

Grazing incidence synchrotron X-ray diffraction of marbles consolidated with diammonium hydrogen phosphate treatments: non-destructive probing of buried minerals

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Abstract

Diammonium hydrogen phosphate (DAP)-based consolidating treatments react with carbonatic stones and form calcium phosphates phases, whose composition depends on the availability of free calcium ions. In this work, an innovative non-destructive approach based on grazing incidence X-ray diffraction (GIXRD) with synchrotron radiation (SR) is used to investigate DAP-treated Carrara marble specimens and to study the influence of the substrate composition on the crystallization of calcium phosphate phases. The outcomes indicate that the presence of compositional micro-heterogeneity of Carrara marble favours the formation of specific phases. Dicalcium phosphate dihydrate, a calcium phosphate with a low Ca/P molar ratio, is formed on carbonatic phases with a low Ca amount, such as dolomite grains and Mg-containing veins. Furthermore, this study highlights the potentialities of SR-GIXRD as a powerful non-destructive tool for the diagnostic of Cultural Heritage objects since it allows investigating the conservation history of stone materials and their interaction with the environment.

Keywords

marble; consolidating treatments; ammonium phosphate; calcium phosphate; synchrotron radiation grazing incidence X-ray diffraction; GIXRD

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1 Introduction

Marble is a lithotype widely used in historical and modern sculptures and architectures and it undergoes to weathering processes when exposed to the outdoor conditions with a consequent formation of decay products, decohesion and sugaring. Historically, the conservation practice requires to apply products able to restore the lost cohesion of the microstructure. This procedure delays the weathering processes of marble artefact and prevents the development of further alterations and decay phenomena. Among the many available consolidating treatments [1–3], the inorganic-mineral treatment based on diammonium hydrogen phosphate (DAP, $(\text{NH}_4)_2\text{HPO}_4$) is one of the most recent and promising treatments for carbonatic stone materials [4–9]. In fact, hydrogen phosphate ions are able to form insoluble calcium phosphates using a small amount of calcium ions dissolved from the substrate. After the treatment, a newly-formed “linking system” of calcium phosphates reduces the cracking, reconnects detached stone grains and blocks the sugaring of weathered marbles [6,8,10–14].

The newly-formed crystalline phases grow with a topotactic mechanism inside the pores and cracks, and on the surface of reacted calcite grains. As showed in a recent study [6] and in some data under publication (in the following text, cited as “data under publication”), the nucleated calcium phosphates are organised on the calcite surface in a layered arrangement of phases called the *newly-formed system*. The *newly-formed system* is composed by a layer of phases well adherent to the substrate, called *shell*, and by aggregates of phases that grow over the *shell*.

When the marble is treated with 0.76 M DAP water solutions by capillarity or poultice, the *shell* is composed of octacalcium phosphate (OCP, $\text{Ca}_8(\text{HPO}_4)_2 \cdot (\text{PO}_4)_5 \cdot 5\text{H}_2\text{O}$) and hydroxyapatite (HAP, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$), while the phases nucleated over the *shell* consists in spotty aggregates of dicalcium phosphate dihydrate (DCPD, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). These crystalline phases are characterized by different stability, solubility and Ca/P molar ratio: HAP: 1.67, OCP: 1.33, DCPD: 1.00 [15]. DCPD is the phase with the lowest Ca/P molar ratio and its formation depends on the low availability of free calcium ions. In fact, in presence of DAP solutions with different molarities (3M and 0.76 M), DCPD crystallizes just with the slight reaction of 0.76 M solutions (data under publication).

However, no data are available on how the composition of the substrate and its micro-structural heterogeneity affect the crystallization of calcium phosphate phases during DAP treatments.

The conventional analytical techniques (XRPD, FTIR, Raman, SEM-EDS) are not fully exhaustive for the characterization of the crystalline phases distribution in the *newly-formed systems* and in the underlying stone substrate [16,17]. Moreover, many of the XRD methods are destructive since they require to grind the sample; this could be a further limit of the conventional analytical approach when the investigated item is an historical marble artwork.

