

# INORGANIC PRODUCTS USED IN THE CONSERVATION OF CULTURAL HERITAGE: INTERACTION WITH CARBONATIC SUBSTRATES AND NEWLY-FORMED CRYSTALLINE PHASES

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## INTRODUCTION

The diammonium hydrogenphosphate (DAP,  $(\text{NH}_4)_2\text{HPO}_4$ ) is an inorganic-mineral consolidant applied to carbonatic matrixes of cultural heritage artefacts (*i.e.*, ornamental stones, plasters, mural paintings; Snethlage *et al.*, 2008; Matteini *et al.*, 2011; Sassoni *et al.*, 2011; Balonis-Sant *et al.*, 2013; Sassoni, 2017, 2018). The treatment is based on the diffusion of water-based DAP solutions within the pores of the stone matrix. The reaction occurs between the phosphate ions of the reagent and the calcium ions of the substrate, and generates a crystal framework of phosphate phases that restores the lost cohesion of the microstructure.

The core idea of the treatment is to form stoichiometric hydroxyapatite (HAP,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ; Matteini *et al.*, 2011), a phase with a lower solubility and slower dissolution rate than the calcite of the substrate (Wang & Nancollas, 2008), which provides stability and durability of the treatment.

Actually, the DAP reaction with polycrystalline substrates (such as calcite of plasters, mortars and stones) is non-stoichiometric and it is influenced by several factors such as, pH, presence of foreign ions, and degree of supersaturation. The consequence is the formation of different calcium phosphates in a complex mixture (Kamiya *et al.*, 2004; Naidu & Scherer, 2014; Possenti *et al.*, 2016; Possenti *et al.*, 2019a,b). Considering that each calcium phosphate has specific properties (*e.g.*, Ca/P molar ratio, solubility, stability; Elliott, 1994; Wang & Nancollas, 2008; Dorozhkin, 2011), the formation of soluble or instable phases in place of HAP might be detrimental for the efficacy and the durability of the consolidating treatment. Then, it is essential to explore the crystallochemical composition of the reaction products in order to understand how to drive the crystallization toward the most stable and insoluble phases.

The crystallization of phosphates takes place by dissolution and recrystallization on pore walls of the stone material (Possenti, 2019) and it modifies the microstructural features of the substrate (*i.e.*, porosity, connectivity, capillarity properties). The characterization of these variations gives rise to a new understanding on the interaction of the treatment with carbonatic substrates and allows evaluating the new properties of the “stone-treatment system”. Therefore, the present work aims to improve the knowledge on the DAP interaction with carbonatic stones focusing on the characterization of: *i*) the crystal-chemistry of the newly-formed phases and how the lithotype peculiarities (*e.g.*, composition and microstructure) and the treatment protocol (*e.g.*, application technique, DAP molarity, pH) interplay in the formation and localization of specific phases; *ii*) the penetration depth of the reaction products inside the stone matrix, as well as the microstructural variations induced by the treatment; *iii*) the DAP potentialities to consolidate stone carved artefacts naturally decayed in polluted urban environment.

The whole research involved innovative multi-analytical approaches based on advanced techniques in non-conventional experimental setup (heating treatments, high resolution ATR  $\mu\text{FT-IR}$  mapping, synchrotron radiation (SR) X-ray diffraction in grazing incidence and transmittance geometry, SR X-ray micro-computed tomography), which, step by step, allowed characterizing the “stone-treatment system” at different scales and resolutions.

The expectation of this study is to develop scientific guidelines to approach the conservation choices in the field with consolidating treatments having improved performances, able to consider the peculiarity of specific case studies and the conservation history of the artworks.

## MATERIALS AND METHODS

### Materials

This study was carried out on three different carbonatic lithotypes, quarried in Italy and widely used in architecture and sculpture as ornamental stones, *i.e.*, the Carrara marble, the Noto yellowish limestone, and the Angera stone.

