsed with deionized water and then dried at room temperature. The features of the different coatings were determined as described in § 2.2.6.

2.2.1. Effect of ethanol concentration

To prevent cracking of the coating, the reduction of the DAP concentration by adding ethanol to the DAP solution was investigated, as first proposed in [22]. The effect of adding increasing amounts of ethanol to an aqueous solution containing 0.1 M DAP and 0.1 mM $CaCl_2$ was evaluated. Ethanol concentrations of 0, 0.6, 2.5, 6, 10 and 30 vol% were tested, in all cases replacing water with ethanol, so as to maintain constant the DAP and $CaCl_2$ concentrations in the total liquid.

2.2.2. Effect of pH

When pH is not controlled, an aqueous solution containing 0.1 M DAP and 0.1 mM $CaCl_2$ has pH 8. Because a higher amount of PO_4^{3-} ions (needed to form HAP) is expected to form from DAP dissociation in water at higher pH [19], the effect of increasing the pH of the DAP solution to 10 was investigated. In a previous study, we tried to increase the pH using NaOH [22], but the resulting coating exhibited limited acid resistance, likely because of the formation of soluble phases [22]. Therefore, in the present study we used NH_4OH to adjust the pH, to prevent the cation from the base from influencing the coating composition. The effect of replacing water with an increasing amount of ethanol (0, 1, 3, 6, 8 and 10 vol%) was also investigated. The possible further reduction of the DAP concentration from 0.1 M to 0.01 M and 0.001 M, when pH is increased to 10 and 6 vol% EtOH is added, was also explored.

2.2.3. Effect of treatment duration

For the formulation that gave the most promising results (viz., 0.1 M DAP + 0.1 mM $CaCl_2$ with 10 vol% EtOH at pH 8), the effect of treating samples for shorter (12 hours) and longer time (48 hours) was investigated.

2.2.4. Effect of double treatments

For the same formulation as above (solution containing 0.1 M DAP, 0.1 mM $CaCl_2$ and 10 vol% EtOH at pH 8), the effect of repeating the treatment twice (after drying after the first treatment) was also investigated.

2.2.5. Effect of alcohol nature

The effect of using IPA instead of EtOH was investigated, by testing a solution containing 0.1 M DAP, 0.1 mM $CaCl_2$ and 10 vol% IPA at pH 8.

2.2.6. Characterization techniques

The coverage of marble surface by the new coatings, their morphology and the possible presence of microcracks were assessed by observation with an environmental scanning electron microscope (FEI Quanta 200 FEG ESEM), equipped with an energy dispersive x-ray spectroscopy device (Oxford Instruments EDS probe). To prevent charging during ESEM observation (performed in high vacuum to increase the image quality), samples were made conductive by carbon coating.

6

The possible presence of pores inside the coatings was assessed by cutting cross sections using a focused ion beam SEM (FEI StrataTM DB 235 FIB). In this case, samples were carbon coated twice: before cutting the cross section in the FIB-SEM and then again before observing the cross section using the ESEM, to make sure that also the cross section itself was conductive.

The mineralogical composition of the coatings was assessed by grazing incidence diffractometry (GID), which reveals the composition of superficial layers without interference from the substrate, thanks to the low penetration depth of the incoming radiation (a few hundreds of nanometers from the surface). A Bruker D8 Discover X-Ray Diffractometer was used (incidence radiation $\theta=0.5°$, detector scan range $2\theta=3-55°$, step size = 0.02 θ, step time = 0.4 s, kV = 40, mA = 40).

The increase in the amount of PO_4^{3-} ions caused by ethanol and IPA addition was determined as follows. Four solutions were prepared containing 0.1 M DAP and 0.1 mM $CaCl_2$ and increasing amounts of alcohol: 0, 10 and 30 vol% EtOH and 10 vol% IPA (the total volume of solvent remaining constant). The PO_4^{3-} concentration in each solution was then measured by first adding a marker based on the ascorbic acid method (HI 93713 reagent, Hanna Instruments) and then measuring the intensity of the colour shift towards blue (which is a function of the PO_4^{3-} concentration) by using a photometer (HI 83200, Hanna Instruments).

2.3. Protective ability

The treatments reported in Table 2 were selected for testing their ability to provide protection against marble dissolution in acid. Cubic specimens were immersed in 200 ml of an aqueous solution of HNO_3 at pH 4.75 (chosen to resemble realistic values of rain pH in Europe nowadays [6]), and the pH increase over time was recorded using a Oakton pH-meter (pH 1100 series). The acid solution was continuously stirred using a magnetic stirrer. To prevent atmospheric CO_2 from altering the solution pH and to prevent evaporation during the test, the beaker containing the solution was sealed using Parafilm® (allowing only the pH probe to pass through the Parafilm® to reach the solution).

Since the edges of the cubic specimens exhibited some coating deterioration at the end of the treatment (because rotation for 24 hours in the plastic containers caused abrasion near the edges), 5 faces of the cubes and the edges of the sixth face were sealed using an impermeable layer of nail polish (Eternal Nail Enamel). In this way, a central area of 8×8 mm^2 was isolated in the centre of the sixth face of the cube and only this area was subjected to the acid attack test. The impermeability of the coating to the acid solution had been preliminarily assessed by testing entirely coated samples, which caused no pH increase for the whole duration of the test. Even if none of the cube faces was polished, still the freshly sawn faces were rougher than the faces sawn by the marble supplier, so each treatment formulation was tested

twice: once on a rougher face and once on a smoother face. The average for the two measurements was then calculated and used to compare the different treatments.

After the test, the coating resistance was also qualitatively evaluated by observing samples subjected to acid attack test by ESEM (after carbon coating).

2.4. Consolidating ability

The ability of the investigated formulations (Table 2) to restore cohesion among calcite grains was tested on artificially aged samples. Such samples were used instead of fresh samples because, in the latter case, the micro-cracks among calcite grains, which consolidants are supposed to bond, would be absent. Therefore, artificially aged samples were produced that exhibited decohesion of grains and micro-cracks similar to those of naturally weathered marble needing consolidation. Artificially aged specimens were produced following a novel method we have recently developed [28]. The idea is to obtain specimens with a gradient in properties (greater damage near the surface, as is the case of naturally weathered marble [27,29]), by placing specimens in contact with a hot plate at a certain temperature for a certain time, calculated by a mathematical model [28]. In the present study, half of the specimens were subjected to 200 °C for 20 seconds and half to 300 °C for 20 seconds. In both cases a 5×1 cm^2 face was placed on the hot plate, while the sides and the top of the specimens were wrapped with a thermal insulator, to ensure mono-directional heat flux. Based on the mathematical model, in these conditions the first 1 cm from the heated surface is expected to undergo a decrease in dynamic elastic modulus (E_d) of -35% and -42%, respectively, whereas the rest of the specimen should remain unaltered [28]. E_d was selected as a meaningful and reliable mechanical parameter to track artificial weathering and then consolidation of the specimens, because E_d has been shown to be very sensitive to the opening and healing of microcracks [30,31].

To evaluate the effects of artificial aging, E_d was determined before heating and after cooling, on exactly the same sample, taking advantage of the non-destructive nature of the measurement. E_d was determined by measuring the ultrasonic pulse velocity v across the 5 cm side of the specimens (parallel to the heated surface) and then calculating E_d according to the formula $E_d = \rho\ v^2$, where ρ is the density. v was measured using a PUNDIT instrument with 54 kHz transducers, inserting a rubber couplant between the specimen and the transducers, to improve the contact. For each sample, the measurement was carried out: (i) in the first 1 cm from the heated surface, i.e. the part damaged during the artificial ageing; (ii) in the opposite part of the specimen (i.e., the part at 4 to 5 cm from the heated surface), that should remain unaltered during artificial ageing.

For each heating temperature (200 or 300 °C), one specimen was consolidated for each formulation reported in Table 2. Specimens were treated by vacuum

impregnation, to ensure the solutions penetrate deeply into the microcracks developed by artificial aging. After reacting for 24 hours, samples were rinsed with deionized water and then dried at room temperature.

Then, E_d measurements were repeated on the treated samples, again in the following two parts: (i) in the first 1 cm from the heated surface (the most damaged part during artificial aging), to assess the treatment ability to restore cohesion among loose calcite grains; (ii) in the part at 4 to 5 cm from the heated surface (unaltered during artificial ageing), to check whether overconsolidation of the sound part occurred.

After the E_d measurement, the formation of new phases in the microcracks among calcite grains was assessed by ESEM observation of fracture samples obtained by chisel from the tested specimens.

2.5. Aesthetic compatibility

Any treatment intended for application to cultural heritage objects is required not to significantly alter the aesthetic appearance of the treated material, so the colour change caused by the investigated treatments was determined. Measurements were performed on the same prismatic specimens (5×5×1 cm^3) used for the E_d tests. The LABCIE colour parameters (L^* = black÷white, a^* = green÷red, b^* = blue÷yellow) were determined using a NH310 colorimeter. The color change (ΔE^*) was calculated as $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$. For each condition, the color change was calculated as the average for three measurements.

3. RESULTS AND DISCUSSION

3.1. Effect of ethanol concentration

When no ethanol is added to a 0.1 M DAP and 0.1 mM CaCl$_2$ solution, no CaP coating is formed over calcite (Figure 2). This is a consequence of the very low amount of PO$_4^{3-}$ ions (needed to form HAP), originating from DAP dissociation at pH 8 (Table 3). When 0.6 or 2.5 vol% ethanol is added, some isolated new CaP phases are formed, but the coating is far from being continuous. When the ethanol amount is increased to 6 vol%, a more uniform coating is formed, however still exhibiting several bare areas (Figure 2). A continuous coating is achieved when the ethanol amount is further increased to 10 and 30 vol% (Figure 2). In the case of 30 vol% addition, some precipitation of CaP particles occurred already in the solution, leading to particle deposition over the coating. This makes the 10 vol% addition preferable, because it allows complete coverage of the marble surface with only a few particles deposited over the coating (Figure 2).

