Diammonium hydrogenphosphate for the consolidation of building materials. Investigation of newly-formed calcium phosphates

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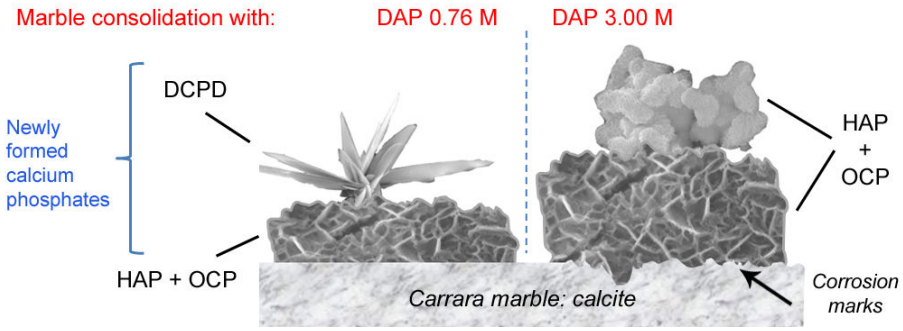
Declarations of interest: none

Highlights

- Diammonium hydrogenphosphate (DAP) solutions consolidate decayed carbonatic stones
- The formed phases depend on treatment method, DAP molarity and stone microstructure
- Cutting-edge techniques are discussed to identify similar crystalline phases
- The formation of hydroxyapatite is unambiguously demonstrated
- Variables which might affect the treatment effectiveness are discussed

Graphical abstract



The graphical abstract and all the figures can be printed in black and white

Abstract

Diammonium hydrogenphosphate (DAP) is a water soluble consolidant for decayed carbonatic materials of historical buildings. The reaction of DAP solutions with polycrystalline calcite of marbles is non-stoichiometric and forms a calcium phosphates mixture whose identification is tricky and controversial. This study investigated how the DAP molarity, the treatment method and the microstructure of the stone influence the formation of specific phases. Thermal treatments and cutting-edge techniques (XRD with synchrotron radiation in transmitting geometry and high resolution FTIR microspectroscopy) were used to overcome the analytical limits of the more conventional methods, shading light to an in depth evaluation of DAP consolidating processes and treatment conditions.

Keywords

Carrara marble; calcium phosphates; consolidation; diammonium hydrogenphosphate; synchrotron X-ray powder diffraction; high resolution FTIR microspectroscopy.

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43 **Manuscript**

44 **1. Introduction**

45 Over the last few years, the use of diammonium hydrogenphosphate (DAP, $(NH_4)_2HPO_4$)
46 solutions has been introduced in the conservation field as a new inorganic-mineral treatments
47 to consolidate or protect carbonatic stone materials of historical monuments.

48 The DAP reaction with carbonatic substrates was investigated in terms of *i.e.:* compatibility
49 with the substrate [1], durability [2], resistance to simulated rain [3] or to phototrophic
50 colonization [4], desulfating agent [5,6].

51 The literature indicates that the reaction between DAP and calcite single crystals leads to the
52 formation of hydroxyapatite (HAP, $Ca_5(PO_4)_3OH$) [7,8], a stable and insoluble phase (K_{sp} 25
53 °C: calcite 4.8×10^{-9} mol/L, hydroxyapatite 1.6×10^{-117} mol/L [9]). More complex is its
54 reaction with carbonatic stones, because in this case it is non-stoichiometric and determines
55 the formation of a mixture of phases with a different Ca/P molar ratio [10–12]. The detected
56 phases after DAP treatments on carbonatic stone substrates are DCPD (brushite,
57 $CaHPO_4 \cdot 2H_2O$) [9,10], MCPM (monocalcium phosphate monohydrate, $Ca(HPO_4)_2 \cdot H_2O$) [5],
58 ACP (amorphous calcium phosphate, $Ca_xH_y(PO_4)_z \cdot nH_2O$ with n = 3–4.5) [10], MCPA
59 (monocalcium phosphate anhydrous, $Ca(HPO_4)_2$), TCP (tricalcium phosphate, $Ca_3(PO_4)_2$) and
60 OCP (octacalcium phosphate, $Ca_8(HPO_4)_2 \cdot 5H_2O$) [10,13]. However, Karampas &
61 Kontoyannis [14] and C. Drouet [15] reported that the straightforward characterization of
62 calcium phosphate phases is challenging due to the limits of a conventional analytical
63 approach; as a consequence, they highlighted the need of new analytical protocols. In
64 particular, one of the most critical issue is to define the most suitable method able to
65 distinguish HAP from OCP, especially if they are poorly crystalline or crystallize in a mixture

66 [14,15]. The structure of OCP consists of apatite-like layers alternated with hydrated layers
67 parallel to (100), deeply similar to HAP crystalline arrangement [16]; thus both of them give
68 rise to severe overlapping of X-ray diffraction peaks and vibrational bands.