The veined variety of Carrara marble (a compact metamorphic stone containing dolomitic veins, Possenti, 2019) and the Noto yellowish limestone variety (a highly porous calcarenite, Barone *et al.*, 2014) were selected in order to study the interaction of DAP solutions with calcite-based lithotypes. Additionally, the veined Carrara marble was also used to investigate how the presence of compositional heterogeneities of the lithotype influences the crystallization of specific phases whereas the Noto yellowish limestone was also used to explore the penetration depth of the treatment and the microstructural variations induced by the crystallization.

The white variety of Angera stone (a sedimentary porous dolostone, Cavallo *et al.*, 2004) was used to give new insights on the DAP reaction with dolomite and on the crystallization of phosphates within decayed stone matrixes.

Prismatic specimens ( $5 \times 5 \times 2 \text{ cm}^3$ ) of quarry and artificially weathered specimens of the three lithotypes, as well as a decayed carved artwork in Angera stone coming from the “Richini courtyard” in Milan (XVII century), were treated by poultice and capillarity for 24 h (Carrara marble and Noto limestone) or 48 h (Angera stone) with 0.76 M and 3.00 M aqueous solutions of DAP (CAS Number 7783-28-0, assay  $\geq 99.0\%$ , reagent grade, Sigma–Aldrich). At the end of the treatment, the specimens were dried in laboratory conditions ( $T = 22 \pm 1 \text{ }^\circ\text{C}$ ,  $\text{RH} = 50 \pm 5\%$ ) for 24 h; then, they were rinsed by poultice in MilliQ water three times and dried again until constant weight (Possenti, 2019; Possenti *et al.*, 2019a,b).

### Methods

The morphology and composition of the specimens before and after the DAP treatments were explored by scanning electron microscopy coupled with energy dispersive X-ray spectrometer (SEM-EDS, JEOL 5910 LV with tungsten filament coupled EDS spectrometer IXRF-2000).

The nature of the newly-formed phosphates was investigated at the MCX beamline of the ELETTRA Synchrotron facility, Trieste (Italy) in two SR-XRD experiments:

1) Investigation of the newly-formed phases and assessment of the HAP formation. The XRD measurements were collected in transmittance geometry ( $\lambda = 0.88523(6) \text{ \AA}$ , exp. No. 20160183), and coupled with heating treatments (heating from room temperature to  $900 \text{ }^\circ\text{C}$  with the gas blower Oxford Danfysik DGB-0002). A detailed description of the experimental conditions is described in (Possenti *et al.*, 2019a).

2) Characterization of the influence of the stone substrate on the crystallization of specific phosphates. The measurements were collected in grazing incidence geometry (SR-GIXRD;  $\lambda = 0.88523(6) \text{ \AA}$ , exp. No. 20160183;  $\lambda = 0.82591(6) \text{ \AA}$ , exp. No. 20167062) with X-ray beam spot size of  $500 \text{ }\mu\text{m} \times 300 \text{ }\mu\text{m}$  ( $h \times v$ ). A detailed description of the experimental conditions is described in (Possenti *et al.*, 2018).

The distribution of the reaction products was investigated by HR  $\mu$ Attenuated Total Reflection Fourier Infrared Spectroscopy (ATR  $\mu$ -FT-IR). The analyses were carried with a LUMOS Standalone FT-IR microscope (Bruker Optik GmbH) equipped with an automated Ge-ATR probe (tip diameter  $\sim 100 \text{ }\mu\text{m}$ ). The  $\mu$ -mapping data were managed with the OPUS-IR™ software (Bruker Optik GmbH, version 7.5). A detailed description of the experimental conditions is described in (Possenti *et al.*, 2019a).

The penetration depth of phosphates within treated stones was investigated by SR X-ray Diffraction in Transmittance geometry (SR- $\mu$ TXRD) on thin sections. The measurements were performed at the ID15b beamline of the European Synchrotron Radiation Facility ESRF (Grenoble – France;  $\lambda = 0.41050(3) \text{ \AA}$ ). The X-ray beam spot size was of  $10 \times 10 \text{ }\mu\text{m}^2$  and the stepsize was  $20 \text{ }\mu\text{m}$ . A detailed description of the experimental conditions is described in (Possenti, 2019).

