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New insights on protective treatments for marble by FIB-SEM

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

[1] Dept. Civil, Chemical, Environmental & Materials Engineering (DICAM),
University of Bologna, Italy

[2] Dept. Civil and Environmental Engineering (CEE), Princeton University, USA

E-mail: enrico.sassoni2@unibo.it

Abstract. In this study, we investigated by FIB-SEM the microstructure of protective coatings formed by two inorganic treatments (namely, ammonium oxalate and ammonium phosphate solutions), with the aim of identifying the factors limiting the protective efficacy of the coatings and outlining possible improvement strategies. In the case of the oxalate treatment, the resulting layer of whewellite was found to contain vertical channels, which can allow water to reach the marble surface and trigger dissolution. Possible prevention of the formation of these channels by addition of a calcium source to the oxalate solution was attempted, but even micromolar additions led to rapid precipitation in the solution. In the case of the phosphate treatment, the resulting hydroxyapatite and octacalcium phosphate coating was found to be cracked and porous. To prevent cracks and pores, diminishing the ammonium phosphate concentration and adding ethanol to the solution were found to be effective strategies, as cracks were prevented and pores were reduced almost to zero. The resulting protective efficacy of the coating was found to be significantly improved, although still not perfect.

1. Introduction

Marble sculptures and architectural decorations exposed outdoors are subject to dissolution in rain, because of the slight solubility of calcite in water [1]. To prevent dissolution, the application of protectives is often necessary. Organic protectives have been widely investigated and applied in the past decades. In spite of their high efficacy in making marble hydrophobic, thus preventing dissolution in rain, organic protectives have exhibited severe compatibility and durability issues [2]. As a consequence, the use of inorganic treatments is often preferred [3].

Inorganic treatments are aimed at forming a superficial layer of a new mineral, able to prevent dissolution of the substrate. For this purpose, the newly formed layer needs to meet several requirements: (i) it must have reduced solubility, compared to calcite; (ii) it needs to be continuous, to prevent bare areas from triggering dissolution; (iii) it needs to be crack-free and pore-free, to prevent rain from reaching the substrate by permeation through the protective layer. Whereas fulfilment of the other requirements can be relatively easily evaluated by standard techniques (e.g., XRD and SEM), assessing the presence of pores inside the coating can be challenging. SEM observation of cross sections encapsulated in resin could be one route, but possible alteration of the cross section by resin penetration and polishing needs to be taken into account.

In this study, we present an example of the use of a focused ion beam (FIB) microscope to obtain cross sections of protective coatings with minimum alteration of the original microstructure. Two inorganic protectives were considered: (i) ammonium oxalate, which is currently the most widely used

inorganic treatment; (ii) ammonium phosphate, which is receiving increasing attention because of its high potential. FIB cross sections revealed the factors limiting the efficacy of the two treatments (namely, the presence of channels in the resulting calcium oxalate layer and the presence of pores in the resulting calcium phosphate layer, respectively). This suggests possible strategies to overcome these limitations: in the case of the phosphate treatment, it was possible to significantly reduce pores and improve the protective efficacy by adding alcohol to the phosphate solution.

2. Materials and methods

2.1. Materials
Cubic samples (1 cm side) of Carrara marble (BasketweaveMosaics.com, USA) were used. Ammonium oxalate (AmOx, $(NH_4)_2C_2O_4 \cdot H_2O$, assay > 99%, Sigma Aldrich), 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) and deionized water were used.
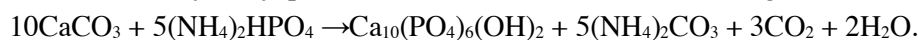
2.2. Treatments
All the treatments were applied by immersing each sample in 200 ml of solution and leaving it to react for 24 hours, the solution being continuously stirred by rotating the container with the solution and the sample. After 24 hours, the sample was rinsed with deionized water and dried at room temperature.