9

In addition to the increased surface coverage, ethanol addition also had a significant effect on the coating microstructure and tendency to crack. If one compares a specimen treated with a solution containing 0.1 M DAP, 0.1 mM $CaCl_2$ and 10 vol% ethanol ("EtOH" sample) with a specimen treated with a 1 M DAP and 1 mM $CaCl_2$ solution ("1 M DAP"), the following observations can be made. In both cases complete coverage of the marble surface is achieved. However, the "1 M DAP" specimen is affected by some cracking, likely developed during drying, while the "EtOH" specimen exhibits no visible cracks (Figure 3). In terms of porosity of the coating, FIB-SEM revealed that numerous large pores are present in the "1 M DAP" specimen (Figure 3), which are expected to negatively affect the acid resistance (cf. § 3.1.6). On the contrary, the "EtOH" specimen exhibits a much denser microstructure and no visible pores (Figure 3), apart from the top of the coating (right after the platinum layer), where the typical flower-like morphology of CaP is present. Notably, at the interface between the calcite substrate and the CaP coating (about 2-4 µm thick), good adhesion seems present (Figure 4).

The addition of ethanol to the DAP solution also influenced the mineralogical composition of the coating (Figure 5). Whereas both HAP and octacalcium phosphate (OCP, $Ca_8(PO_4)_6H_2 \cdot 5H_2O$) are present in the "1 M DAP" specimen (consistently with previous observations [3]), only OCP forms when ethanol is added to the DAP solution ("EtOH" specimen). This is in agreement with the previously reported decrease in Ca/P ratio of the final calcium phosphate when ethanol is added to DAP solution [32]. In spite of being slightly more soluble than HAP (the solubility at 25 °C being ~0.0081 g/l for OCP and ~0.0003 g/l for HAP [29]), OCP is still less soluble than calcite (~0.014 g/l [29]). Therefore, formation of a non-porous and non-cracked layer of OCP over marble is expected to provide significant acid protection, superior to a cracked and porous layer of less soluble HAP.

The modifications in the coating features upon ethanol addition to the DAP solution are thought to originate from the effects that ethanol has (i) on the ions in the DAP solution and (ii) on the calcite surface:

i) When ethanol is added to an aqueous solution containing calcium and phosphate salts, the precipitation of calcium phosphates is influenced by ethanol in several (sometimes opposing) ways. Even if a decrease in crystallinity of the new CaP has been reported in some cases [32,33], ethanol is thought to enhance the CaP crystallinity [34-36] and to increase the crystallite size, because it increases the supersaturation in the medium [37]. Moreover, ethanol has been reported to intensify the interactions between the ions in the solution, because of the decrease in the dielectric constant [32]. An additional important effect of ethanol is the weakening effect it has on the hydration sphere of ions in the solution. In fact, DAP speciation in water leads to formation of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$ ions, whose relative amount depends on the solution pH [3,19]. Each species in the solution is surrounded by water molecules, constituting the so-called hydration sphere. Based on molecular dynamics simulations, the hydration shell of PO_4^{3-},

10

HPO_4^{2-}, $H_2PO_4^-$ ions has been reported to consist of 16, 20 and 20 water molecules, respectively, which are tightly bound to the ions [38]. Ethanol is able to weaken the bonds in the hydration sphere of ions dissolved in water-ethanol solutions [34,39], thus decreasing the dehydration energies and facilitating the precipitation process [39]. Upon ethanol addition to an aqueous solution of DAP, a decrease in HPO_4^{2-} content and an increase in PO_4^{3-} content have been reported [40]. This is confirmed by direct measurements of PO_4^{3-} concentration in solutions with increasing amounts of ethanol, carried out in the present study (Table 3). Compared to the case of no ethanol addition (PO_4^{3-} concentration of 0.22 mg/L), the amount increases to 0.32 and 0.76 mg/L for ethanol additions of 10 and 30 vol%, respectively (Table 3). Moreover, a further aspect that is expected to enhance CaP formation in a water-ethanol solution is the fact that OH^- groups in the ethanol molecule are adsorbed to the surface of the CaP nuclei, thus decreasing their interface energy [35]. Combined with the higher supersaturation in water-ethanol systems (compared to the aqueous systems) [35,39], this leads to a decrease in the critical nucleation free energy, so that CaP nuclei are easier to form in water-ethanol systems [35].

ii) When a water-ethanol solution is in contact with calcite (independently of the presence of phosphate ions in the solution), ethanol adsorbs to the calcite surface, orienting itself with the hydrophilic OH^- group pointing towards the ionic calcite surface and the hydrophobic CH_3 group pointing away from the surface towards the bulk solution [41]. This might be counterproductive for the goal of forming a coating over calcite, because adsorbed ethanol could actually provide a barrier to crystal growth perpendicular to calcite surface, since a hydrophobic layer is formed after the first monolayer of ethanol molecules adsorbs to the surface [42]. This risk is also enhanced by the fact that ethanol molecules are able to displace water molecules already adsorbed to the calcite surface [42]. Because ethanol adsorption to calcite surface might have a negative effect on the CaP coating formation, using a different solvent that adsorbs less strongly to calcite might be preferable, which is the reason why we also investigated the use of IPA instead of ethanol (cf. § 3.1.5).

3.2. Effect of pH

Increasing the pH of the DAP solution to 10 using NH_4OH had a huge effect on the CaP coating development, as illustrated in Figure 6. Even with no ethanol addition, at pH 10 abundant formation of new phases occurred when marble was treated with a 0.1 M DAP and 0.1 mM $CaCl_2$ solution, while no formation took place at pH 8 (Figure 2). This is a consequence of the higher amount of PO_4^{3-} ions originating from DAP dissociation at high pH [19]. However, because of excessive growth, the CaP coating is extensively cracked (Figure 6), which prevents effective acid protection. To try to avoid cracking, two routes were tested. First, increasing ethanol additions to the DAP solution were tested, to develop a more adherent coating with more refined

microstructure. As illustrated in Figure 6, a reduction in cracking and flake detachment was achieved, but cracks were not completely eliminated. Moreover, the combination of high pH and high ethanol additions led to an excessive PO_4^{3-} amount, which resulted in abundant precipitation of CaP particles over the coating (Figure 6). Therefore, considering that at higher pH a lower concentration of DAP could be enough to achieve complete surface coverage, a progressive reduction in DAP concentration from 0.1 M to 0.01 M and 0.001 M was tested (the $CaCl_2$:DAP concentration always being 1:1000). As illustrated in Figure 7, a DAP concentration of 0.01 M at pH 10 was enough to obtain complete coating of the surface. However, the coating exhibited some cracking (Figure 7). A further reduction of the DAP concentration by 10 times led to no coating formation (Figure 7), because the PO_4^{3-} content became too low. Since the boosting effect of high pH was always linked to cracking in the tested conditions, only treatments at pH 8 were considered for the prosecution of the study.

3.3. Effect of treatment duration

Considering that ethanol addition significantly favours formation of the new CaP coating, the effect of reducing the treatment duration from 24 to 12 hours was investigated. At the same time, because an evolution of the phase composition and microstructure has been reported in the literature passing from 24 to 48 hours (however in different conditions, especially without stirring of the DAP solution [43]), a longer reaction time was also considered. However, in the case of a solution containing 0.1 M DAP, 0.1 M $CaCl_2$ and 10 vol% ethanol, no remarkable difference in the coating morphology was noticeable for the different reaction times investigated (Figure 8), hence treatment for 24 hours (as recommended in [3]) was adopted for further comparisons.

3.4. Effect of double treatments

Because repeated treatments had been found to significantly improve the surface coverage of marble particles by CaP coatings [22], the effect of repeating the "EtOH" treatment twice was investigated. As reported in Figure 3, this led to formation of huge CaP flakes on top of the coating, visible both from observation of the treated surface and in the FIB cross section (Figure 3). Even if the underlying layer exhibits a much denser microstructure than the superficial flakes, the adhesion at the coating-substrate interface seems worse compared to the single application, likely because the second treatment caused excessive growth and partial detachment of the coating from the substrate.

3.5. Effect of alcohol type

As pointed out in § 3.1.1, in addition to the positive effect on the hydration sphere of ions in the solution, according to the literature ethanol also has the effect of being

adsorbed onto the calcite surface, which might be counterproductive. Therefore, we investigated the effect of using IPA instead of EtOH. IPA was selected because it has lower adsorption affinity to calcite (i.e., it binds less strongly) than EtOH [44]. In principle, methanol would have an even lower adsorption affinity [44], but it was discarded because of its toxicity. Moreover, the adsorption onto calcite by IPA molecules is expected to be lower than that by ethanol, because of steric effects. Similarly, the coverage of calcite surface was found to be lower for t-butanol (having CH_3 groups protruding laterally, hence taking more space) compared to ethanol [45]. This is expected to allow for an increased reactivity of the calcite surface in the water-IPA system, compared to the water-ethanol system, as well as for an increased reactivity of the ions in the solution.

Consistently with the theoretical expectations, the amount of PO_4^{3-} ions in solution when 10 vol% IPA was added was found to be much higher than when the same amount of ethanol was added (0.71 mg/l vs 0.32 mg/l, respectively), basically corresponding to a 30 vol% ethanol addition (0.76 mg/l) (Table 3). Accordingly, the microstructure of the CaP coating formed with IPA addition was even denser than in the case of ethanol, the interface between the calcite substrate and the coating being hardly distinguishable (Figure 3). In terms of composition, the coating consisted of OCP, as in the case of ethanol addition (Figure 5).

3.6. Protecting ability

For the most promising formulations of the phosphate treatments (namely, "EtOH", "EtOH twice", "IPA" and the reference "1 M DAP", Table 2), as well as the reference conditions "UT" and "AmOx", the results of the acid attack test are illustrated in Figure 9. Results are expressed in terms of pH increase over time of the acid solution simulating rain, in which the samples had been immersed. The appearance of the coating before and after the acid attack test is illustrated in Figure 10.

First, the stability of the solution pH when no sample was immersed was checked and no pH increase was in fact recorded. The "UT" sample caused a quick increase of pH during the test (Figure 9). This increase is due to H^+ ions in the solution being consumed as Ca^{2+} ions are released from calcite [1]. Since the Ca^{2+} concentration increases as the test proceeds, the rate of dissolution decreases, because the dissolved Ca^{2+} ions remain in the solution [1]. At the end of the test, the marble surface is significantly etched, so that single grains and grains boundaries become apparent (Figure 10).

The "1 M DAP" treatment was able to provide some protection against dissolution, as denoted by the fact that the respective curve lies well below the untreated reference (Figure 9). For instance, if one compares the time required for the solution pH to increase by 1 unit (from 4.75 to 5.75), the "1 M DAP" treatment allowed an increase from 3.9 h ("UT") to 7.3 h ("1 M DAP") (Table 2). However, at the end of the acid attack test, the coating exhibited several areas where it had been detached and removed (Figure 9). This is a consequence of the presence of cracks and pores

inside the coating (Figure 2), which allowed the acid to reach the marble substrate and trigger its dissolution, thus leading to coating detachment in some areas.