The Rietveld refinement was carried out by using the GSAS package on a silicon standard to estimate the uncertainty of the experimental wavelength of all the XRD experiments and to carry out the whole pattern profile fitting.

The variations induced by the DAP treatments to the pore network were investigated by Synchrotron Radiation X-ray Micro-Computed Tomography (SR- $\mu$ CT,  $\lambda = 0.49610(2)$  Å, exp. No. MA311) at the ID11 beamline of ESRF (Grenoble, France). The SR- $\mu$ CT projections were elaborated with the SYRMEP Tomo Project (STP) and processed by using FIJI ImageJ. The Pore3D software library was used for the image analysis. Details on the beamline setup and the image manipulation processes can be found in (Possenti *et al.*, 2019c).

## RESULTS AND DISCUSSION

### DAP reaction with calcite

The DAP reaction with calcite promotes the formation of calcium phosphates arranged in a *shell* on the surface of calcite grains. This phenomenon takes place either on compact lithotypes as well as on porous substrates. On compact matrixes, the newly-formed phases mainly form an external layer on the surface of the stone. On porous matrixes, the DAP solution penetrates into the pores and calcium phosphates crystallize mainly on pore walls.

The phases of the *shell* have different crystal habit and their relative abundance is controlled by the lithotype. In fact, the thin rose-like phases (thickness < 100 nm, dimensions  $\sim 1$ -2  $\mu$ m) are predominant on the Carrara marble whereas spherical units and aggregates of spherical units in elongated arrangement (diameter  $\sim 300$  - 900 nm) are mainly on the Noto limestone (Fig. 1a, b).

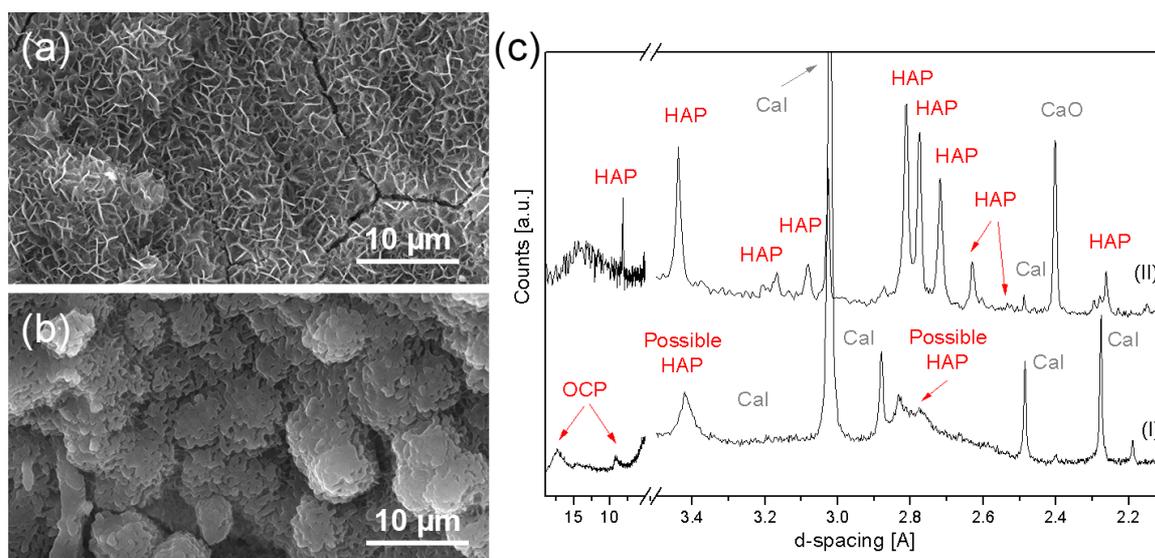


Fig. 1 – SEM images showing the different morphology of the *shell* formed on Carrara marble (a) and on Noto limestone (b) after the consolidation with DAP. SR-XRD patterns (c) of the newly-formed calcium phosphates: after the DAP treatment (pattern I) and after the heating treatments at 900 °C (pattern II). HAP = hydroxyapatite, Cal = calcite, OCP = octacalcium phosphate, CaO = lime formed as heating by-product.