69 DAP treatments can be performed without the addition of calcium ions or with an external
70 calcium source by adding calcium soluble salts [10,17,18]. The first method imply a slow
71 reaction with the substrate, which ideally favours a higher diffusion inside the substrate. The
72 formation of phases depends on the specific surface area of calcite grains and the descending
73 reactivity. The core idea of the second approach is to use calcium ions immediately available
74 for the reaction, accelerating the formation of calcium phosphates and resulting in the quicker
75 coverage of the marble surface with a film formation [17].

76 Despite the high number of studies on the crystallization of calcium phosphates and their
77 formation on the surface of carbonatic substrates, only a few studies [10,19,20] explored the
78 formation of calcium phosphate phases on marbles treated with DAP and using calcite of the
79 substrate as unique source for calcium ions.

80 For these reasons, the goal of this research is to determine how the crystallization of calcium
81 phosphates on Carrara marble after DAP consolidating treatments is influenced by the stone
82 substrate (micro-structural variations due to the conservation state) and by the treatment
83 method (application technique and DAP solution molarity) without using a further calcium
84 source. In this study, a set of quarried and decayed Carrara marble specimens were treated
85 with different method using DAP solutions of different molarities. Commercial powders of
86 calcium phosphates were used as references; OCP, a metastable phase not available for sale,
87 was synthesized and the structure of the obtained poly-crystalline material was refined by the
88 Rietveld method using high quality X-ray synchrotron powder diffraction data. To
89 unambiguously characterize the formation of newly-formed phosphate phases with similar
90 crystalline structure in multi-phase mixture and their arrangement on the marble surface, an

ad hoc multi-analytical approach was developed combining conventional and cutting-edge techniques (XRD with synchrotron radiation in transmitting geometry, high resolution FTIR microspectroscopy). Moreover, thermal treatments were performed to unequivocally demonstrate the presence of the newly-formed HAP, overcoming the analytical limits of the more conventional methods.

2. Materials and methods

2.1. Materials

The study was performed on prismatic specimens (5x5x2 cm) of quarried white Carrara marble (a compact metamorphic carbonatic stone with homogeneous texture and composition); part of them was artificially decayed (heating ramp up to 200 °C for 3 hours), in order to induce micro-structural variations and grain detachment and to simulate naturally weathered marbles.

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

OCP, not available on sale, was synthesised at our laboratory, with a modified LeGeros procedure [21]. The reagents for OCP synthesis were purchased by Merck, Darmstadt Germany: $NaH_2PO_4 \cdot H_2O$ (CAS Number 10049-21-5, assay ≥ 99.0%, reagent grade), $Ca(CH_3COO)_2 \cdot xH_2O$ (CAS Number 62-54-4, assay ≥ 99.0%, reagent grade), HCl. 250 mL of 0.04 mol/L $NaH_2PO_4 \cdot H_2O$ (pH adjusted at 4.50 by the addition of 6.45 mL of 1 mol/L HCl solution) were added drop wise with a speed of 1.39 mL/min in quiescent 250 mL of 0.04 mol/L $Ca(CH_3COO)_2 \cdot xH_2O$ at 70 °C (± 1°C). At the end of the reaction, the pH was 4.28. The solid precipitated was kept in contact with the mother solution for 20 minutes; after that, it

was isolated by filtration, rinsed with deionised water and dried at room temperature. The nature of the precipitate was checked with a structure refinement by the Rietveld method using the X-ray synchrotron powder diffraction pattern (further details in the section 2.2.2). The high-quality refinement ($R(F^2)$ = 0.0435, *wRp* = 0.0588) confirmed the formation of monophasic OCP with a triclinic structure (space group: *P*-1), with unit-cell parameters: *a* = 19.677(5) Å, *b* = 9.533(3) Å, *c* = 6.835(2) Å, α = 90.14(3) °, β = 92.55(4) °, γ = 108.31(3) °, *V* = 1215.7(4) $Å^3$, in good agreement with the data previously reported in the literature [16,22].