Grazing incidence X-ray diffraction (GIXRD) is a well established technique for the investigation of polycrystalline thin layers and surface analyses [18–20], as well as in Cultural Heritage field [21–24], since it allows collecting XRD data without damaging the investigated object. The technique probes the superficial portion of a material with small incidence angles between the X-rays and the surface of the sample. The incidence angle (Φ) and the X-rays energy determine the penetration depth of the X-rays in the material. GIXRD measurements can be performed with conventional XRD instruments equipped with Göbel mirrors [24] or with synchrotron radiation (SR), which provides a tunable wavelength or energy and a small beam size.

In this study, we carry out a completely non-destructive SR-GIXRD investigation of the crystalline phosphate phases nucleated on marble surface after DAP-treatments and a depth profile of the underlying stone substrate. The analyses were performed on marble specimens treated by capillarity by 0.76 M DAP solutions, with the final aim to explain the relationship between the crystallization of calcium phosphates and the mineralogical composition of the marble substrate.

2 Materials and methods

2.1 Materials

Veined Carrara marble is a compact metamorphic carbonatic stone largely used in sculptures and architectures. For the experiments of this study, prismatic specimens (5x5x2 cm) were obtained from a freshly quarried block.

The consolidating treatments were performed with 0.76 M aqueous solution of DAP (CAS Number 7783–28-0, assay ≥ 99.0 %, reagent grade, Sigma-Aldrich). The 0.76 M DAP molarity, corresponding to a 10 % w/w, is the DAP concentration used *in situ* consolidating practice [25]; moreover, this molarity promotes a beneficial consolidating action and is found to be only little aggressive on the marble substrate (data under publication).

The marble specimens were treated by capillarity for 24 hours, using a set of paper filters (thickener layer of about 1 cm) and a sheet of Japanese paper between the specimen and the paper filters, in order to avoid sticking. The treatment was performed in sealed boxes to avoid the evaporation of the solution. At the end of the treatment, the specimens were let to dry in laboratory conditions ($T = 22 \pm 1$ °C, $RH = 50 \pm 5$ %) for 24 hours. After this time, they were rinsed three times in MilliQ water and left to dry in laboratory conditions until constant weight.

2.2 Methods

2.2.1 Conventional X-ray powder diffraction (XRPD)

Preliminary information on the crystalline phases nucleated on the treated marble surface were collected with a Panalytical X'Pert PRO X-ray powder diffractometer, equipped with a Cu-K α radiation source ($\lambda \sim 1.54$ Å), a PW 3050/60 goniometer, anti-scatter slit and divergence slit (1° and 1/2° respectively), a PW3040/60 generator and a X'Celerator solid state detector PW3015/20 nickel filtered. The newly-formed calcium phosphates were scratched from the whole treated finely ground surface and spread on zero background holders. The XRD patterns were collected in Bragg-Brentano geometry in the angular range 3° – 75° of 2θ , with a stepsize of 0.017 °, scan-step time of 200 s, accelerating voltage of 40 kV and electric current at the Cu anode of 40 mA.

2.2.2 Synchrotron radiation grazing incidence X-ray diffraction (SR-GIXRD)

The GIXRD experiments were carried out at the MCX beamline [26] of the ELETTRA Sincrotrone Trieste S.C.p.A facility (Basovizza, Trieste Italy). The analyses were performed on the treated specimens without any sampling. The *in-situ* diffraction measurements were collected with the high-resolution four circle Huber diffractometer using a focalized monochromatic beam of $\lambda = 0.88523(6)$ Å

(exp. No 20160183) and of $\lambda = 0.82591(6) \text{ \AA}$ (exp. No 20167062) in the 2θ angular range of $1.5 - 50^\circ$, with a step size of 0.01° . The Rietveld refinement on silicon standard was used to estimate the uncertainty of the experimental wavelengths. The X-ray diffraction data were collected in grazing angle geometry with fixed incident grazing angles (Φ): $0.5, 1.0, 2.5$ and 5.0° . The specimens were investigated also with $\Phi = 7.0^\circ$ but no significant differences were observed, thus the XRD patterns are not reported. The acquisition setup and the incidence angles were optimised considering the critical angle, the surface topology and the spatial resolution. The X-ray beam spot size was of $300 \mu\text{m}$ (vertical) x $500 \mu\text{m}$ (horizontal), allowing the investigation of a micro-portion of marble surface.