Focusing on the nature of the new phases, the crystallochemical characterization is challenging, as they are micro-crystals in a complex mixture, and in minor fraction with respect to the minerals of the substrate. For this reason, an advanced protocol based on X-ray diffraction (XRD) with synchrotron radiation (SR) has been developed. The SR-XRD protocol revealed that the *shell* is composed of octacalcium phosphate (OCP,  $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$ ) mixed with calcite of the substrate (Fig. 1c). The presence of HAP, initially ambiguous (Possenti *et al.*, 2019a), has been demonstrated by SR-XRD combined with heating treatments. Moreover, the protocol showed that the newly-formed HAP is poorly crystalline but mainly stoichiometric and that it is in

mixture with a minor fraction of non-stoichiometric carbonate-substituted apatites. This is due to a complex interplay of factors, including the kinetic of the reaction, the pH evolution during the crystallization and the descending  $\text{Ca}^{2+}$  ions availability, which prevented the formation of well ordered crystals (Possenti *et al.*, 2019a). Over the *shell*, there is the spotty formation of other phosphates. These phases have different morphology and composition. In particular, spherical aggregates ( $\sim 5 \mu\text{m}$  diameter) of thin, rose-like crystals composed of OCP and HAP are formed on area treated with 3.00 M DAP solutions whereas crystals with a blade-like morphology of dicalcium phosphate dihydrate (DCPD,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) are formed on specimens treated with 0.76 M ones (Fig. 2). Their formation is determined by the availability of free  $\text{Ca}^{2+}$  ions, which, in turn, depends on the DAP

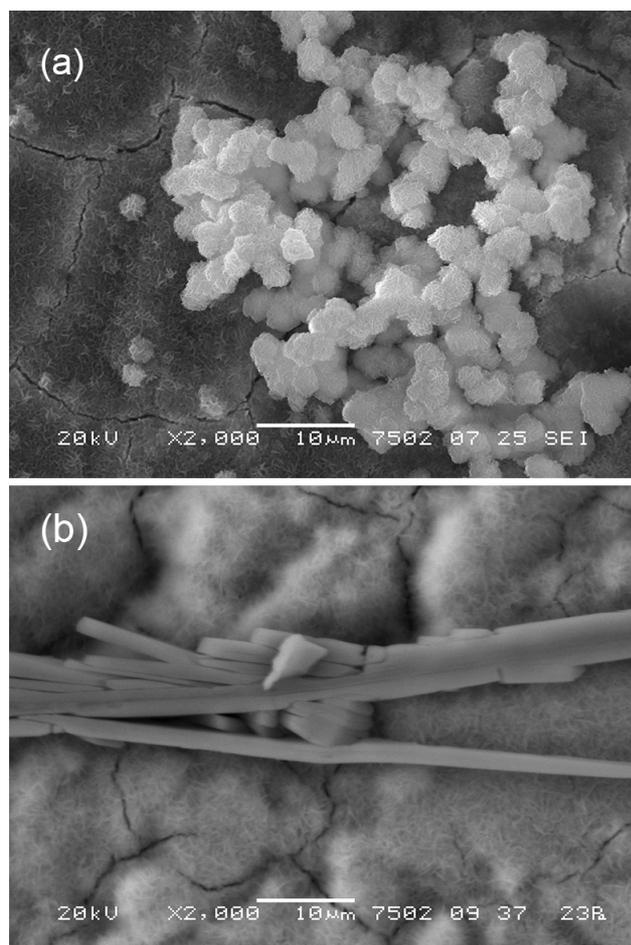


Fig. 2 – SEM images showing the spotty growth of calcium phosphates over the *shell*: spherical aggregates of thin, rose-like crystals formed after the treatment with 3.00 M DAP solutions (a) and crystals with a blade-like morphology formed after the consolidation with 0.76 M solutions (b).

pre-reacted substrate as growth seed for the new crystallization. These morphological features clearly show that the phosphate formation does not fill the voids and, consequently, demonstrate that DAP treatments preserve the highly porous nature of the lithotype.