For the ammonium oxalate treatment (labelled "AmOx"), samples were treated with an aqueous solution of 5 wt.% AmOx, as proposed in [3,4]. The aim of the treatment is to transform calcite into calcium oxalate monohydrate (whewellite), according to the reaction [3]:

$$CaCO_3 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4 \cdot H_2O + 2NH_3 + H_2O + CO_2.$$

For the first formulation of the ammonium phosphate treatment (labelled "DAP1"), samples were treated with an aqueous solution containing 1 M DAP and 1 mM $CaCl_2 \cdot 2H_2O$, as proposed in [5]. The aim is to transform calcite into hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$), according to the reaction [6]:

$$10CaCO_3 + 5(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 5(NH_4)_2CO_3 + 3CO_2 + 2H_2O.$$

$CaCl_2 \cdot 2H_2O$ was added to the DAP solution based on previous results, indicating that $CaCl_2$ helps achieve complete coverage of marble surface [5].

Based on FIB-SEM results, a possible improvement of the DAP1 formulation was then investigated, with the aim of reducing the porosity of the resulting coating. For the improved formulation (labelled "DAP2"), samples were treated with a water-ethanol (90-10 vol%) solution containing 0.1 M DAP and 0.1 mM $CaCl_2$. Ethanol was added based on previous results, indicating that HAP formation is favoured by addition of ethanol to the precipitation medium [7].

2.3. Characterization

2.3.1. Coating composition and microstructure. The coating composition was determined by grazing incidence X-ray diffraction (GID), using a Bruker D8 Discover X-Ray Diffractometer. By analysing the sample with an X-ray beam with very little inclination with respect to the analysed surface ($\theta = 0.5°$), the reduced depth of penetration of the X-ray beam into the sample yields information about the composition of the superficial coating with little interference from the substrate.

The coating morphology was analysed by an environmental scanning electron microscope (FEI Quanta 200 FEG ESEM), after making the samples conductive by carbon coating.

The coating microstructure was analysed by a focused ion beam SEM (FEI StrataTM DB 235 FIB), after carbon coating. The steps in cutting a cross section of a coating are illustrated in Figure 1 in the case of the DAP1 treatment: (1) the location for cutting the cross section is first identified; (2) a platinum layer is deposited to preserve the morphology of the coating; (3) the cross section is cut by milling with Ga^{3+} ions at high current (30 kV, 23 nA); (4) the cross section is finally polished by milling with Ga^{3+} ions at low current (30 kV, 40 pA)
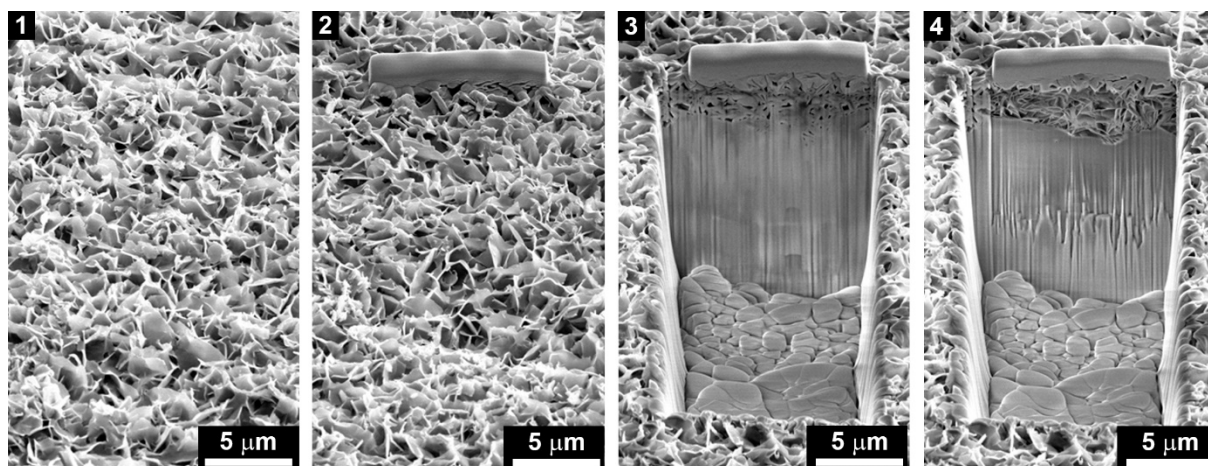
Figure 1. Stages of FIB-SEM analysis (here illustrated for the DAP1 coating): (1) surface of the sample to be analysed, tilted by 52° with respect to the horizontal; (2) platinum layer deposited over the surface, to protect the coating morphology; (3) rough cross section obtained by milling at high current; (4) polished cross section obtained by milling at low current.