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).

3 Results and discussion

The XRPD patterns of quarried Carrara marble mainly show calcite (foremost peaks at 3.85 \AA , 3.03 \AA , 2.49 \AA , 2.28 \AA , 2.09 \AA), while in correspondence of sporadic stone veins, dolomite (peaks located at 2.88 \AA) is detected as well, sometimes associated with quartz (peaks located at 3.34 \AA) and other silicates.

As reported in some data under publication, the 0.76 M DAP treatments performed by capillarity on Carrara marble form a complex mixture of calcium phosphate phases. Due to the low porosity of quarry marbles, the calcium phosphates crystallization mainly occur on the surface of marble specimens forming the *newly-formed system*. The XRPD patterns of the phases as scratched from the surface always reveal the presence of OCP and HAP (Fig. 1). In addition, the formation of ammonium calcium phosphates hydrate ($(\text{NH}_4)_3\text{CaP}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$, main peaks at 6.93 \AA and 5.94 \AA and $\text{NH}_4\text{CaP}_3\text{O}_9\cdot 3\text{H}_2\text{O}$, main peak at 6.36 \AA) and of DCPD (marker peaks 7.59 \AA and 4.24 \AA) is randomly documented. The ammonium calcium phosphate phases are soluble reaction by-products and are transformed in more insoluble phases (OCP and HAP) after a further rinsing. In case these ammonium calcium phases might form on historical marble artworks, they are expected to be dissolved and easily transformed in OCP and HAP in wet environments. No phase transformations occur for DCPD crystals. The occasional occurrence of dolomite peaks in the XRPD patterns (patterns a, b and d of Fig. 1) does not allow modelling any relationship with the newly-formed phases.

In general, the calcium phosphates are trace phases within the calcite bulk and display a very weak XRPD signal. Even when the sampling is extremely focused just to the surface, the XRPD pattern shows the prevalence of calcite peaks of the matrix. Therefore, the detection of calcium phosphates is frequently ambiguous and no characteristic Bragg peaks can be observed in the XRPD pattern (e.g. Fig. 1, pattern d). Here, the actual presence of newly-formed phases was checked by SEM-EDS and P was mapped as marker element for newly-formed phosphates. EDS spectra showed a very low P intensity as well. This suggests that, locally, the formation of newly-formed calcium phosphates in a scratched sample might be underestimated, if their amount is below or close the XRPD detection limits.

Moreover, XRPD prevents a deeper insight on the variables which affect the formation of DCPD and ammonium calcium phosphates hydrate since it provides an average information of the whole surface

and does not supply a local information on the relationship between the substrate and the phases nucleated over it. The investigation at the micro-scale level of the superficial crystalline phases can be performed with a high-resolution Attenuated Total Reflection Fourier Transform Infrared micro-mapping (micro-ATR-FTIR) which allows localizing spotty DCPD crystals on DAP treated marbles (data under publication). However, this technique is blind towards the underlying substrate and it provides superficial information only.