Focusing on the distribution of the newly-formed phases, the calcium phosphates permeate the lithotype down to several millimetres (8-12 mm), forming a crystal network that reconnects the outer part of the stone matrix to the inner one. The phosphate phases are more abundant in the most superficial portion of stone materials, whereas they undergo a slight but progressive reduction toward the inner portions. A sort of accumulation on the surface is somehow expected, as it is the portion of stone materials which is directly in contact with the source of DAP solution, and also because the solution which penetrates through the first

molarity and the mineralogical composition of the underlying substrate. In fact, as demonstrated by SR grazing incidence X-ray diffraction (SR-GIXRD), when the reaction environment is rich of calcium (*e.g.*, substrate composed only of calcite, high DAP molarity), the calcium phosphates have a high Ca/P molar ratio (HAP 1.67, OCP 1.33). On the other side, when there is a minor calcium content (*e.g.*, substrate with dolomitic veins or with compositional heterogeneities, low DAP molarity), the overgrowth phases have a low Ca/P molar ratio (DCPD 1.00, Possenti *et al.*, 2018; Wang & Nancollas, 2008).

#### *Diffusion of calcium phosphates within the Noto limestone*

The penetration depth and the spatial distribution of the reaction products are key factors to determine the efficacy of a consolidating product (Graziani *et al.*, 2018). Thus, the diffusion of calcium phosphates and the effects induced by the crystallization were both investigated.

By the investigation of the treated stone matrix by SEM-EDS, it was possible to identify the calcium phosphates on the boundaries of calcite grains as well as inside the micro-porosity of calcite grains (Fig. 3). Focusing on the reaction profile, calcite grains show irregular boundaries, demonstrating the occurrence of a topotactic reaction in which the reagent partially dissolves the substrate, while P-containing phases employ the

millimetres is still rich of reagent. At the same time, the newly-formed phases close to the surface do not form an external thick, compact crust, but, on the contrary, they are localized in the voids and generate a network highly interconnected that binds calcite grains.

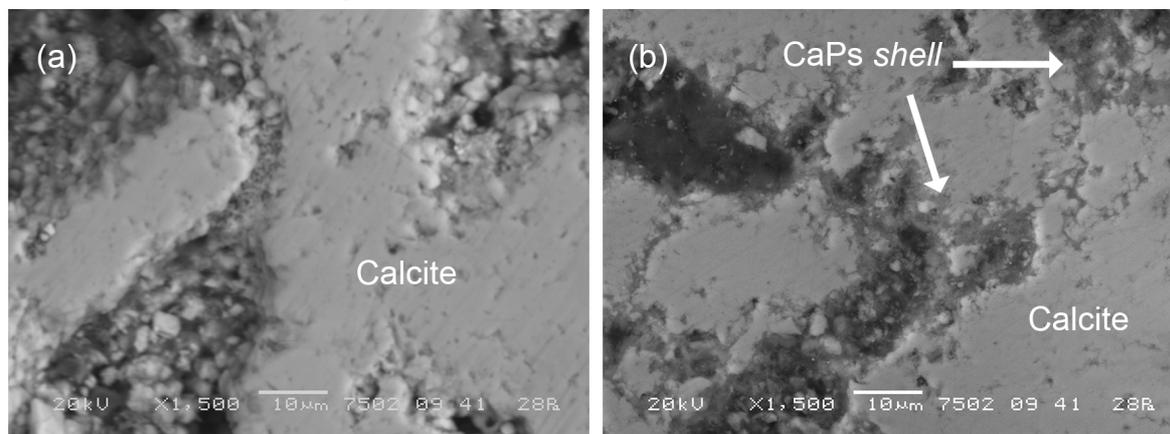


Fig. 3 – SEM images of untreated (a) and treated (b) Noto limestone embedded in polished cross sections. The (b) image shows the well distinguishable formation of the calcium phosphate *shell* on the boundaries of calcite grains.