2.3.2. Coating performance. The coating performance was assessed in terms of ability to delay dissolution of marble samples immersed in a HNO_3 aqueous solution at initial pH 4.8, simulating slightly acidic rain. Marble dissolution was monitored by measuring the increase in pH as a function of time, using an Oakton pH-meter (pH 1100 series). For better comparability, an area of 8×8 mm^2 was isolated in one face of the cubic samples, the other surfaces being coated by an impermeable layer of nail polish. For each condition, two samples were analysed and the results were averaged.

3. Results and discussion

3.1. Ammonium oxalate treatment

GID detected whewellite ($CaC_2O_4 \cdot H_2O$) as the only new phase formed after treatment, as expected (Figure 2). Whewellite has a solubility product ($K_{sp} \approx 10^{-9}$) lower than that of calcite ($K_{sp} \approx 5 \cdot 10^{-9}$) [1], so some protection of the underlying marble from dissolution in acid is expected.

From SEM observation of the sample surface, whewellite appeared to uniformly cover marble surface, with no visible bare areas or micro-cracks (Figure 3, "before" condition). Nonetheless, limited protective efficacy was achieved (Figure 4). In fact, initially the AmOx curve is below that of the untreated reference, which indicates that some delay in marble dissolution is achieved. However, after about 400 min the two curves overlap, which indicates that the protective action is lost. Consistently, when the AmOx sample was analysed by SEM at the end of the acid attack test, no trace of the whewellite coating was found and only bare marble was visible (Figure 3, "after" condition).

One reason for the limited protective efficacy could be the solubility of the new mineral. Although lower, the solubility product of whewellite is very similar to that of calcite, hence dissolution of the whewellite coating after prolonged exposure in the acid solution seems plausible (however, no data were found in the literature about the dissolution rate of whewellite in pure water [1]).