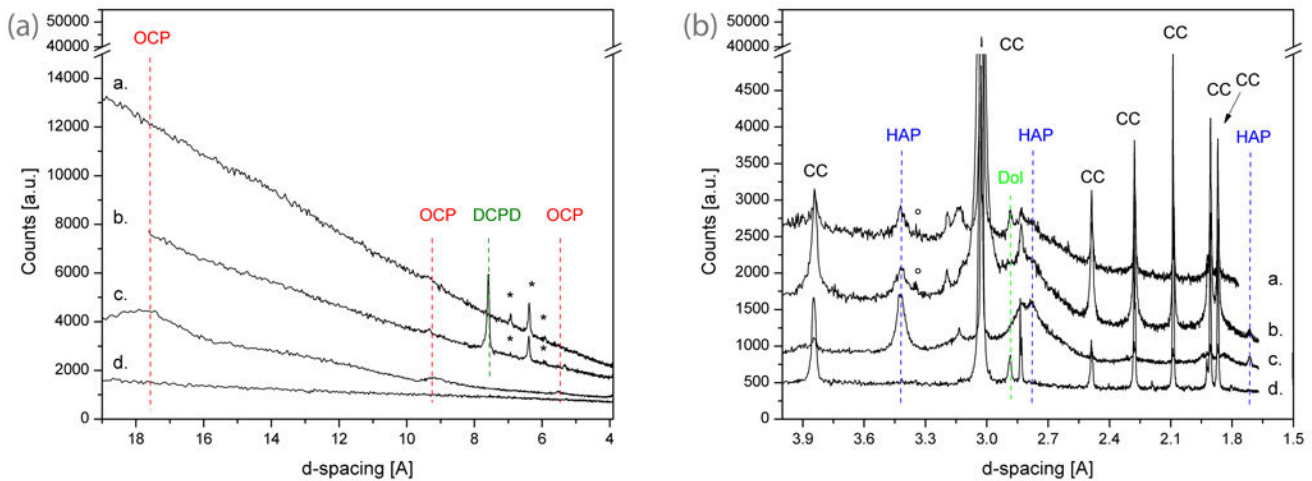


Fig. 1 (a) XRPD patterns of the powders scratched from the surface of four different treated marble specimens. (b) A zoom between 4.0 and 1.5 Å. CC calcite, Dol dolomite, OCP octacalcium phosphate, HAP hydroxyapatite, DCPD dicalcium phosphate dihydrate, * ammonium calcium phosphates hydrate, ° quartz

SR-XRD measurements performed with a grazing incidence setup (GIXRD) are used to overcome the analytical limits of conventional techniques. In our GIXRD experiments, the angles with lower incidence (0.5 and 1.0°) enhance the X-ray diffraction of the superficial layers and thus they allow characterizing the nature of the *newly-formed system*. Higher incidence angles (2.5 and 5.0°) are used to better investigate the mineralogical composition of the stone substrate below the calcium phosphate *newly-formed system* and to understand how the compositional micro-heterogeneity of the stone substrate influences the growth of specific calcium phosphates phases.

The measurements were carried out on a pure calcitic portion, in proximity to a dolomitic vein and exactly over a dolomitic vein.

Fig. 2 shows the GIXRD patterns of the sequence acquired on pure calcitic portion. The GIXRD patterns acquired at 0.5° and 1.0° Φ strongly enhance the intensity of calcium phosphates peaks and allow the straightforward identification of OCP in mixture with HAP. GIXRD pattern clearly show that HAP peaks are broader and weaker than OCP ones; as discussed in a previous paper (data under publication), this is due to the formation of HAP in a poorly-crystalline carbonate-substituted form. The GIXRD pattern acquired for $\Phi 2.5^\circ$ clearly shows that the stone substrate is composed only of calcite; no dolomite peaks are detectable even when the bulk of the stone matrix is investigated with $\Phi 5.0^\circ$.

In general, the GIXRD patterns show that the higher is the incidence angle, the higher is the intensity of the minerals of the stone matrix (in this case, calcite), while no important intensity increase is documented for OCP and HAP peaks.