The investigations carried out by SR- $\mu$ TXRD provided a qualitative 2D characterization of the crystalline phases formed within the lithotype. The SR- $\mu$ TXRD data showed that the nature and the spatial localization of the calcium phosphate varied along with the penetration depth. In particular, OCP is detected close to the surface while HAP is constantly present. The formation of different phases, with a different Ca/P molar ratio and acidity, is due to the DAP reaction mechanism and the reactivity of the substrate, and in particular to the ions availability, the composition of the stone matrix and the pH evolution during the reaction.

The crystallization of phosphates on pore walls of the stone substrate modifies the microstructure of the porous system. These variations, explored by mercury intrusion porosimetry and by SR- $\mu$ CT, involve the decrease of the total open porosity, a variation of the pore size distribution with a shift toward finer pores and a reduction of the average pore radius. However, thanks to the topotactic reaction, the treated stone matrix preserves its original high connectivity, with more than  $\sim 95\%$  of the total porosity composed by a system of open and interconnected 3D cells (Possenti *et al.*, 2019c). The crystallization also induces changes in the capillarity properties, which record a decrease of the sorptivity speed and of the amount of absorbed water per surface unit. These new features are positive, as they correspond to a reduced propensity of the lithotype to quickly absorb water (potentially harmful in the field), although they preserve the original hydrophilic properties and the permeability of the stone materials to water flows.

#### *DAP consolidating treatments on a pilot case study in Angera stone*

Similarly to what observed on Noto limestone and Carrara marble, the DAP reaction with dolomite induces the crystallization of newly-formed phases, that reconnect the stone grains detached by the degradation induced by the urban environment.

Thus, the crystallochemical composition, the spatial distribution of the reaction products, as well as the effects induced to Angera stone by the crystallization, were both investigated.

The phosphate phases were detected down to 3-5 mm from the treated surface, with a gradient from the surface to the inner portions. Even though the lithotype was subjected to several cleaning procedures, the stone matrix still contained soluble salts due to the decay (Na- and N-rich compounds detected by EDS and WDS) in the most external millimetre. No phosphates were detected in correspondence of these regions, indicating that a matrix containing similar decay products was not reactive to DAP treatments and it remained locally incoherent after the consolidation.

The reaction products are composed of struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) and a calcium phosphate phase with a poorly-ordered structure, either on pilot area treated by 0.76 M DAP solutions or with 3.00 M ones (Fig. 4). The nature of the ambiguous calcium phosphate phase was investigated by XRD coupled with thermal treatments and they demonstrated that it is a poorly-crystalline but mainly stoichiometric HAP.