The marble specimens were treated by poultice and capillarity with two different molarities (0.76 M and 3.00 M) of DAP aqueous solutions. The 0.76 M concentration corresponds to a 10% w/w and it was selected on the basis of previous experiments [10] and on the *in situ* DAP consolidating practice [23]; the choice to include also 3.00 M concentration was suggested by the literature [13], where this value was used to obtain the formation of a thicker layer of calcium phosphates. After 24 hours, the treatments were removed and the specimens were left drying at room temperature for 24 hours; at complete drying, the specimens were rinsed twice by immersion in MilliQ water and dried again.

2.2. Methods

2.2.1. Scanning electron microscopy coupled with energy dispersive X-ray spectrometry

Morphological investigations of the newly-formed phases formed on marble were performed in low and high vacuum mode by JEOL 5910 LV scanning electron microscope (SEM) coupled with energy dispersive X-ray spectrometer (EDS) IXRF-2000 (0–20 keV). The shape of newly-formed crystalline phases has been investigated by zenithal observations of the surface of treated specimens; the growth of the phases from the surface, the action of the

138 treatment on calcite and the arrangement of the new phases on the substrate have been
139 analysed on cross sections.

140

141 *2.2.2. X-ray powder diffraction techniques*

142 The XRD pattern of references (commercial calcium phosphates and Carrara marble) were
143 investigated in Bragg-Brentano geometry with a Panalytical X'Pert PRO X-ray powder
144 diffractometer (XRD), equipped with a Cu-Kα radiation source (λ ~ 1.54 Å), a PW 3050/60
145 goniometer, anti-scatter slit and divergence slit (1° and 1/2° respectively), a PW3040/60
146 generator and a X'Celerator solid state detector PW3015/20 nickel filtered. The accelerating
147 voltage and electric current at the Cu anode were set to 40 kV and 40mA, respectively.
148 Powdered samples were finely ground and spread on zero background holders. Diffraction
149 data were collected at room temperature (rT, 25 °C) and after heating treatments (250 °C and
150 850 °C) in the angular range 3°–75° 2ϑ, with a stepsize of 0.17° and scan-step time of 21.32 s.

151 The X-ray diffraction patterns of synthesized OCP and of calcium phosphates formed after
152 DAP treatments were collected at the ELETTRA Synchrotron facility, Trieste (Italy) in order
153 to investigate the presence of minor phases and to discriminate slight differences between
154 similar crystalline structures. The experiments were performed in transmission mode at the:

155 - XRD1 beamline [24]: measurements of the synthesized OCP. The diffraction data
156 were collected with a monochromatic wavelength of λ = 0.700784(6) Å, using a
157 Pilatus 2M hybrid-pixel area detector at rT and after heating treatments (250 °C and
158 850 °C). The investigation of the synthesized OCP with a synchrotron radiation was
159 required to: i) perform a structural refinement by the Rietveld method; ii) assess the
160 absence of apatite, as minor phase, and consequently to validate the synthesis route;

iii) investigate the phase transformation induced by heating and detect low fraction or secondary phases as thermal by-products.

- MCX beamline [25]: measurements of calcium phosphates formed after DAP treatments scratched from the marble surface. In-situ diffraction data were collected with the high-resolution four circles Huber diffractometer from rT to 900 °C using a gas blower (Oxford Danfysik DGB-0002) with a heating ramp speed of 5 °C/min, to investigate the phase transformation in response to heating. The X-ray diffraction patterns were collected at specific temperatures where phase transitions are expected (250 °C, 750 °C, 850 °C). Additional patterns were collected at 100 °C, 500 °C, at 900 °C and after cooling to rT. The diffraction patterns were collected using a focalized monochromatic beam of λ = 0.885227(6) Å in the 2ϑ angular range of 1.5 – 50°, with a step size of 0.01°.

A whole pattern profile fitting of the diffraction data was performed by the Rietveld method, using the GSAS package (http://www.ccp14.ac.uk/solution/gsas/; profile function: pseudo-Voigt, background function: Chebyshev polynomial).