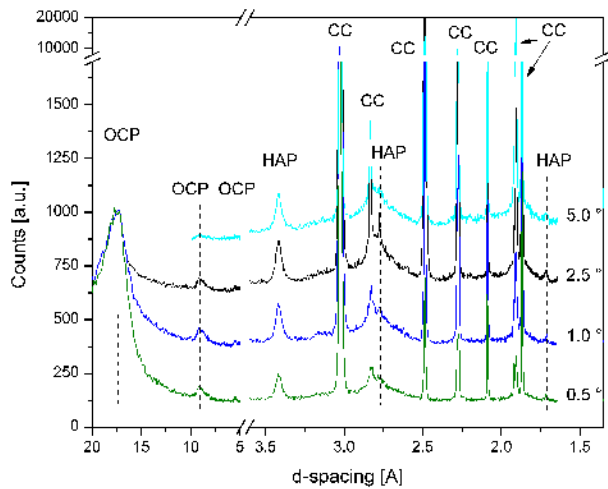


Fig. 2 GIXRD patterns of the surface of a treated marble specimen. *CC* calcite, *OCP* octacalcium phosphate, *HAP* hydroxyapatite

The GIXRD patterns acquired in proximity to a dolomitic vein show a slightly different mineralogical composition (Fig. 3). In this case, the stone substrate is composed of calcite with a low amount of dolomite; OCP and HAP are confirmed to be the detected phases in the *newly-formed system*. The higher is the incidence angle, the higher is the intensity of dolomite peaks. This is due to the better X-ray scattering that occur at higher incidence angle, as previously observed for calcite peaks. At the same time, it cannot be excluded that the increase of the Bragg peaks intensity of dolomite for higher Φ might be due also to the presence of dolomite crystals just below the surface. This is supported by the investigations carried out exactly over a dolomitic vein (Fig. 4).

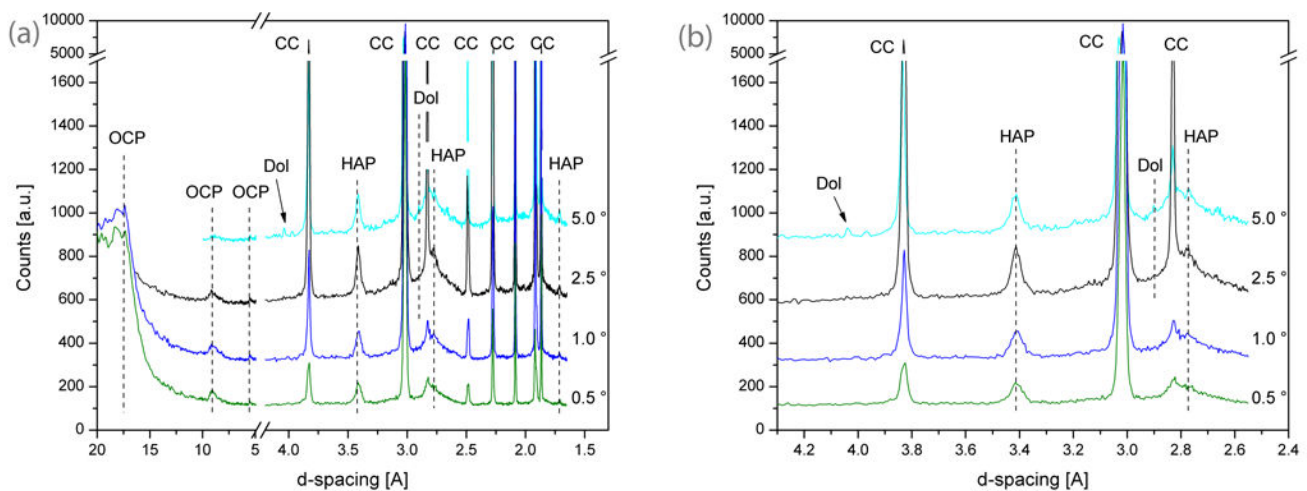


Fig. 3 (a) GIXRD patterns of the surface of a treated marble specimen showing dolomite peaks. (b) A zoom between 4.3

and 2.4 Å shows the increase of dolomite peaks intensity. *CC* calcite, *Dol* dolomite, *OCP* octacalcium phosphate, *HAP* hydroxyapatite