When the DAP concentration was reduced and ethanol was added to the solution, cracking was prevented and a much denser microstructure was achieved (Figure 2), which allowed a significant improvement in the protecting ability ("EtOH" sample in Figure 2). The time required for pH increase from 4.75 to 5.75 was more than doubled (from 3.9 h to 8.3 h, Table 2), and the "EtOH" curve remained below the untreated reference "UT" for the whole duration of the test (Figure 9). When observed after the acid attack test (Figure 10), the coating exhibited no diffused detachment (unlike the "1 M DAP" sample), but still some cracking, which allowed the acid to reach the substrate and cause the increase in pH registered after some time.

When repeated twice, the EtOH treatment performed a little worse, the curve basically overlapping with that of the "1 M DAP" sample (Figure 9) and the time for pH shift decreasing to 6.8 h (Table 2). Accordingly, diffused cracking was noticed when the sample was analysed after the acid attack test (Figure 10). The worsening of the treatment performance when repeated twice is in agreement with the less dense microstructure observed in the "EtOH twice" specimen (Figure 2), likely related to the excessive growth of the film during the second application.

The acid resistance of the "IPA" sample resulted improved with respect to the "EtOH" sample, especially at the beginning of the test (Figure 9), the time required for pH increase to 5.75 being the longest (8.7 h against 8.3 h for the "EtOH" sample and 3.9 h for the "UT" reference, Table 2). The ESEM observation of the coating after the acid attack test revealed that no diffuse detachment occurred, even if cracks are visible (similarly to the case of the "EtOH" sample) (Figure 10).

The "AmOx" sample, taken as a reference because it is commonly used in the onsite practice, exhibited the lowest protecting efficacy among all the investigated treatments (Figure 8). It only allowed an initial slowing down of the acid attack to marble surface, the time required for pH shift from 4.75 to 5.75 only increasing from 3.9 h ("UT") to 4.4 h ("AmOx") (Table 2). Afterwards, the curve rapidly reaches the untreated reference, meaning that the protecting efficacy is lost. Accordingly, the whewellite crystals that covered marble surface before the test are completely removed after the acid attack, revealing the underlying marble substrate, diffusely etched (Figure 10). This behaviour is a consequence of the solubility of the whewellite layer formed after treatment, which is only slightly lower than that of calcite (Table 1]). Moreover, the presence of vertical channels between the whewellite crystals (Figure 3) likely reduces the acid resistance of the coating, because these channels allow acid to reach the marble substrate. The presence of these channels is thought to be a consequence of the fact that Ca^{2+} ions needed for whewellite formation only come from dissolution of the substrate, so the presence of interconnected pores is necessary to allow the dissolved Ca^{2+} ions to move from the calcite-whewellite interface to the whewellite-solution interface, where the reaction is

proceeding [46]. Attempts to avoid this problem by adding calcium ions to the solution, as is done in the DAP solutions, was unsuccessful, owing to rapid precipitation of particles in the solution [47].

It is important to point out that, even if initially they exhibited sensibly different behaviours, the curves of the different phosphate treatments converge as the test proceeds, so that after 12 h only minor differences are present (Figure 9). This is a consequence of the fact that, even if the coating exhibits complete coverage and no cracks, still some sporadic defects can be noticed. As illustrated in Figure 11, when impurities are present over the marble surface, the formation of the coating is interrupted. The remaining bare areas are weak points, from where the attack on the marble surface can start and propagate to the adjacent areas, where the coverage was originally good. Moreover, it was observed that the continuity of the coating is sometimes abruptly interrupted at the boundary between two grains, so that one calcite grain has perfect coverage and the adjacent one remains almost bare (Figure 11). This is thought to be a consequence of the different orientation of calcite grains, which might be more or less favourable for the development of the CaP coating. In fact, epitaxial growth of HAP over calcite has been reported in the literature, but only along privileged crystallographic directions of the calcite and HAP crystals [48]. Along these directions, the distance between the phosphate groups in the HAP crystal closely matches the distance between carbonate groups in the calcite crystal, so that epitaxial growth can occur [48]. However, in marble where calcite grains have random orientation, this is generally not the case. Epitaxial growth might occur over those grains that have a particularly favourable orientation (over these grains, HAP nucleation is also favoured by the reduction in supersaturation needed for nucleation [48]) and from these grains the coating can spread to the adjacent ones with different orientation. However, when the coating development reaches grains with a particularly unfavourable orientation, formation over these grains may be impeded. Possible routes to overcome the influence of the underlying calcite crystals orientation on the development of the phosphate coating are currently being investigated.

In summary, the protecting efficacy decreased in the order IPA > EtOH > EtOH twice ≈ 1 M DAP > AmOx ≈ UT. It should be noted that the adopted acid attack test is very useful to quickly screen different protective treatments, but it is not entirely representative of the behaviour in the field. In fact, in this experimental set-up the dissolved Ca^{2+} ions are retained in the solution, which reduces the rate of diffusion of products away from the surface, thus reducing the dissolution rate [1]. Therefore, for those formulations that exhibited the best behaviour in the described test, the performance in more realistic conditions should be evaluated. This can be done by means of the custom-designed apparatus for reproducing rain drops over samples and collecting the runoff solution for analysis, as described in [49]. This is going to be the next step of the present research.

3.7. Consolidating ability

The variations in dynamic elastic modulus E_d of marble specimens after accelerated ageing and consolidation are reported in Figure 12, while the new phases formed inside the microcracks between calcite grains are illustrated in Figure 13.

After accelerated ageing by contact with a hot plate for 20 seconds, in the first 1 cm from the heated surface the specimens exhibited a 38% E_d decrease after heating at 200 °C and a 44% E_d decrease after heating at 300 °C (Figure 12). These values are in very good agreement with those predicted by the mathematical model (35% and 42%, respectively) [28], which was used to calculate the heating temperature and time required to produce damage similar to that experienced in the field by naturally weathered marble [27-29]. At the same time, the upper 1 cm of the sample underwent no substantial E_d decrease (Figure 12), as expected.

Consolidation by the "1 M DAP" treatment proved to be the most effective among all the investigated treatments, being able to increase E_d in the weathered part up to 139% (samples heated at 200 °C) and 151% (samples heated at 300 °C) of the initial value. The higher consolidating efficacy in samples with higher initial damage is consistent with previous results obtained on limestone [21]. The fact that the "1 M DAP" treatment was able to increase mechanical properties the most, in spite of the presence of cracks and pores in the formed CaP layer, derives from the following fact. Whereas in the case of *protection* it is essential that the formed coating continuously cover the surface and be crack- and pore-free, in order to prevent acid from reaching the substrate, this is not as important in the case of *consolidation*. In this latter case, the main requirement is that the newly formed material be able to seal the tip of the cracks among grains [50]. If the crack tip is effectively sealed, then the continuity of the coating and the presence of cracks and pores are not as detrimental as in the case of acid protection (however, cracks in the coating might propagate to the crack between grains, so uncracked coatings are nevertheless preferable). A potentially negative aspect of the high consolidating effectiveness of the "1 M DAP" treatment is that not only the initially deteriorated part (lower 1 cm), but also the initially sound part (upper 1 cm) underwent a significant mechanical improvement (Figure 12). This is undesired, because over-strengthening of the sound part might lead to mechanical incompatibility between the treated part and the substrate, potentially leading to its detachment [51,52]. Therefore, treatments able to restore mechanical properties of the weathered part, without causing excessive strengthening of the sound part are recommended [51,53].

The "EtOH" treatment was able to significantly improve E_d in the weathered part of the specimens (lower 1 cm), E_d being increased up to 88% and 84% of the initial value in samples heated at 200 and 300 °C, respectively (Figure 12). After a second application, E_d was basically completely restored in all specimens (E_d brought back to 106% and 93% of the initial value in samples heated at 200 and 300 °C, respectively), in both cases without causing excessive over-strengthening of the sound part (maximum E_d increase up to 114%). In the case of mechanical

16

consolidation, the fact that the microstructure of the "EtOH twice" specimens was a little less dense than specimens treated only once is not expected to be a major issue, for the reasons explained above for the "1 M DAP" treatment.

As expected, the "IPA" treatment exhibited higher consolidating efficacy than the "EtOH" treatment, E_d being restored to 94% ("IPA") instead of 88% ("EtOH") in specimens heated at 200 °C and 87% ("IPA") instead of 84% ("EtOH") in specimens heated at 300 °C. Also in this case, a second application allowed to fully restore the initial modulus in the weathered part (E_d up to 107% and 109% in specimens heated at 200 and 300 °C, respectively). In this case, however, the sound part underwent a more intense consolidation (E_d up to 122% and 130% in specimens heated at 200 and 300 °C, respectively), which might be undesired.

Specimens consolidated by "AmOx" exhibited remarkable mechanical improvement, second only to the "1 M DAP" specimens (Figure 12). In fact, the initial modulus in the weathered part was completely restored and even enhanced after a single application (E_d up to 129% and 107% in specimens heated at 200 and 300 °C, respectively), with considerable strengthening also of the sound part (E_d up to 122-125%). Such mechanical improvement is notable, considering that in a previous study we found the consolidating ability of the ammonium oxalate treatment to be very modest [29]. The poor consolidating behaviour of ammonium oxalate was ascribed to the reduced depth of formation of whewellite [29], owing to the very rapid reaction between the ammonium oxalate solution and calcite [54]. In addition to the different thickness of samples to be consolidated (1 cm in the present case, 2 cm in the previous case [29], a possible explanation for the better results obtained in this study may be the different application technique. While in the previous study the ammonium oxalate solution had been applied by brushing [29], in the present study it was applied by vacuum impregnation, which likely allowed to achieve a deeper and quicker penetration of the consolidating solution into marble microcracks, leading to higher strengthening. However, it should be noted that, given the low resistance of the newly formed whewellite to dissolution in acid, it is not unlikely that most of the mechanical improvement induced by the "AmOx" treatment could be lost after prolonged exposure to rain.

3.8. Aesthetic compatibility

The results of the colour change measurements are reported in Table 4. All the treatments caused colour changes below the so-called "just noticeable difference" detectable by human eye ($\Delta E^* = 2.3$) [55]. Considering that color changes up to $\Delta E^* = 5$ are commonly accepted after conservation works [56], all the treatments can be regarded as fully compatible from an aesthetic point of view (at least on the investigated marble). It is noteworthy that the color change increased slightly as the DAP concentration increased and as the number of applications increased, but in all cases it was below the human eye detection limit.