In addition, SEM observation of FIB cross sections (Figure 3, right) revealed a further possible reason for the measured performance. Whewellite crystals seem to be separated by small vertical channels, connecting the marble/whewellite interface with the upper whewellite surface. These channels can allow acid to reach the marble surface, thus triggering its dissolution and leading to pH increase over time. These vertical channels resemble those described in the case of mineral replacement [8], where the presence of channels is essential for the growth of the new mineral.
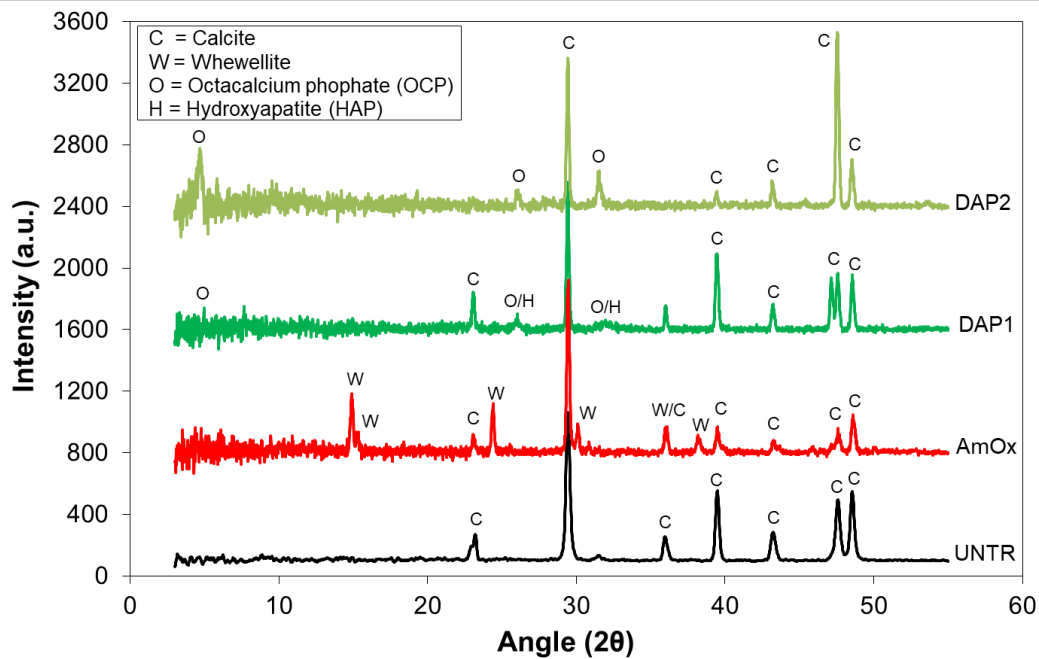
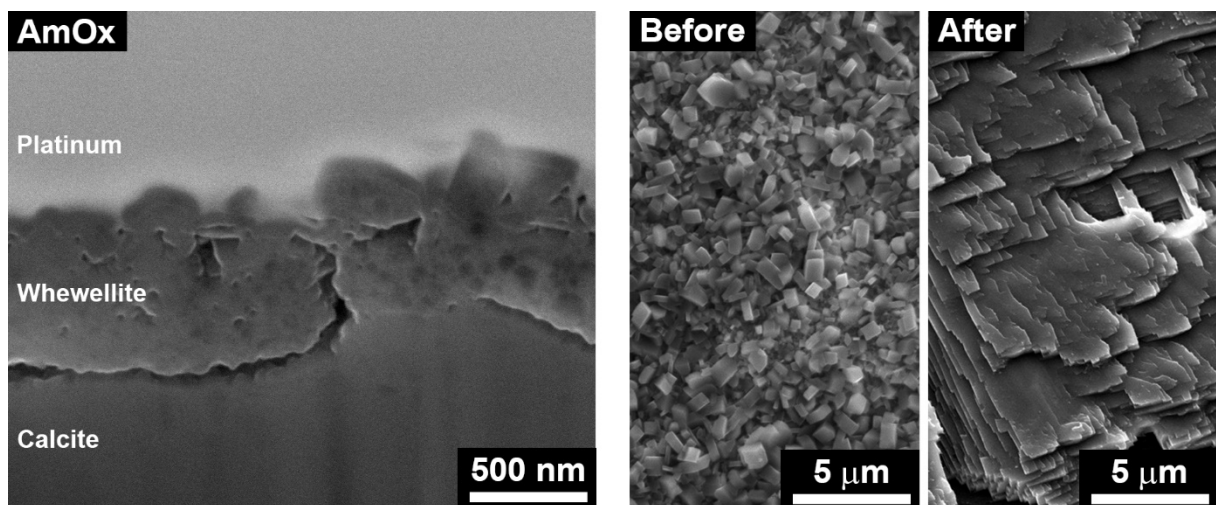**Figure 2**. Mineralogical composition of untreated and treated samples.

Figure 3. FIB cross section before acid attack (left) and surface (right), before and after acid attack, of AmOx sample.

Indeed, for the reaction to proceed and the new mineral to keep on forming, ions dissolved from the original mineral need to cross the new mineral and reach the interface between the new mineral and the solution [8]. In the present case, calcium ions necessary for whewellite formation only come from dissolution of the marble substrate, hence it is reasonable that the vertical channels are formed during whewellite formation to allow its growth.