2.2.3. High resolution ATR-FTIR microspectroscopy

ATR μFT-IR measurements of calcium phosphates were carried out in order to investigate the microscale distribution of crystalline phases with a LUMOS standalone FT-IR microscope (Bruker OptikGmbH), equipped with a motorized XYZ sample stage and automated Ge-ATR probe (tip diameter about 100 μm), driven by a piezo, included into the 8x cassegrain objective (NA = 0.6). Considering the Ge refractive index value (4), the theoretical lateral resolution of about 1 μm [26] was obtained collecting the spectra with a 4.0 x 4.0 μm^2 aperture, step size (along x and y) around 3.5 μm, 16 or 32 scans and different ATR pressure (low, medium, high). The data were treated with the OPUS-IR™ software (Bruker Optik GmbH, version 7.5).

3. Results and discussion

3.1 Analysis of the newly-formed phases

After DAP treatments, the surfaces of all the specimens show the formation of calcium phosphates (Ca and P clearly detected by EDS) with different morphologies (rose-like with irregular contours, spherical units or aggregates of spherical units in elongated arrangements, plate-like blades) arranged in a *shell* around calcite grains and between grain boundaries. Moreover, some specimens exhibit further calcium phosphate crystals grown over the *shell*. Here, the *shell* and the calcium phosphate crystallized over the *shell* are called "*newly-formed system*" (Fig. 1a-1d).

In all the specimens, the XRD patterns of the *shell*, collected with a conventional instrument and by using a synchrotron radiation to improve the signal intensity, show the characteristic Bragg peaks of OCP in mixture with calcite (Fig. 2a and Fig. 2b). The XRD peaks of calcite are due to the presence of calcite grains detached during the treatment and embedded in the *shell*, as shown in Fig. 1b. The XRD peaks of OCP at 18.56 Å (d_{100}), 9.36 Å, 9.03 Å and 5.49 Å are broad, weak and with relative intensities slightly different from the synthesized reference material, suggesting that this phase is probably formed as sub-micrometric crystals or contains structural defects and vacancies. The presence of HAP in these XRD patterns is ambiguous. Two peaks, corresponding to inter-planar distances of 3.42 Å and 1.71 Å (indicated in Fig. 2a by the dotted lines), could be attributed to HAP. However, the severe overlap of OCP and HAP diffraction patterns (due to the close relationship between the two structures) prevents the univocal identification of HAP.

The spectra acquired by high resolution ATR-FTIR microspectroscopy of references powders of OCP and HAP permit to clearly distinguish the two phases by the characteristic vibrations

in the fingerprint region of PO_4^{2-} groups [27] and HPO_4^{2-} groups [28–30]. However, even with this technique, it is not possible to unequivocally identify HAP in the *shell* because all the acquired spectra reveal hybrid vibrational patterns between HAP and OCP that can be considered the convolution of vibrational features of the two phases (Fig. 3a and Fig. 3b, spectrum 1 and 2); this ambiguity persists down to the microscale, as demonstrated by the spectra collected on areas of 1x1 μm^2. These findings indicate that OCP and the not well defined apatites are not formed as single, crystalline, micrometric individuals but, instead, they are most likely formed as sub-micrometric multiphase mixture. Furthermore, the detection of CO_3^{2-} vibrational bands at 1460 cm^{-1}, 1399 cm^{-1} and 868 cm^{-1} suggest the formation of carbonate-substituted non-stoichiometric apatite, with the typical surface layers hosting groups such as CO_3^{2-}, HPO_4^{2-} instead of PO_4^{3-} [27,31]. Therefore, the *shell* consists by a complex mixture of sub-micrometric non-stoichiometric phases due to their nucleation in a not ideal reaction environment.