4. CONCLUSIONS

The present study was aimed at (i) investigating the effect of adding different alcohols to aqueous solutions of diammonium hydrogen phosphate (DAP), used to create a passivating layer of calcium phosphates over marble; (ii) optimizing the treatment conditions and (iii) evaluating the protecting and consolidating efficacy of the newly developed treatments, in comparison with a commercial benchmark. Based on the results, the following conclusions can be derived:

1) The addition of 10 vol% ethanol to an aqueous solution containing 0.1 M DAP and 0.1 mM $CaCl_2$ allows complete coverage of marble by a crack-free and pore-free coating of octacalcium phosphate (OCP). Formation of this dense coating was possible thanks to the effect of ethanol, which weakens the hydration sphere of ions in the DAP solution, thus making them more reactive. Accordingly, when ethanol is added to the DAP solution, an increase in the concentration of PO_4^{3-} ions (needed to form OCP and hydroxyapatite) was found. However, ethanol is also adsorbed on calcite surface, which might be counterproductive, because the layer of adsorbed ethanol molecules may act as a barrier preventing further reaction of calcite with the bulk phosphate solution.

2) The addition of 10 vol% isopropanol (instead of ethanol) to a 0.1 M DAP and 0.1 mM $CaCl_2$ solution was found to increase the concentration of PO_4^{3-} ions in the solution more than an equal amount of ethanol. Correspondingly, the resulting CaP coating exhibited very dense microstructure and good adhesion to the substrate. This is a consequence of the fact that isopropanol is adsorbed to calcite surface less strongly and less densely than ethanol, because of steric effects.

3) In terms of ability to protect marble from dissolution in acid, the phosphate treatments involving ethanol and especially isopropanol were able to significantly improve marble durability. The time required for the pH of the acid solution to increase by 1 unit was more than doubled in both cases, which implies a significant increase in the life of a monument after treatment with these formulations. Notably, both treatments provided more protection than ammonium oxalate, which is currently the most widely used inorganic product for marble protection.

4) In terms of ability to consolidate weathered marble, the treatments involving ethanol and isopropanol were able to significantly improve marble cohesion after a single treatment and fully restore it after a second treatment. A previously developed formulation of the phosphate treatment (namely, an aqueous solution of 1 M DAP and 1 mM $CaCl_2$) caused greater mechanical improvement, even if the resulting coating contains cracks and pores (detrimental for acid protection, but not as much for consolidation). Ammonium oxalate provided greater mechanical improvement than alcohol-containing formulations of the phosphate

18

treatment, but the latter treatments have the advantage of providing also good protection from dissolution in rain, whereas the mechanical improvement brought by ammonium oxalate might be lost after exposure in the field.

ACKNOWLEDGMENTS

REFERENCES

[1] S. Naidu, J. Blair, G.W. Scherer, Acid-resistant coatings on marble, Journal of the American Ceramic Society 99 (2016) 3421-3428

[2] P.V. Brady, Physics and chemistry of mineral surfaces, New York, CRC Press, 1996

[3] S. Naidu, G.W. Scherer, Nucleation, growth and evolution of calcium phosphate films on calcite, Journal of Colloidal and Interface Science 435 (2014) 128-137

[4] F.W. Lipfert, Atmospheric damage to calcareous stones comparison and reconciliation of experimental findings, Atmospheric Environment 23 (1989) 415-29

[5] F. Sandrolini, E. Franzoni, E. Sassoni, P.P. Diotallevi, The contribution of urban-scale environmental monitoring to materials diagnostics: a study on the Cathedral of Modena (Italy), Journal of Cultural Heritage 12 (2011) 441-450

[6] A. Bonazza, P. Messina, C. Sabbioni, C.M. Grossi, P. Brimblecombe, Mapping the impact of climate change on surface recession of carbonate buildings in Europe, Science of the Total Environment 407 (2009) 2039-50

[7] Y. Niu, X. Li, Z. Huang, C. Zhu, Chemical characteristics and possible causes of acid rain at a regional atmospheric background site in eastern China, Air Quality, Atmosphere and Health, DOI 10.1007/s11869-017-0486-8

[8] US-NAPAP Program "United States National Acid Precipitation Assessment Program" (http://ny.water.usgs.gov/projects/NAPAP/)

[9] UNECE ICP Materials Program "United Nations Economic Commission for Europe International Cooperative Program on effects on materials including historic and cultural monuments" (http://www.unece.org/env/lrtap/workinggroups/wge/materials.html)

[10] EU 5FP Project MULTI-ASSESS "Model for multi-pollutant impact and assessment of threshold levels for cultural heritage", Publishable Final Report, 2005

[11] EU 6FP Project CULT-STRAT "Assessment of air pollution effects on cultural heritage – Management strategies", Publishable Final Report, 2007

[12] EU 6FP Project NOAH'S ARK "Global climate change impact on built heritage and cultural landscapes", Publishable Final Report, 2007

[13] E. Carretti, L. Dei, Physicochemical characterization of acrylic polymeric resins coating porous materials of artistic interest, Progress in Organic Coatings 49 (2004) 282-289

[14] E. Hansen, E. Dohene, J. Fidler, J. Larson, B. Martin, M. Matteini, C. Rodrìguez-Navarro, E.S. Pardo, C. Price, A. de Tagle, J. M. Teutonico, N. Weiss, A review of selected inorganic consolidants and protective treatments for porous calcareous materials, Reviews in conservation 4 (2003) 13-25

[15] M. Matteini, Inorganic treatments for the consolidation and protection of stone artefacts, Conservation Science in Cultural Heritage 8 (2008) 13-27

[16] B. Doherty, M. Pamplona, Costanza Miliani, M. Matteini, A. Sgamellotti, B. Brunetti, Du-rability of the artificial calcium oxalate protective on two Florentine monuments, Journal of Cultural Heritage 8 (2007) 186-192

[17] P. Meloni, F. Manca, G. Carcangiu, Marble protection: An inorganic electrokinetic approach, Applied Surface Science 273 (2013) 377-385

[18] A. Burgos-Cara, E. Ruiz-Agudo, C. Rodriguez-Navarro, Effectiveness of oxalic acid treatments for the protection of marble surfaces, Materials and Design 115 (2017) 82–92

[19] S.V. Dorozhkin, Calcium orthophophates, Biomatter 1 (2011) 121-164

[20] S. Naidu, E. Sassoni, G.W. Scherer, New treatment for corrosion-resistant coatings for marble and consolidation of limestone, in Stefanaggi M., Vergès-Belmin V. (Eds), "Jardins de Pierres – Conservation of stone in Parks, Gardens and Cemeteries", Paris (F) 22-24 June 2011, p. 289-294

[21] E. Sassoni, S. Naidu, G.W. Scherer, The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones. J Cult Herit 12 (2011) 346-355

[22] G. Graziani, E. Sassoni, E. Franzoni, G.W. Scherer, Hydroxyapatite coatings for marble protection: Optimization of calcite covering and acid resistance, Applied Surface Science 368 (2016) 241-257

[23] A.G. Evans, M.D. Drory, M.S. Hu, The cracking and decohesion of thin films, Journal of Materials Research 3 (1988) 1043-1049

[24] G. S. Wheeler, S. A. Fleming, S. Ebersole, "Evaluation Of Some Current Treatments For Marble"; pp. 439-443 in "La conservation des monuments dans le bassin mediterraneen: Actes du 2° symposium international". Geneve, 19-21/11/1991, 1992.

[25] G. Royer-Carfagni, Some Considerations On The Warping Of Marble Façades: The Example Of Alvar Aalto's Finland Hall In Helsinki, Const. Build. Mater. 13 (1999) 449-457

[26] S. Siegesmund, K. Ullemeyer, T. Weiss, and E. K. Tschegg, Physical Weathering Of Marbles Caused By Anisotropic Thermal Expansion, Int. J. Earth Sci., 89 (2000) 170-182

[27] E. Sassoni and E. Franzoni, Sugaring Marble In The Monumental Cemetery In Bologna (Italy): Characterization Of Naturally And Artificially Weathered Samples And First Results Of Consolidation By Hydroxyapatite, Applied Physics A: Materials Science & Processing 117 (2014) 1893-1906

[28] E. Sassoni, G. Graziani, E. Franzoni, G.W. Scherer, New method for controllable accelerated aging of marble: Use for testing of consolidants, Journal of the American Ceramic Society (submitted)

[29] E. Sassoni, G. Graziani, E. Franzoni, Repair of sugaring marble by ammonium phosphate: comparison with ethyl silicate and ammonium oxalate and pilot application to historic artifact, Materials and Design 88 (2015) 1145-1157

[30] T. Weiss, P.N.J. Rasolofosaon, and S. Siegesmund, Ultrasonic wave velocities as a diagnostic tool for the quality assessment of marble; pp. 149-164 in Natural stone, weathering phenomena, conservation strategies and case studies. Geological Society, London, Special Publications, 205, 2002.