To prevent formation of these vertical channels, an attempt was made to externally supply calcium ions (similarly to the case of the DAP1 treatment) [9]. However, because of the rapid precipitation of particles even for micromolar additions of $CaCl_2$ to the AmOx solution, the attempts to prevent formation of these vertical channels were unsuccessful [9].
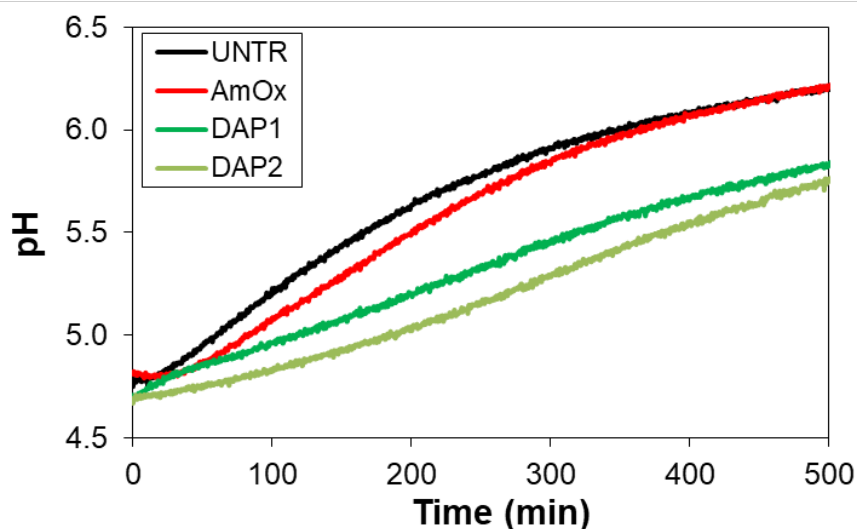
Figure 4. Increase of pH as a function of time for untreated and treated samples.

3.2. Ammonium phosphate treatment – First formulation

In the case of the DAP1 treatment, GID suggests formation of both HAP ($Ca_{10}(PO_4)_6(OH)_2$) and octacalcium phosphate (OCP, $Ca_8(PO_4)_6H_2 \cdot 5H_2O$) (Figure 2), consistently with previous results about the addition of $CaCl_2$ to the DAP solution [5,10]. The solubility product of HAP is many orders of magnitude lower than that of calcite ($K_{sp} \approx 10 \cdot 10^{-59}$ and $5 \cdot 10^{-9}$, respectively [1]), hence formation of HAP is expected to provide significant protection to marble surface. OCP has a solubility product ($K_{sp} \approx 10^{-48}$ [11]) higher than HAP, but still much lower than calcite, hence its formation is not expected to negatively affect the protectiveness of the coating, especially because it significantly helps achieve complete coverage of marble surface [5].

However, SEM analysis of the sample surface (Figure 5, "before" condition) revealed that the coating is cracked, which presumably occurred during drying, because its thickness exceeds the critical value below which cracking is thermodynamically inhibited [12]. This surely negatively affects the protective ability of the coating. Consistently, the acid attack test (Figure 4) indicates that the coating provides some protection to the marble surface, but still much less than expected based on the solubility products: the DAP1 curve is always well below that of the untreated reference, but a progressive increase of pH occurs with time. Accordingly, at the end of the test the coating exhibits visible degradation and bare areas are visible (Figure 5, "after" condition). To prevent cracking of the coating, decreasing the DAP concentration might be one route, with the aim of reducing the coating thickness. However, if the coating is also porous, permeation of acid through the coating might further reduce the protective ability.

FIB cross sections provided a fundamental piece of information about the presence of inherent porosity, as the DAP1 coating was found to be highly porous (Figure 5, left). The coating porosity surely reduces its protective efficacy, so it needs to be eliminated. This was attempted by developing the DAP2 treatment formulation.

