



New insight on the interaction of diammonium hydrogenphosphate conservation treatment with carbonatic substrates: A multi-analytical approach☆



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ABSTRACT

The inorganic-mineral treatment with diammonium hydrogenphosphate (DAP; $(\text{NH}_4)_2\text{HPO}_4$) is one of the most recent developed for conservation purposes. Its reaction with calcite (CaCO_3) of the stone induces the crystallization of calcium phosphates, able to restore the mechanical integrity of deteriorated substrates by physical and chemical binding of the grain boundaries.

Due to the complexity of DAP reaction mechanism a deep insight into the relation between consolidating action and newly-formed mineralogical phases is essential. This study focuses on morphological, mineralogical and spectroscopic characterization of calcium phosphates precipitated in calcium carbonate substrates after DAP treatment (hydroxyapatite, brushite, octacalcium phosphate, amorphous calcium phosphate) with the final aim to correlate the formed phases with the effectiveness of the treatment. The influence of the specific substrate, grain size and duration of treatment on the precipitation of calcium phosphates has been investigated and the stratigraphic succession of the phases inside the *shell* crystallized around the calcite grains is suggested.

Due to the difficulty to obtain a straightforward identification of calcium phosphates in a complex mixture, advantages and drawbacks of a multi-analytical approach (X-ray diffraction, scanning electron microscopy with energy dispersive spectroscopy, micro-Raman and FTIR spectroscopies) are critically proposed. The outcomes have a direct impact in the *in-situ* DAP application, in terms of conservation efficacy and treatment modality.

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1. Introduction

Inorganic-mineral products are effective consolidating treatments due to their chemical compatibility with stone substrates and durability of the newly-formed mineralogical phases. In the last few years new treatments based on ammonium phosphates and artificial calcium phosphates have been proposed [1,2] and several experimental studies performed [1–14]. The development of ammonium phosphate-based treatment is inspired by its chemical reactivity with carbonatic substrates, able to restore the mechanical integrity of deteriorated stones by physical and chemical binding of the grain boundaries and fracture surfaces. The advantages of this new treatment are mainly related to its high compatibility with the substrate [1,2], the absence of reagent and reaction products toxicity [1,2] and the high solubility of ammonium phosphates in water, permitting the preparation of

solutions at higher concentration with respect to the other inorganic products [1].

The new treatment induces the crystallization into the depth of the stone matrix of newly-formed mineralogical phases characterized by highly insolubility and able to resist to acid attacks [15]. Moreover, it has potential desulfation properties and its consolidating action provides a passivation towards acid atmospheric agents. Preliminary studies demonstrated that after the treatment the total open porosity of the substrate is essentially unaltered [2,3,6,9], the water sorption capability reduced [1,2] and the optical characteristics of the stone slightly changed [1,2]. In literature, most of the studies aim at the investigation of mechanical, micro-structural and physical changes of the substrates after the phosphate consolidating treatment [2–4,6,8,9,13], while preliminary tests performed by M. Balonis-Sant et al. [7] and by Yang et al. [10–12] focus on the application of ammonium phosphate treatments on wall paintings and decayed stone prepared in laboratory. Moreover, the evaluation of the effectiveness, compatibility and durability of the ammonium phosphate treatment on carbonatic substrates has been discussed in recent studies [1–6,8,13–14].

Despite several precursors are available (ammonium dihydrogenphosphate, ADP, $\text{NH}_4\text{H}_2\text{PO}_4$; diammonium hydrogenphosphate, DAP,

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(NH₄)₂HPO₄ ammonium phosphate, AP or TAP, (NH₄)₃PO₄) at present DAP is the most studied reagent [1]. The treatment is based on a mild, controlled, chemical reaction between calcite exposed to a DAP solution, with the consequent formation of calcium phosphates. According to the reaction reported by Ni et al. [16]:



the expected reaction product at room temperature is the mineral hydroxyapatite (HAP, Ca₅(PO₄)₃(OH)) which constitutes the inorganic component of teeth and bones. HAP is durable and notably less soluble than calcite, making possible an effective consolidating action for carbonatic stones [1].

Nevertheless, it is well known [1,2,17–20] that the production of HAP is typically non-stoichiometric, especially if the reaction occurs in presence of carbonate ions. In this case, apatite formation involves the crystallization carbonate-substituted hydroxyapatites (C-HAP) and it could take place simultaneously to the precipitation of several intermediate metastable phases, such as monocalcium phosphate monohydrate and anhydrous (Ca(H₂PO₄)₂·H₂O or MCPM; Ca(H₂PO₄)₂ or MCPA respectively), dicalcium phosphate dihydrate and anhydrous (brushite, DCPD, CaHPO₄·2H₂O; monetite, DCPA, CaHPO₄ respectively), octacalcium phosphate (OCP, Ca₈(HPO₄)₂(PO₄)₄·5H₂O), amorphous calcium phosphate (ACP, Ca_xH_y(PO₄)_z·nH₂O, with n = 3–4.5) and/or calcium-deficient HAP (CDHA, Ca_{10-x}(HPO₄)_x(PO₄)_{6-x}(OH)_{2-x}, with 0 < X < 1). Reaction conditions (e.g., degree of supersaturation, temperature and pH) strongly influence the crystallization of these minerals as suggested by a wide literature on thermodynamics and kinetics of calcium phosphates crystallization.