[31] A. Luque, E. Ruiz-Agudo, G. Cultrone, E. Sebastiàn, S. Siegesmund, Direct observation of microcrack development in marble caused by thermal weathering, Environ. Earth Sci. 62 1375-1386 (2011)

[32] A. Rodrigues, A. Lebugle, Influence of ethanol in the precipitation medium on the composition, structure and reactivity of tricalcium phosphate, Colloids and Surfaces A: Physicochemical and Engineering Aspects 145 (1998) 191-204

[33] L. El Hammari, H. Merroun, T. Coradin, S. Cassaignon, A. Laghzizil, A. Saoiabi, Mesoporous hydroxyapatites prepared in ethanol-water media: Structure and surface propertis, Materials Chemistry and Physics 104 (2007) 448-453

[34] E. Lerner, R.Azoury, S. Sarig, Rapid precipitation of apatite from ethanol-water solution, Journal of Crystal Growth 97 (1989) 725-730

[35] X. Ji, P. Su, C. Liu, J. Li, H. Tan, F. Wu, L. Yang, R. Fu, C. Tang, B. Cheng, A novel ethanol induced and stabilized nanorods: hydroxyapatite nanopeanut, J Am Ceram Soc 98 (2015) 1702-1705

[36] T. Goto, I. Yong Kim, K. Kikuta, C.Ohtsuki, Hydroxyapatite formation by solvothermal treatment of a α-tricalcium phosphate with water-ethanol solution, Ceramics International 38 (2012) 1003-1010

[37] M. Sadat-Shojai, M.T. Khorasani, E. Dinpanah-Khoshdargi, A. Jamshidi, Synthesis methods for nanosized hydroxyapatite with diverse structures, Acta Biomaterialia 9 (2013) 7591-7621

[38] C. Ebner, U. Onthong, M. Probst, Computational study of hydrated phosphate ions, Journal of Molecular Liquids 118 (2005) 15-25

[39] M.S. Tung, T.J. O'Farrell, Effect of ethanol on the formation of calcium phosphates, Colloids and Surfaces A: Physicochemical and Engineering Aspects 110 (1996) 191-198

[40] E. Babaie, H. Zhou, B. Lin, S.B. Bhaduri, Influence of ethanol content in the precipitation medium on the composition, structure and reactivity of magnesium-calcium phosphate, Materials Science and Engineering C 53 (2015) 204-211

[41] I.S. Pasarìn, M. Yang, N. Bovet, M. Glyvradal, M.M. Nielsen, J. Bohr, R. Feidenhans'l, S.L.S. Stipp, Molecular ordering of ethanol at the calcite surface, Langmuir 28 (2012) 2545-2550

[42] D.J. Cooke, R.J. Gray, K.K. Sand, S.L.S. Stipp, J.A. Elliott, Interaction of ethanol and water with the {1014} surface of calcite, Langmuir 26 (2010) 14520-14529

[43] E. Possenti, C. Colombo, D. Bersani, M. Bertasa, A. Botteon, C. Conti, P.P. Lottici, M. Realini, New insight on the interaction of diammonium hydrogenphosphate conservation treatment with carbonatic substrates: A multi-analytical approach, Microchemical Journal 127 (2016) 79–86

[44] D.V. Okhiremenko, J. Nissenbaum, M.P. Andersson, M.H.M. Olsson, S.L.S. Stipp, Energies of the adsorption of functional groups to calcium carbonate polymorphs: The importance of -OH and -COOH groups, Langmuir 29 (2013) 11062-11073

[45] N. Bovet, M. Yang, M.S. Javadi, S.L.S. Stipp, Interaction of alcohols with the calcite surface, Phys. Chem. Che. Phys. 17 (2015) 3490-3496

[46] A. Putnis, Transient porosity resulting from fluid-mineral interaction and its consequences, Reviews in Mineralogy & Geochemistry 80 (2015) 1-23

[47] S. Wang, "Formation of Nonporous Calcium Oxalate for Calcite Protection", Princeton University, 2017, unpublished work

[48] P. Álvarez-Lloret, A. B. Rodriguez-Navarro, G. Falini, S. Fermani, M. Ortega-Huertas, Crystallographic control of the hydrothermal conversion of calcitic sea urchin (Paracentrotus lividus) into apatite, Crystal Growth & Design 10 (2010) 5227-5232

[49] G. Graziani, E. Sassoni, G.W. Scherer, E. Franzoni, Resistance to simulated rain of hydroxyapatite- and calcium oxalate-based coatings for protection of marble against corrosion, Corrosion Science 127 (2017) 168–174

[50] G.W. Scherer, G.S. Wheeler, Silicate consolidants for stone, Key Engineering Materials 391 (2009) 1-25

[51] E. Sassoni, G. Graziani, E. Franzoni, An innovative phosphate-based consolidant for limestone. Part 1: Effectiveness and compatibility in comparison with ethyl silicate, Construction and Building Materials 102 (2016) 918-930

[52] E. Sassoni, G. Graziani, E. Franzoni, An innovative phosphate-based consolidant for limestone. Part 2: Durability in comparison with ethyl silicate, Construction and Building Materials 102 (2016) 931-942

[53] P. Maravelaki-Kalaitzaki, N. Kallithrakas-Kontos, D. Korakaki, Z. Agioutantis, S. Maurigiannakis, Evaluation of silicon-based strengthening agents on porous limestones, Progress in Organic Coatings 57 (2006) 140-148

[54] I. Osticioli, G. Botticelli, P. Matteini, S. Siano, R. Pini, M. Matteini, Micro-Raman analysis on the combined use of ammonium oxalate and ammonium phosphate for the consolidation and protection of carbonate stone artifacts, Journal of Raman Spectroscopy, DOI: 10.1002/jrs.5150

[55] G. Sharma, Color fundamentals for digital imaging, In *Digital color imagining handbook*, Sharma, G., Ed.: CRC Press; 2003