3.3. Ammonium phosphate treatment – Improved formulation

Compared to DAP1, the DAP2 formulation has two differences: (i) the lower concentration of DAP (0.1 M instead of 1 M) and $CaCl_2$ (always in 1:1000 ratio to the DAP concentration), with the aim of forming a thinner coating, thus possibly preventing cracking; (ii) the addition of ethanol (10% in volume), with the aim of favoring formation of calcium phosphates and possibly preventing pore formation. Indeed, ethanol molecules are known to weaken the hydration sphere of phosphate ions in solution [13] and

previous tests have shown that coverage of calcite particles by HAP is improved when ethanol is added to the DAP solution [7].
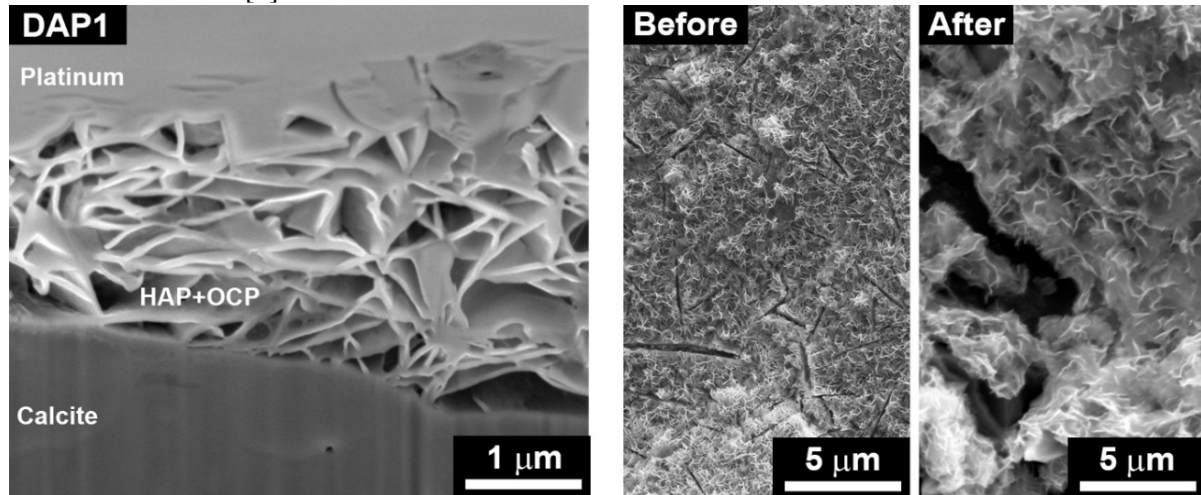

Figure 5. FIB cross section before acid attack (left) and surface (right), before and after acid attack, of the DAP1 sample.
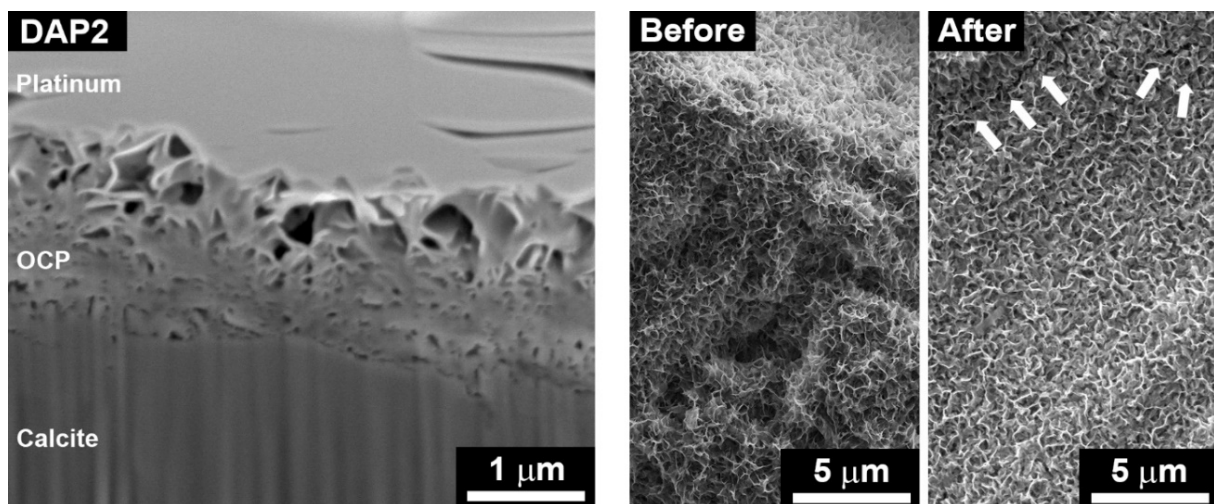