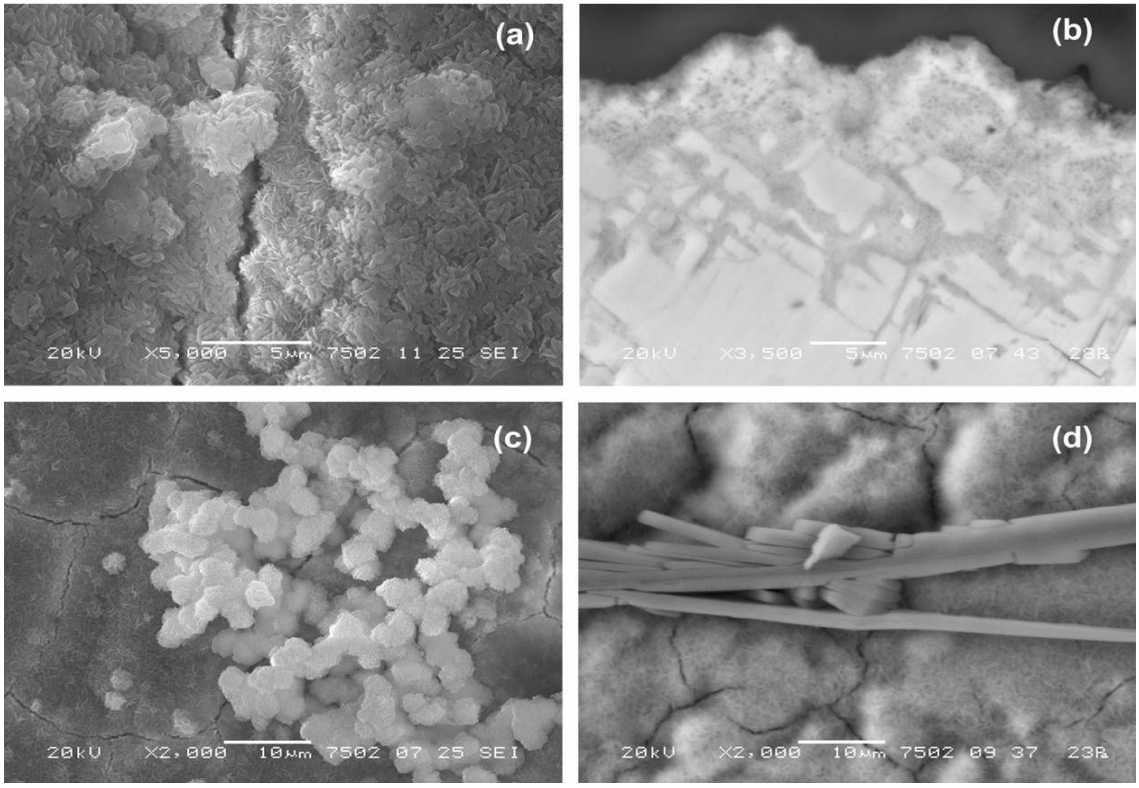
Over the *shell*, the composition of newly-formed phases depends on the molarity of the solution. In fact, after 3.00 M DAP treatments, spherical aggregates of thin, rose-like blades are formed over the *shell* and they are composed of OCP, calcite and ambiguous HAP (Fig. 1c, Fig. 2a and Fig. 2b). Instead, the 0.76 M DAP solutions form acicular plate-like crystals (Fig. 1d) heterogeneously distributed over the *shell*; these crystals are composed of DCPD, as clearly identified with high resolution ATR-FTIR microspectroscopy by the marker HPO_4^{2-} vibrations at 1125 cm^{-1}, 1051 cm^{-1}, 985 cm^{-1} [14,27] (Fig. 3a and Fig. 3b, spectrum 3) and confirmed by a very weak XRD peak (Fig. 2a and Fig. 2b).

DCPD is an acid calcium phosphates, it has a Ca/P molar ratio of 1.00 and its growth is most likely due to two simultaneous factors: the Ca/P molar ratio [5,32] and the decrease of pH of the solution. Its nucleation requires the availability of HPO_4^{2-} groups and a low Ca^{2+} concentration. The DAP speciation in water leads to the formation of a much higher amount

of HPO_4^{2-} ions, compared to PO_4^{3-} ions [20], therefore its formation seems to be favoured during the reaction, alongside HAP. Actually, its crystallization also requires an acidification of the solution, conditions not suitable for the formation of OCP and HAP. Such reaction conditions probably occur in the final steps of the reaction of 0.76 M DAP solutions, when the pH decreases, due to the release of H^+ from the reagent speciation, and slows the HAP and OCP formation (phases preferentially formed under basic or neutral conditions [11]). The decrease of pH, combined to the crystallization of OCP and HAP (which consume Ca^{2+} and PO_4^{3-} ions), actually favours the formation of DCPD. At the same time, the growth of the *shell* starts to represents a barrier for the release of further Ca^{2+} ions from the marble substrate, which further inhibit the formation of phases with high Ca/P molar ratio. Moreover, since the 0.76 M DAP solutions have a "reduced capability" to dissolve Ca^{2+} ions, the treatments with this molarity are definitely less aggressive on the stone substrate and, for this reason, the *shell* is well adherent to the substrate. On the contrary, since 3.00 M DAP solutions dissolve a high amounts of Ca^{2+} ions from the substrate, these treatments are more aggressive on the substrate, calcite shows deep corrosion marks and the *shell*, thicker than those of 0.76 M solutions, is evidently detached from the substrate.