[56] J. Delgado Rodrigues, A. Grossi, Indicators and ratings for the compatibility assessment of conservation actions. J Cult Herit 8 (2007) 32-43
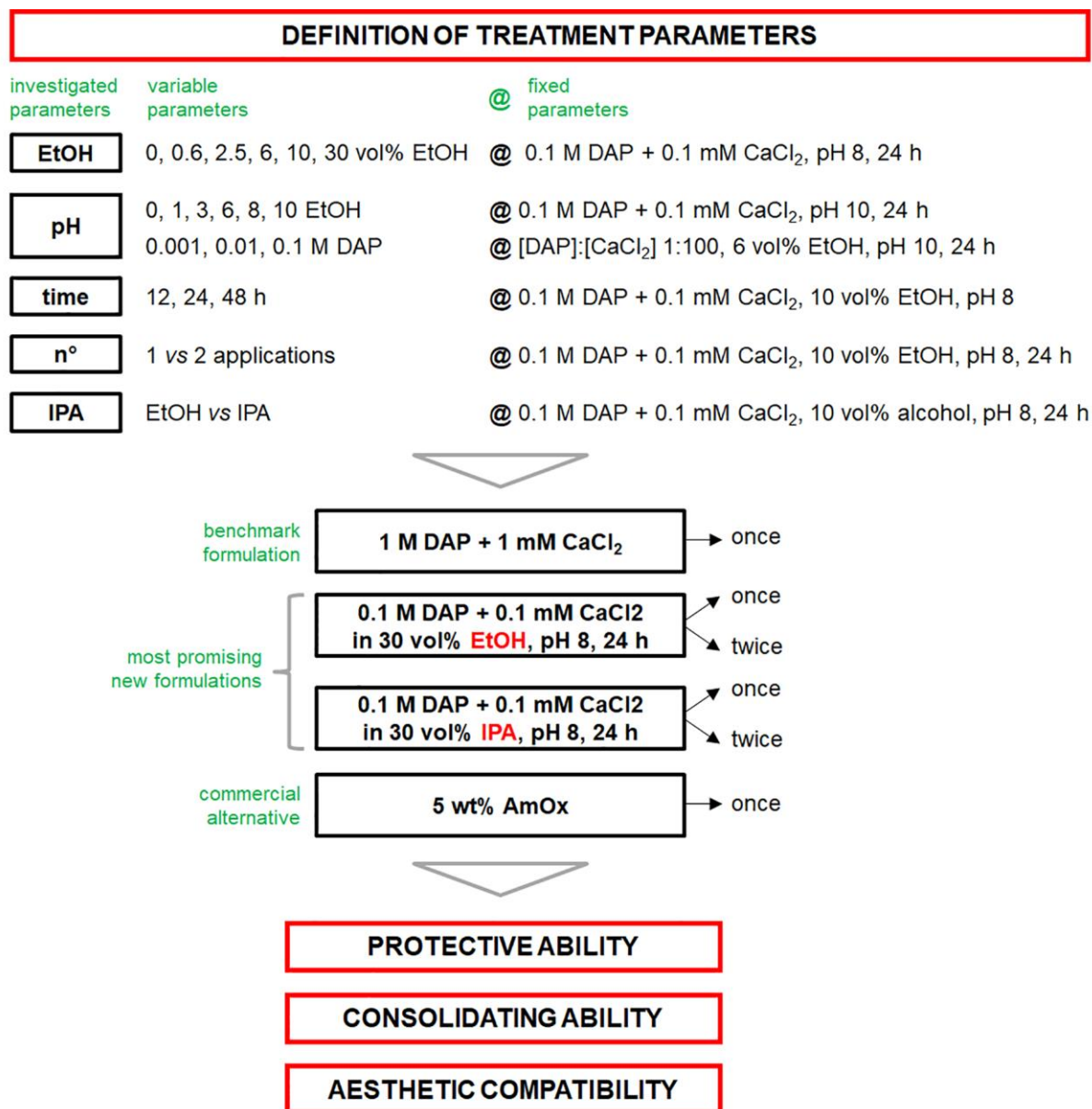
Figure 1. Scheme illustrating the investigated parameters and the whole rationale of the study.
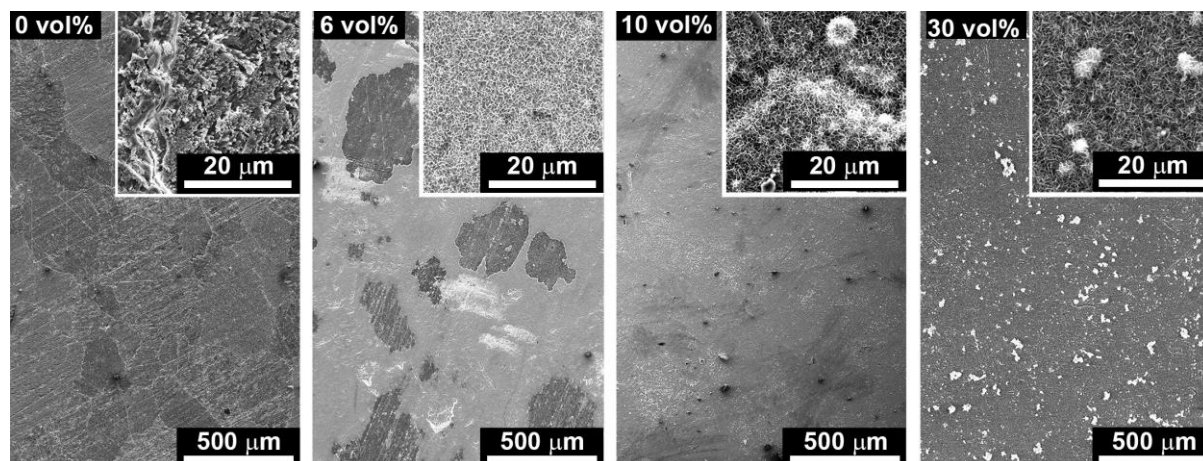
Figure 2. Coverage of marble surface by CaP coatings formed by reaction with a 0.1 M DAP and 0.1 mM CaCl₂ solution containing increasing amounts of ethanol.
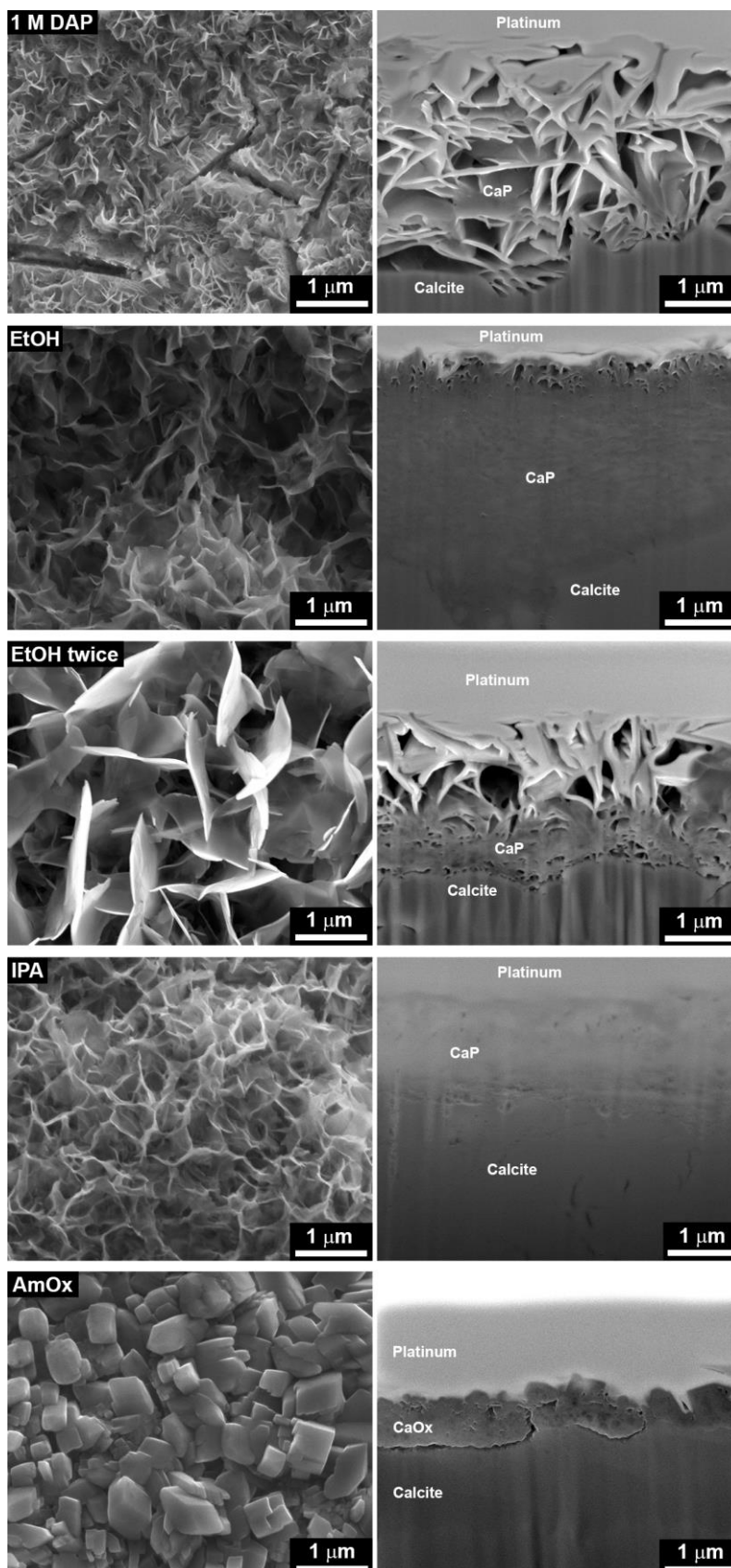
Figure 3. Surface morphology (left) and cross section (right) of marble samples subjected to different treatments.
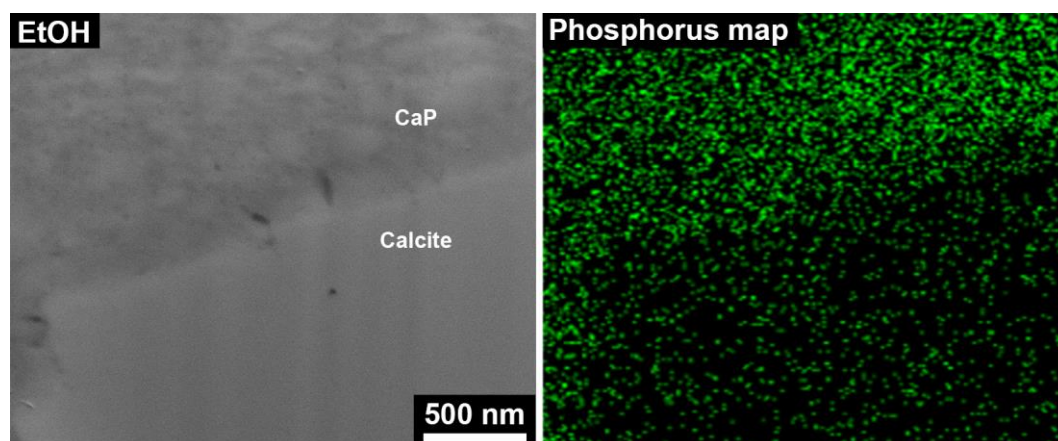
Figure 4. Interface between the calcite substrate and the CaP coating (left) and corresponding phosphorus map (right).
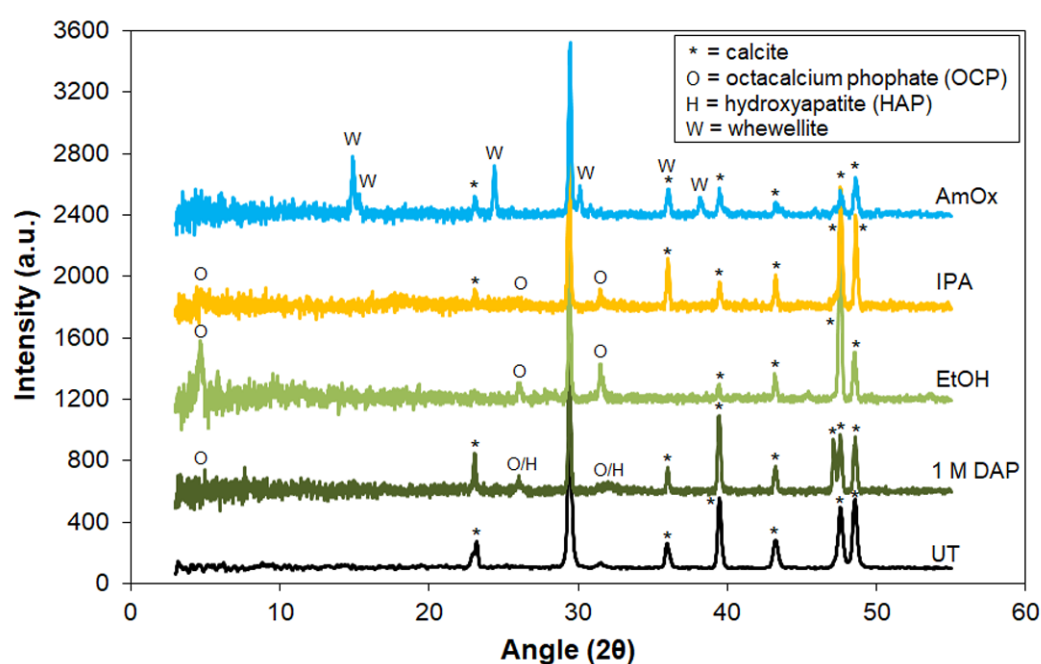
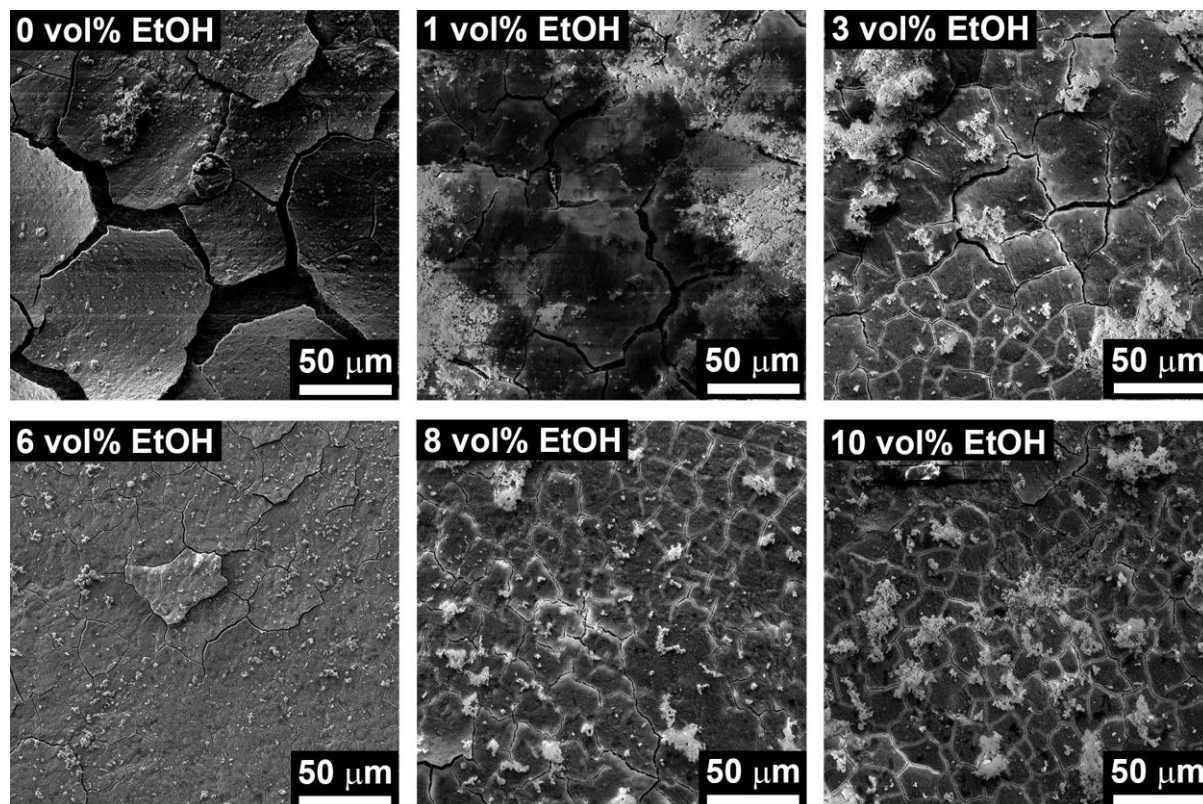**Figure 5**. Mineralogical composition of untreated and treated specimens.