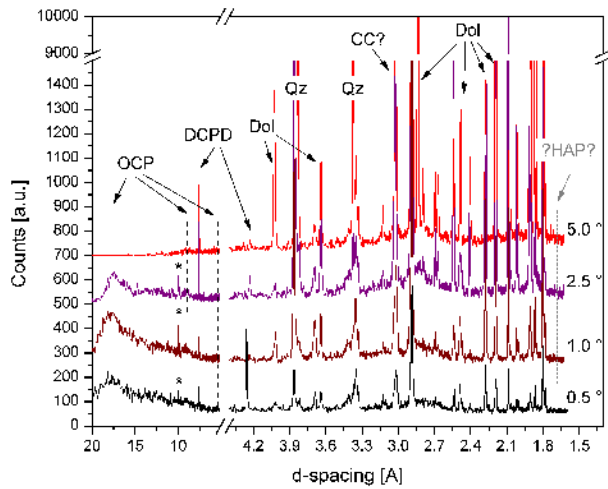


Fig. 4 GIXRD patterns of the surface of a treated marble specimen in correspondence of a dolomitic vein. *Dol* dolomite, *CC* calcite, *OCP* octacalcium phosphate, *HAP* hydroxyapatite, *DCPD* dicalcium phosphate dihydrate, *QZ* quartz, * phyllosilicates

In this case, as showed from the GIXRD patterns acquired with Φ of 5.0 ° and 2.5 °, the investigated area is composed of dolomite coexisting with phyllosilicates and quartz. Calcite, if existing in this area, shows strong shifts of its XRD peaks position and its detection is uncertain. On this area, the GIXRD patterns record the nucleation of DCPD crystals in addition to OCP. The identification of HAP is strongly ambiguous because its marker peak at 1.71 Å (interplanar distance of (004)) is never distinguishable from the baseline.

The investigation with GIXRD of the marble portion exactly below the DCPD crystals sheds light on the relationship between the formation of DCPD and the mineralogical composition of the stone substrate. DCPD is a calcium phosphate with a low Ca/P molar ratio and in these experimental conditions its formation is found to be dependent from the low availability of free Ca^{2+} ions due to the composition of the underlying stone substrate. In fact, the amount of Ca^{2+} ions released from dolomite is significantly lower than the amount released from calcite, due to the different carbonate composition of the two minerals and the consequently lower Ca/ CO_3 molar ratio per formula unit (calcite Ca/ CO_3 molar ratio: 1; dolomite Ca/ CO_3 molar ratio: 0.5). Furthermore, dolomite is less reactive to the acid dissolution, which takes place during the DAP reaction, and, as a consequence, the DAP reaction with dolomite is definitely slower if compared to the kinetics with calcite (the conversion rate of dolomite is about eight times slower than the conversion rate of calcite [27]). No Mg-phosphates are detected by GIXRD data. However, the absence of Mg-phosphates is expected since the release of Mg^{2+} ions from dolomite is even more delayed than Ca^{2+} ions [28]. The coexistence of dolomite and silicates with a very low amount of calcite clearly demonstrates the presence of a vein that determines variations in terms of composition, texture and microstructure. This provides a reasonable explanation for the spotty and irregular formation of DCPD crystals and for the homogeneous formation of OCP and HAP on pure calcite areas.

4 Conclusions

The remarkable core idea of this paper is that SR-GIXRD is a powerful non-destructive tool for the investigation of the conservative history of stone materials and their interaction with the environment.

The optimized experimental setup provided unambiguous information on the nature of the crystalline phases and allowed to disclose their inter-dependence between the calcium phosphate *newly-formed system* and the minerals of the marble portion underlying.

Compared to more conventional XRD techniques, the SR-GIXRD approach overcomes many analytical limits and can be successfully used to investigate the micro-heterogeneities of a material very quickly, supplying noticeable advantages in terms of flexibility, spatial resolution and depth profiling.

Moreover, the present study paves the way to a completely new strategy for layered systems investigation, able to identify crystalline phases of pigments, deposits, degradation and corrosion products.

Conflict of Interest: The authors declare that they have no conflict of interest.

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