The thickness of the *newly-formed system*, as demonstrated by measurements carried out on polished cross sections, is strongly influenced by the treatment methods. In fact, poultice and capillarity are characterized by a different contact at the interface between the marble and the thickener (either cellulose pulp or paper filter): the cellulose pulp provides a continuous contact not allowing a "free growth" of calcium phosphate crystals; for this reason the *newly-formed system* is thin (2-10 μm). On the contrary, with capillarity the contact shows several vacancies determining the occurrence of gaps with a certain amount of free solution without spatial limitations. As a consequence, the *newly-formed system* is thicker (10-20 μm).

259 The stone microstructure influences the thickness of the *newly-formed system* as well. The
260 decohesion of weathered substrates determines a higher porosity, and consequently higher
261 specific surface area and reaction rate; therefore the *newly-formed system* is slightly thicker
262 for decayed specimens.



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264 **Fig. 1.** SEM images of calcium phosphates formed after DAP treatments: (a) surface of marble showing the
265 newly-formed calcium phosphate phases after 3.00 M DAP treatment; (b) polished cross section of calcium
266 phosphates *newly-formed system* which embeds calcite grains detached during the 3.00 M DAP treatment; (c)
267 spherical structures formed over the *shell* after 3.00 M DAP treatments; (d) acicular plate-like crystals formed
268 over the *shell* after 0.76 M DAP treatments.

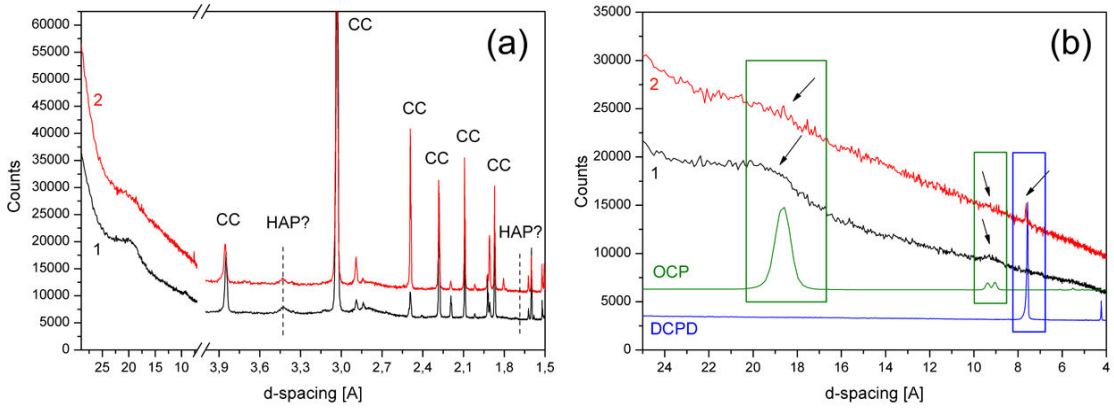

Fig. 2. XRD patterns of calcium phosphates formed on specimens treated by 3.00 M (pattern 1) and 0.76 M (pattern 2) DAP solutions: (a) calcite peaks (CC) embedded in the calcium phosphate *shell* and peaks compatible with HAP (dotted lines); (b) formation of OCP and a mixture of OCP and DCPD.