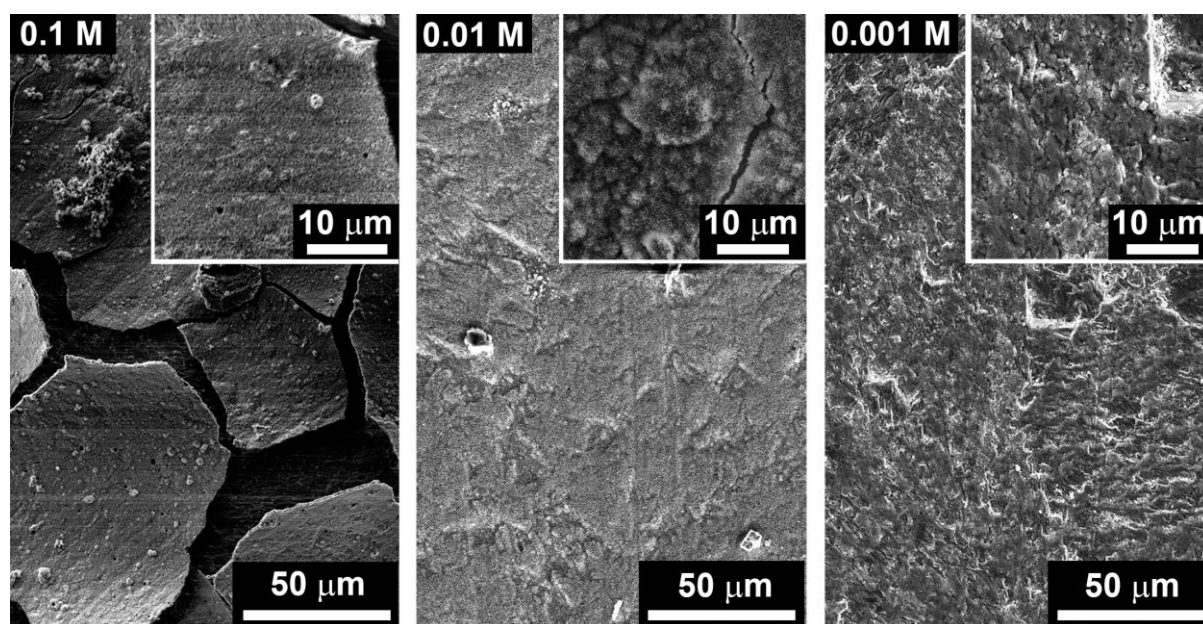**Figure 6**. Morphology of CaP coatings formed at pH 10 for increasing amount of ethanol addition to the DAP solution.

Figure 7. Morphology of CaP coatings formed at pH 10 for decreased DAP concentration and no ethanol addition to the DAP solution.
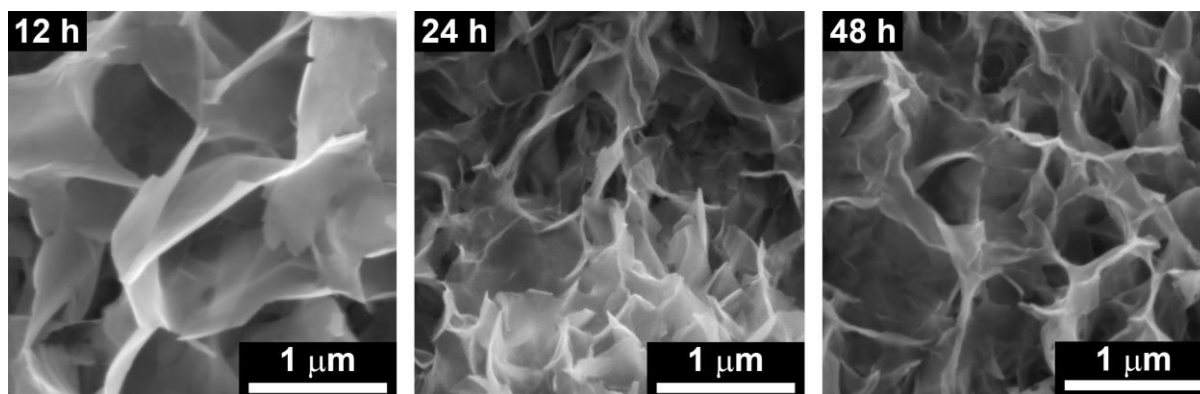
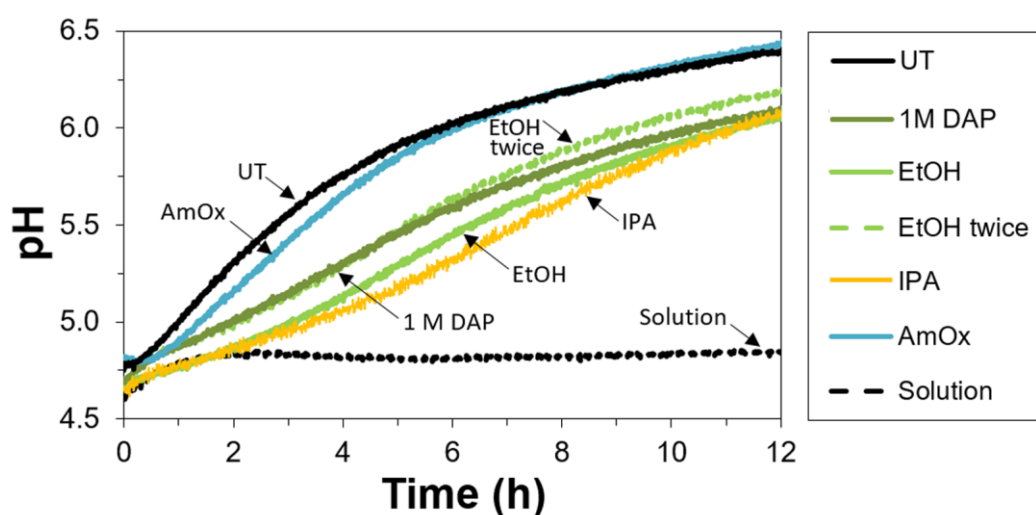**Figure 8**. Morphology of CaP coatings formed after treatment for increasing time.