Figure 6. FIB cross section before acid attack (left) and surface (right), before and after acid attack, of the DAP2 sample.

In terms of composition of the coating, the DAP2 treatment led to formation of OCP, while no HAP peak was clearly evident (Figure 2). As discussed above, OCP is far less soluble than calcite, hence a good protecting ability can be expected, provided that the coating is crack-free and pore-free. SEM observation of the sample surface revealed no visible cracking (Figure 6, "before" condition), which is a further positive feature towards achieving a satisfactory protective action.

FIB-cross sections revealed a remarkable reduction in porosity of the DAP2 coating (Figure 6). The flower-like morphology typical of HAP and OCP is still visible on top of the coating, but the underlying part, in contact with marble surface, is significantly denser. Such a decrease in porosity is thought to derive from the beneficial effect of ethanol, which makes phosphate ions more reactive to form new calcium phosphate phases [13].

As a consequence of the absence of cracks and the densification of the microstructure, the acid resistance of the DAP2 coating results improved compared to DAP1 (Figure 4). With respect to the

untreated reference, the DAP2 sample reached the same value of pH after about twice as much time, which means that marble was provided with a significant improvement in durability.
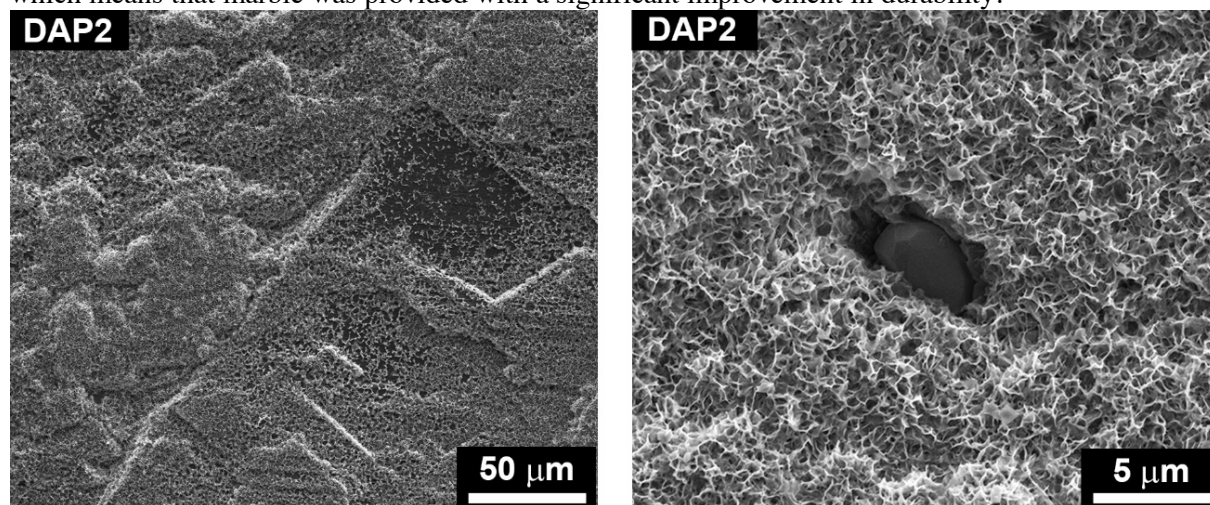

Figure 7. SEM images illustrating the presence of defects in the DAP2 coating in correspondence of calcite grains with unfavourable orientation (left) and impurities (right).