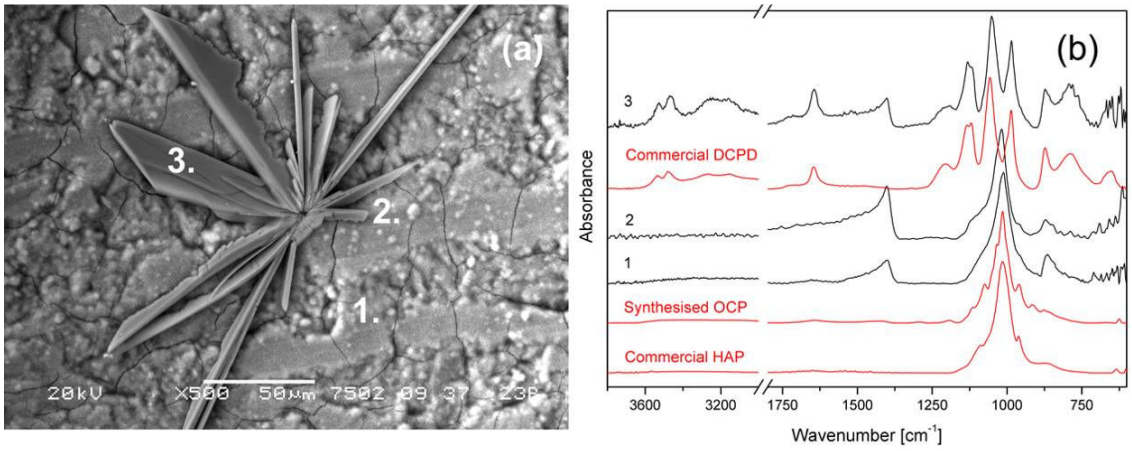

Fig. 3. (a) SEM image of the *newly-formed system*; (b) FTIR spectra of the calcium phosphates *shell* (spectra 1 and 2) and DCPD acicular platelets in characteristic anisotropic plate-like aggregates (spectrum 3) crystallised over the *shell* after 0.76 M DAP treatments.

3.2 Confirm of HAP formation by thermal treatments

OCP has been described as a precursor in the formation of HAP [33] and it is highly likely that OCP acts as growth seeds on the calcite grains for the nucleation of HAP.

For this reason, a set of thermal treatments were carried out to demonstrate the presence of HAP in the *newly-formed system* since heating is proved to be an effective approach to discriminate phases which exhibit similar crystalline structure at room conditions [14,30,34,35]. This procedure was performed first on references and then on the calcium phosphates of the *newly-formed system*.

Heating of synthesized OCP at 250 °C leads to the first phase transition with the formation of an amorphous phase. The OCP main transformation occurs after heating at 850 °C, when the amorphous-apatite/collapsed-OCP is completely transformed into a mixture of β-TCP (β-$Ca_3(PO_4)_2$) and β-CPP (β-$Ca_2P_2O_7$) [30,35,36]. The calculated ratio of the phases, as resulted from the Rietveld refinement, is: 66.8 wt % and 33.2 wt % of β-TCP and β-CPP respectively, in agreement with literature data [30]; these findings basically validated the synthesis route.

Heating of commercial HAP showed no detectable phase changes until 750 °C; from 850 °C the XRD and FTIR spectra revealed the formation of very sharp peaks of β-TCP and HAP [14,34,37], with β-TCP predominant respect to HAP. The growth of sharp peaks is due to the increase, with heating, of the crystallinity degree of poorly-crystalline HAP, while the formation of β-TCP is due to the presence of "impurities", such as HPO_4^{2-} or CO_3^{2-} in the commercial HAP. The formation of a relevant amount of β-TCP indicates that this reference material is poorly-crystalline and non-stoichiometric. On the contrary, the heating of poorly-crystalline stoichiometric HAP should not produce any heating by-product (*i.e.* β-TCP) but only the increase of the crystallinity degree [14,37]. For the characterization of the *newly-formed system*, the XRD peaks corresponding to the *d* spacing of 2.81 Å, 2.77 Å, 2.71 Å and 2.62 Å were used as HAP markers as they do not present significant superimposition with other phases.

Since the references showed that the main transformation occurred at 850 °C, the following discussion focuses on the phase transformation occurred above 850 °C.