Figure 9. Acid resistance (in terms of pH increase over time) of untreated and treated specimens (the curves are averages for two specimens, one tested on the rougher surface and one tested on the smoother surface). The curve of the acid solution alone (with no sample) is illustrated as well.
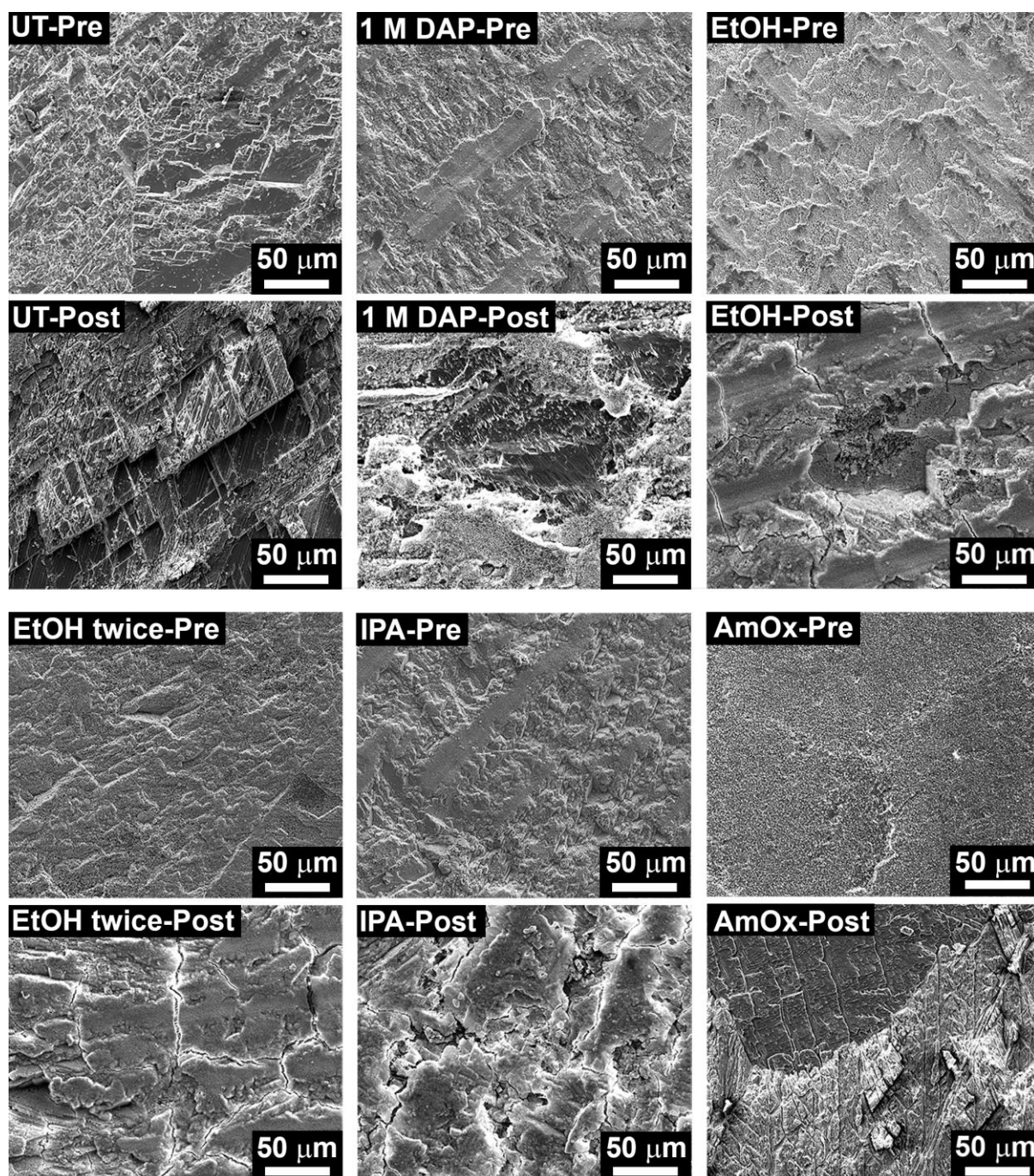
Figure 10. Surface morphology of untreated and treated specimens, before ("-Pre") and after ("-Post") the acid attack test.
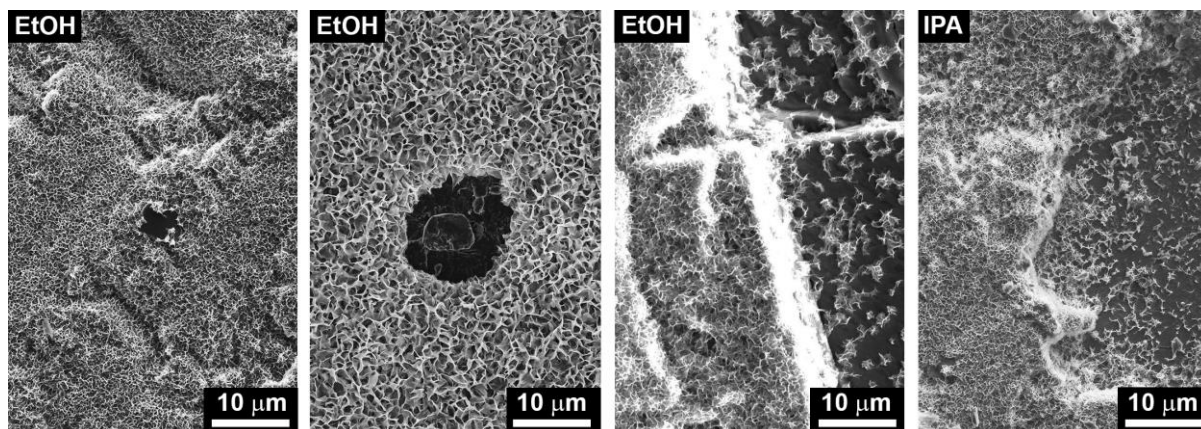
Figure 11. Interruptions in the CaP coating due to the presence of impurities (left two images) and due to the different crystallographic orientation of calcite grains (right two images).
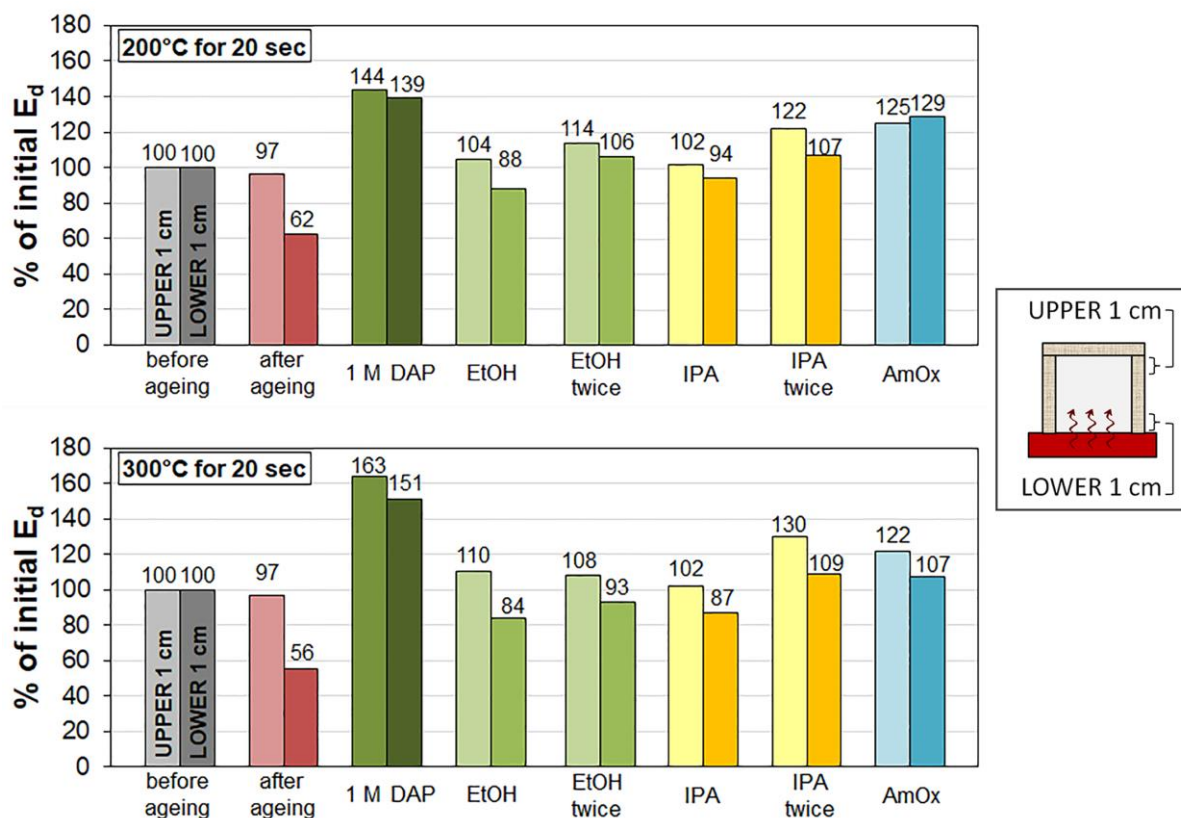

Figure 12. Variations in dynamic elastic modulus (E_d), with respect to the initial value, after accelerated ageing and after consolidation by different treatments. Values refer to the lower and upper 1 cm of the specimens, which had been subjected to accelerated ageing as illustrated in the inset: one face of the specimens was put in contact with the hot plate (in red), while the sides and the top were wrapped with a high temperature resistant insulator (in grey), to ensure the uni-directional heat flux.
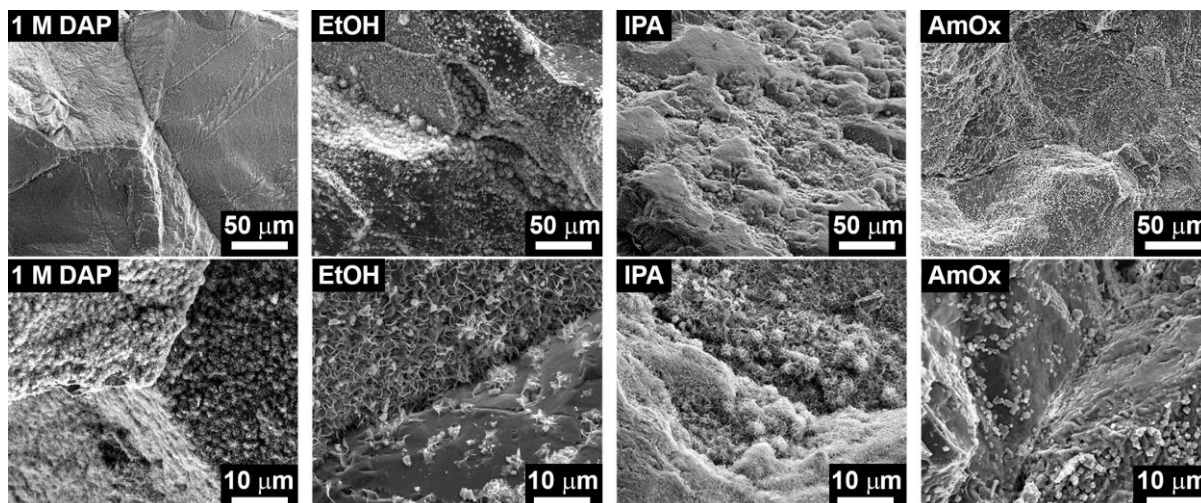
31

Figure 13. New phases formed inside microcracks between calcite grains after consolidation by different treatments.

Table 1. Solubility product K_{sp} at 25 °C [1], dissolution rate R at pH 5.6 [2,3] and lattice parameters [3] of calcite, whewellite and HAP (n.a. = not available). In the case of calcite, two molecules per unit cell are considered to show the match with HAP.

Mineral	K_{sp}	R (mol/(cm^2·s))	a (Å)	b (Å)	c (Å)
Calcite (2×)	$5 \cdot 10^{-9}$	$\sim 10^{-10}$	9.98	9.98	33.82
Whewellite	10^{-9}	n.a.	6.29	14.58	10.16
HAP	$10 \cdot 10^{-59}$	$\sim 10^{-14}$	9.43	9.42	6.88

Table 2. Labels, description of the treatment conditions considered for the acid attack test and time required for the solution pH to increase from 4.75 to 5.75.

Label	Treatment conditions	Time for pH increase by 1 (h)
UT	Untreated	3.9
1 M DAP	1 M DAP + 1 mM CaCl$_2$	7.3
EtOH	0.1 M DAP + 0.1 mM CaCl$_2$ + 10 vol% EtOH	8.3
EtOH twice	0.1 M DAP + 0.1 mM CaCl$_2$ + 10 vol% EtOH, twice	6.8
IPA	0.1 M DAP + 0.1 mM CaCl$_2$ + 10 vol% IPA	8.7
AmOx	5 wt% ammonium oxalate	4.4

Table 3. Concentration of PO_4^{3-} ions in 0.1 M DAP and 0.1 mM $CaCl_2$ solutions with different alcohol additions (values are averages for 3 samples, difference between the average and maximum/minimum values in brackets).

Sample	PO_4^{3-} concentration (mg/L)
0.1 M DAP + 0.1 mM $CaCl_2$	0.22 (± 0.12)
0.1 M DAP + 0.1 mM $CaCl_2$ + 10 vol% EtOH	0.32 (± 0.01)
0.1 M DAP + 0.1 mM $CaCl_2$ + 30 vol% EtOH	0.76 (± 0.12)
0.1 M DAP + 0.1 mM $CaCl_2$ + 10 vol% IPA	0.71 (± 0.15)

Table 4. LABCIE colour parameters and colour change after treatment (L^* = black÷white, a^* = green÷red, b^* = blue÷yellow, $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$). Values are average for 3 measurements.

Sample	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE^*
Untreated	83.46	-0.44	1.24	-	-	-	-
1 M DAP	81.46	-0.64	0.69	-1.99	-0.20	-0.55	2.08
EtOH	82.10	-0.41	1.17	-1.36	0.03	-0.06	1.36
EtOH twice	82.00	-0.43	0.68	-1.46	0.01	-0.56	1.56
IPA	82.04	-0.81	0.56	-1.42	-0.38	-0.68	1.62
IPA twice	81.46	-0.70	0.29	-2.00	-0.26	-0.94	2.23
AmOx	82.04	-0.68	0.35	-1.41	-0.24	-0.89	1.69