Nonetheless, the acid protection is not complete, as pH increases over time, although more slowly than in the case of untreated marble. Closer observation of the DAP2 sample by SEM revealed that, although the coating is crack-free and continuous, still some calcite grains exhibit poor coverage: an abrupt change is present between these isolated badly covered calcite grains and the surrounding ones, perfectly covered with the coating (Figure 7, left). This is thought to be a consequence of the different crystallographic orientation of calcite grains: whereas coverage of marble surface by the coating is generally good and even epitaxial growth of HAP (or OCP) might take place over calcite grains with favorable crystallographic orientation (e.g., when the distance between atoms in the calcite crystal is similar to the distance of atoms in the HAP or OCP crystals), the coating growth is more difficult over grains with unfavorable orientation. Similarly, the coating is interrupted where impurities are present (Figure 7, right). The presence of these interruptions in the coating continuity allows acid to trigger marble dissolution from these bare areas and then spread to the adjacent areas. This also leads to cracking of the coating, as revealed by SEM observation of DAP2 samples after acid attack (Figure 6, "after" condition – newly formed cracks are indicated by white arrows).

Possible strategies to promote the growth of the coating also over these calcite grains with unfavorable crystallographic orientation are currently being investigated.

4. Conclusions

In this paper, focused ion beam (FIB) microscopy was used to investigate the microstructure of two different inorganic coatings for marble protection, with the aim of identifying the factors limiting the performance of the treatments and outlining possible strategies for their improvement.

In the case of the ammonium oxalate treatment, calcium oxalate monohydrate (whewellite), slightly less soluble than calcite, was formed. Cross sections obtained by FIB-SEM revealed that vertical channels are present in the whewellite layer. These channels can allow acid to reach the marble/whewellite interface and hence trigger dissolution of the substrate. The channels are thought to originate from the mechanism of whewellite formation: calcium ions needed to form whewellite only come from dissolution of marble, hence the channels are needed to ensure that the calcium ions can cross the whewellite layer and reach the whewellite/solution interface, where the reaction is proceeding. To prevent formation of these vertical channels, an attempt was made to add calcium ions directly into

the ammonium oxalate solution. However, because of the rapid precipitation of particles even for micromolar additions of $CaCl_2$ to the ammonium oxalate solution, the attempts were unsuccessful.

In the case of the ammonium phosphate treatment, hydroxyapatite and octacalcium phosphate (both significantly less soluble than calcite) were formed when a 1 M DAP and 1 mM $CaCl_2$ solution was used. The coating exhibited cracks (presumably owing to the excessive thickness of the coating) and pores, whose detection was possible by FIB-SEM analysis. Even though the coating is able to delay dissolution of treated marble, still protection is not complete. The new insight made possible by FIB suggests a possible strategy to improve the coating performance: reducing the DAP concentration, to prevent excessive film growth and cracking, and adding ethanol to the DAP solution, to enhance the reactivity of phosphate ions in the solution. FIB cross sections confirmed that, by treatment with a 0.1 M DAP and 0.1 mM $CaCl_2$ solution also containing 10 vol% ethanol, cracks are prevented and pores are almost completely absent. Accordingly, the protective action was found to be improved compared to the first formulation of the phosphate treatment. Nonetheless, protection of marble is not complete yet, because a few calcite grains with unfavorable crystallographic orientation exhibit poor coverage by the coating. Further strategies to improve marble coverage by the coating and hence the protective performance of the coating are currently being investigated.

Acknowledgements

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