Fig. 4a shows the pattern of thermal treatments performed on a *newly-formed system* and it is representative of the results obtained in all the specimens. In the range between 850 °C and 900 °C, the broad weak band between 2.90 Å and 2.62 Å changes into a sequence of sharper, well-defined peaks centred at 2.84 Å, 2.80 Å, 2.75 Å and 2.65 Å. These peaks, as well as the sharper peaks at 8.22 Å, 3.47 Å and 2.28 Å, are unambiguously attributed to the crystallinity increase of HAP above 850°C that minimizes the overlap with the other phases. Therefore, the initial presence in the *newly-formed system* of nano-crystalline non-stoichiometric HAP is definitely confirmed in every specimen (Fig. 4b). The formation of β-TCP is documented by the peaks at 3.20 Å, 2.86 Å, 2.33 Å, 2.15 Å and 2.03 Å, even though they are very weak. β-TCP is the transformation product of both OCP and non-stoichiometric apatite, and after heating of the *newly-formed system* it is rather scarce; these data indicate that in the original *newly-formed system* i) OCP and non-stoichiometric apatite (such as carbonate-substituted apatite detected by FTIR) were only minor phases; ii) HAP, the main phase, was mainly poorly-crystalline or nano-crystalline but stoichiometric.

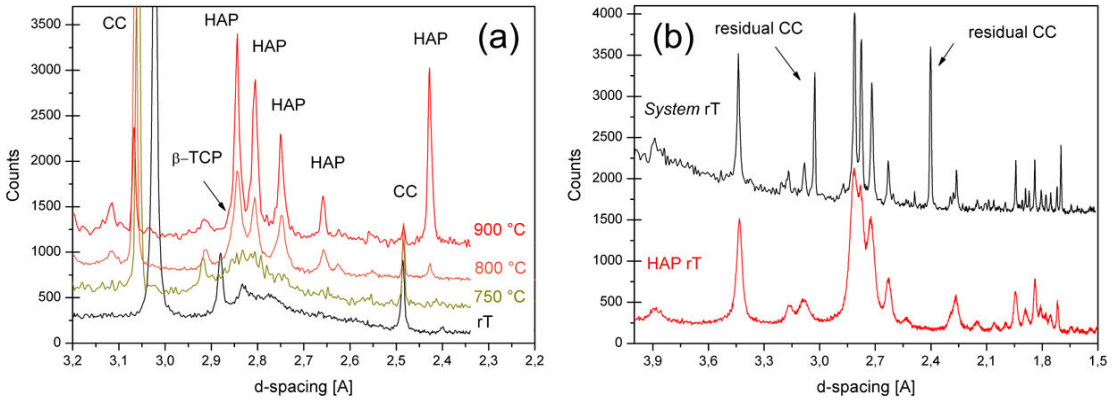

Fig. 4. XRD patterns of the calcium phosphate *newly-formed system*: (a) acquired *in-situ* during the thermal treatments, showing the transformation of the broad band between 2.90 Å and 2.62 Å into a sequence of sharper, well-defined peaks of HAP centred at 2.84 Å, 2.80 Å, 2.75 Å and 2.65 Å. Weak β-TCP peaks and peaks of residual calcite (CC) are also present; (b) comparison of the heated *newly-formed system* after cooling to rT and commercial HAP.

4. Conclusions

The nature and the arrangement of the newly-formed phases after DAP treatment on Carrara marble were properly characterized through the development of a comprehensive multi-analytical approach. X-ray diffraction with synchrotron light in transmitting geometry and thermal treatments were used to investigate the presence of HAP overcoming some analytical limits of the more conventional methods. The potentialities of high lateral resolution ATR-FTIR microspectroscopy have been assessed for the unambiguous identification of DCPD and minor phases (*i.e.* carbonate-substituted apatite).

The experimental findings of this study clearly showed that DAP consolidating treatments performed on massive Carrara marble specimens form a *newly-formed system* of calcium phosphates that depends on the DAP molarity, the treatment method and the microstructure of the substrate. In general, the composition and the localization of the phases, as well as the thickness of the *newly-formed system,* directly depend on the availability of free Ca^{2+} ions and on the reaction kinetics.

The formation of hydroxyapatite in a poorly-crystalline or nano-crystalline stoichiometric form is unambiguously demonstrated by thermal treatments. OCP, non-stoichiometric apatite and DCPD are only minor phases.

From the conservation point of view, even though DCPD is more soluble than HAP and OCP, its formation in heterogeneously distributed aggregates is highly positive because: i) it can be considered a further sacrificial phase for the protection of the treated surfaces from environmental agents; ii) DCPD is a precursor in the formation of apatite and it tends to transform into HAP by dissolution and re-precipitation processes; iii) the formation of DCPD reflects a minor chemical attack on the substrate.

Conflicts of interest

The authors declare that there are no conflicts of interest to declare

Declarations of interest

None

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