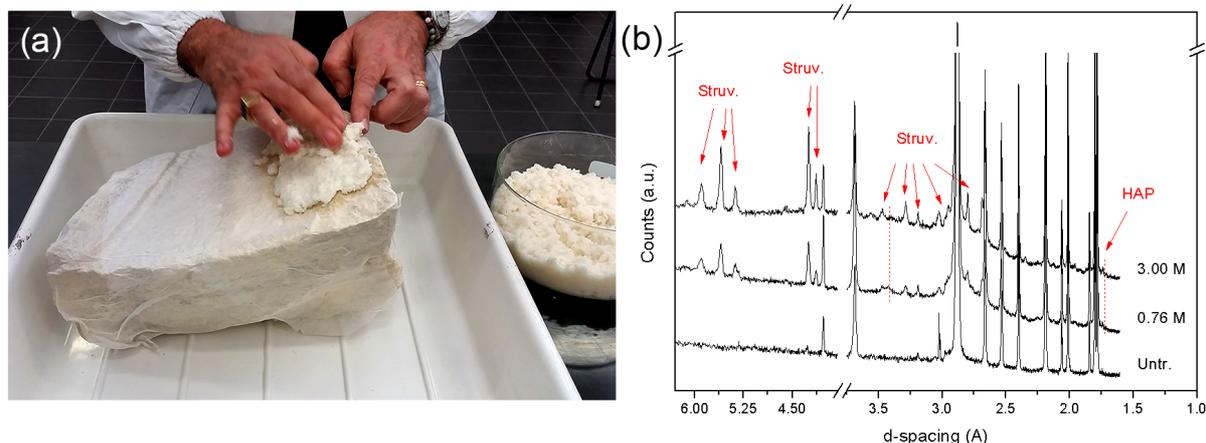


Fig. 4 – Consolidating treatments carried out on the carved element in Angera stone coming from the “Cortile del Richini” (a) and XRD patterns (b) of the untreated (Untr.) and treated stone. Struv. = struvite, HAP = hydroxyapatite.

The HAP formed on dolomite appears more “amorphous” than that formed on calcite. On the other side, struvite formed on Angera stone does not show the typical morphology and crystal size known in literature. This shows that a complex combination of factors, including the kinetics of reaction, the pH of the solution from which struvite and hydroxyapatite may precipitate, the supersaturation and the presence of “foreign” ions, directly influence the nucleation and crystallization process. In particular, the Ca and Mg ions are the “nutrient” for the formation of calcium and magnesium phosphates, and, at the same time, they are “impurities” in the solution from which the two Mg- and Ca-phosphate phases may precipitate (Possenti *et al.*, 2019b).

The widespread crystallization of phosphates within the stone matrix modifies the microstructure, capillarity and colour of the lithotype. In particular, as showed by the MIP investigations, the DAP treatment induces a variation of the total open porosity, a decrease of the average pore radius, an increase of the total specific surface area and a change of the pore size distribution with a % shift toward more finer pores.

Concerning the sorptivity properties, the DAP treatments determine a reduction of the water absorbed by capillarity of about ~ -90%, as showed by water absorption tests with the contact sponge method (European Standard UNI 1142:2011).

Focusing on the perceived colour, principal alteration occurs in terms of  $L^*$  parameters (lightness) which decreases after the treatment, whereas  $a^*$  and  $b^*$  parameters experience very limited modifications. In general, the  $a^*$  values increase whereas the  $b^*$  values are basically unvaried or slightly decreased. Generally speaking, the perceived colour shows a darkening and a shift toward the yellow and red chromatism, which can be perceived by the human eye as a saturation of the stone colour. Most likely, this variation is due to the migration of iron-based chromophores, which occurs in response to the chemical and mechanical decay which characterize the carved artefact. For both the DAP molarities, the colour difference ( $\Delta E$ ) between untreated and treated regions are visible by human eye.

All these variations (porosity, capillarity, and colour) are more pronounced for the area treated by the 3.00 M DAP solutions than with the 0.76 M ones.

## CONCLUSIONS

The DAP reaction with carbonatic lithotypes forms new phosphate phases arranged in a crystal framework with consolidating properties. The consolidating treatment modifies the properties of the lithotype,

thus the crystal-chemistry of the newly-formed phases and the microstructural features induced by the crystallization were both investigated. The investigations showed that the crystallization of the new phosphate phases depends on several factors mutually interfering (e.g., the kinetic of the reaction, the availability of free calcium ions, the pH evolution during the treatment, the stone substrate, the application method and duration, and the DAP molarity) and explored how these variables determine the composition and distribution of the reaction product within the stone matrix. For these reasons, the experimental findings obtained in this research project are expected to serve as guidelines to support the application of DAP consolidating treatments to complex matrixes in conservation field. Furthermore, the multiscale protocol, here developed and based on advanced techniques, can be considered a new analytical route to deepen the research scenario on inorganic treatments and their interaction with real conservation worksites and decay processes.

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