Due to the complexity of DAP reaction mechanism, a deep insight into the relation between consolidating action and newly-formed mineralogical phases is essential; to the best of our knowledge, no information is available in literature on the variables affecting DAP consolidating treatment and on the methods able to identify calcium phosphates in mixture with calcite.

This study combines morphological, mineralogical and spectroscopic data of calcium phosphates precipitated in calcium carbonate substrates after DAP treatment, with the final aim to correlate the formed phases with the effectiveness of the treatment. Three different calcium carbonate powders have been treated by immersion in a DAP solution to investigate the influence of the specific substrate, grain size and duration of treatment on the precipitation of calcium phosphates. A first attempt to identify the position of the newly-formed mineralogical phases from the inner domains of calcite crystal to its external edges has been also proposed. It is worth to note that the straightforward identification of a calcium phosphate in a complex mixture is challenging and it should be carefully carried out by the combination of appropriate methods [21,22]. This is the reason why in this work we propose a multi-analytical approach, using X-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM–EDS), micro-Raman and FTIR spectroscopies to investigate both reference mineralogical phases and crystals formed after the treatment. The informations obtained by these complementary analytical techniques are reported and the potentialities of the proposed multi-analytical approach in the investigation calcium phosphates mixture are discussed.

2. Materials

2.1. Phosphate references

DAP (CAS Number 7783–28–0, assay ≥ 99.0%, reagent grade), DCPD (CAS Number 7789–77–7, assay ≥ 98.0%, reagent grade) and HAP (CAS Number 1306–06–5, reagent grade) were purchased by Sigma-Aldrich.

DCPA (CAS Number 7758–87–4) was obtained by dehydration of DCPD, with a heat treatment at 180 °C in air for 2 h, as reported by Drouet [21].

OCP (CAS Number 13767–12–9) was synthesized in laboratory as reported by Brown et al. [23] (slow hydrolysis of DCPD in a 0.5 M solution of sodium acetate at 40 °C) and by Drouet [21] (hydrolysis of DCPD in presence of DAP, at 37 °C for 24 h). Although both methods were not able to produce pure OCP reference, the synthesized powders has been used to identify the typical OCP pattern in a calcium phosphate mixture.

2.2. Carbonatic powders

Synthetic calcite (CAS Number 13397–26–7, reagent grade – Carlo Erba) and carbonatic powders from sedimentary (Noto limestone) and metamorphic (Carrara marble) stones were used. Powders of Noto limestone were obtained by grinding, while powders of Carrara marble were prepared by an artificial weathering method (starting from Franzoni et al. [24]) to avoid grinding damage of calcite crystals of metamorphic origin. This method consists of heating marble fragment for 2 h at 400 °C and quickly cooling with liquid nitrogen for a few seconds.

The powders obtained both from Noto limestone and Carrara marble were selected by wet sieving with MilliQ water (18.2 MΩ cm) to obtain different grain sizes according to the stone microstructure.

2.3. DAP treatment

The carbonatic powders were treated with a 10% DAP aqueous solution (0,76 M) for 24, 48 and 168 h without stirring. During the reaction, pH values were monitored by a Mettler Toledo™ FG2 FiveGo™ Portable pH meter. After the treatment, the powders were sieved, dried at ambient condition for 24 h, rinsed twice by immersion in MilliQ water, filtered and dried again. Then, the analyses were carried out directly on the powders as well as on the powders embedded in epoxy resin. In Table 1 the scheme of the specimens preparation is reported.

3. Methods

3.1. X-ray diffraction

Treated samples and reference minerals were analysed with Panalytical X'Pert PRO X-ray powder diffractometer (XRD) equipped with a Cu Kα radiation source, a PW 3050/60 goniometer, anti-scatter slit and divergence slit (1° and 1/2° respectively) in Bragg–Brentano geometry, a PW 3040/60 generator and a X'Celeator solid state detector PW3015/20 nickel filtered. The accelerating voltage and electric current at the Cu anode were 40 kV and 40 mA, respectively.

Powdered samples were finely ground and spread on an amorphous silicon holder. Diffraction patterns were recorded in the following angular ranges:

- 3°–75° 2θ: stepsize of 0.17°, scan speed of 0.2089°/s, to characterize the whole diffractometric pattern of the samples;
- 2°–22° 2θ, 23.5°–26.5° 2θ, 30°–34° 2θ: stepsize of 0.008°, scan speed of 0.0033°/s; these selected ranges were chosen with the aim to exclude the strong calcite peaks and perform an easier discrimination of the newly-formed calcium phosphate, especially when they have a low intensity. In particular, in the 2°–22° 2θ range, the (100) reflection typical of OCP (approximately at 4.70–4.80° 2θ) and the (020) and (021) crystal planes of DCPD (at 11.70° and 20.80° 2θ) occur. In the 23.5°–26.5° and 30°–34° 2θ ranges some of the main reflections of HAP due to the (002), (211), (112), (300) crystal planes located at 25.91°, 31.74°, 32.18° and 32.86° 2θ, and other secondary XRD peaks of DCPD and OCP are present.

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