Diammonium hydrogenphosphate treatment on dolostone: the role of Mg in the crystallization process

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Abstract: The diammonium hydrogenphosphate (DAP, $(NH_4)_2HPO_4$) reaction with calcite has been extensively investigated. The availability of free calcium ions in the reaction environment has been acknowledged as a crucial factor in the crystallization of calcium phosphates with a high (hydroxyapatite, Ca/P 1.67) or low Ca/P molar ratio (dicalcium phosphate dihydrate, Ca/P 1.00; octacalcium phosphate, Ca/P 1.33). On the contrary, no data are available on the DAP interaction at room temperature with dolomite in terms of reaction mechanism and composition of the reaction products. Here, a multi-analytical approach based on SEM-EDS and X-ray powder diffraction before and after heating treatments is proposed to explore how the formation of calcium phosphates occur on Mg-enriched substrates and if the presence of magnesium ions during the reaction influences the crystallization process of calcium phosphates. The DAP reaction with polycrystalline dolomite gives rise to the formation of struvite and of poorly crystalline hydroxyapatite. Calcium and magnesium ions mutually interfered in the crystallization of magnesium and calcium phosphates, respectively, whose effects influence the properties (size, micro-morphology, composition and crystallinity)of the newly-formed phases.

Keywords: calcium phosphate; hydroxyapatite; magnesium phosphate; struvite; dolomite; consolidating treatment; cultural heritage; ammonium phosphate

1. Introduction

Diammonium hydrogenphosphate (DAP, $(NH_4)_2HPO_4$) is a promising inorganic consolidating treatment for decayed carbonatic stones [1–4]. The DAP consolidating treatment aims at restoring the stone matrix through a partial transformation of the original material in newly-formed phosphate phases. Ideally, crystalline hydroxyapatite (HAP, $Ca_5(PO_4)_3OH$) is formed by combining calcium ions of the substrate with phosphate groups of the reagent [5,6].

The DAP reaction with calcite ($CaCO_3$) of carbonatic stones has been extensively investigated during the last years, [7,8] and recent findings showed that the DAP reaction with polycrystalline calcite of carbonatic stones is non-stoichiometric [9], which implies that many crystalline phases may form in complex mixtures with a nanocrystalline and/or partially-substituted HAP [1,5,6,9–12]. Furthermore, it has been demonstrated that the composition of the new phases depends on several variables, as *e.g.*, the reaction condition (pH, ion strength), the stone substrate (lithotype, microstructure) and the treatment protocol (duration, application method, DAP molarity) [10,13–16].

The DAP reaction in presence of low amount of calcium ions (*e.g.,* when DAP is used with a low molarity [9] or on calcite substrates with Mg-containing veins [17]) follows a different crystallization process. In particular, the availability of free calcium ions is a crucial factor in the crystallization; phases with a low Ca/P molar ratio (*e.g.,* dicalcium phosphate dihydrate DCPD $CaHPO_4{\cdot}2H_2O$, Ca/P molar ratio 1.00, and octacalcium phosphate OCP $Ca_8(HPO_4)_2{\cdot}5H_2O$, Ca/P molar ratio 1.33), [13,14]) are formed instead of HAP [9,18] (Ca/P molar ratio 1.67) in reaction environments with a low concentration of calcium ions.

Over the centuries, several carbonatic stones with magnesiac nature have been used for artefacts and buildings. A crucial issue is the challenging conservation of Angera stone, a sedimentary dolostone widely used as ornamental lithotype in the North of Italy and severely affected by decay [19]. The literature on the investigation of DAP treatments applied to calcite-based materials of cultural heritage is progressively increasing, while, surprisingly, the DAP reaction with magnesium carbonates is still quite unexplored.

Clearly, the DAP reaction with magnesium carbonates is expected to give rise to a set of crystalline phases different to those formed with calcium carbonate. However, even though the transformation of magnesium carbonates into magnesium phosphates with hydrothermal conditions [20], or by calcination [21], is well-known in literature, only a few studies investigated the carbonate-to-phosphate conversion at room temperature [22,23], which normally is the operative condition of conservation treatments.

This study focuses, for the first time, on the reaction of polycrystalline dolomite with DAP solutions at room temperature in order to explore how: i) DAP treatments react with dolostones; ii) the nucleation of calcium phosphates occur in presence of Mg-enriched substrates; iii) the presence of magnesium and calcium ions during the reaction influences the crystallization process of calcium and magnesium phosphates.

The DAP treatments were carried out by using DAP water solutions with two different molarities on quarry specimens. The formation of specific crystalline phases and their diffusion inside the stone matrix are investigated following a multi-analytical approach (SEM-EDS, X-ray diffraction before and after heating treatments) and critically discussed.

2. Materials and Methods

2.1. Materials

The Angera stone, a dolostone quarried in the northern Italy (Piedmont) and widely used in the Lombard architecture as ornamental building material since the Roman age, has been used for this study [24]. The lithotype is characterized by a very fine grain size and a high porosity (18-26 %, depending on the Angera stone variety). The stone is mainly composed of dolomite ($CaMg(CO_3)_2$) in association with a low fraction of clay minerals and iron oxides [19,25–28].

The experiments were performed on the white variety of Angera stone, as it is the variety which undergoes to the most severe decay processes in the environmental conditions. They were carried out on a set of freshly quarried prismatic specimens (50×50×20 mm) in order to explore the crystallization of phosphates from DAP solutions at room temperature on dolostones.

The Angera stone specimens were treated by a 0.76 M or of a 3.00 M aqueous solutions of DAP (CAS Number 7783–28-0, assay ≥ 99.0%, reagent grade, Merck, Darmstadt Germany). The concentration 0.76 M (corresponding to a 10% w/w) was selected on the basis of previous experiments [10] and on the consolidating practice in conservation worksites [29]; the choice to include also 3.00 M concentration was suggested in previous studies available in the literature [7,30], where this value was used to enhance the crystallization of calcium phosphates. The consolidating DAP solution was applied by poultice (dry cellulose pulp, MH 300 Phase, Italy; ratio ~ 5:1 DAP solution: dry cellulose pulp), as it is one of the most common application methods in the conservation field. The treatment time was 48 hours, during which the specimens were wrapped in a plastic film to avoid the evaporation of the solvent. After 48 hours, the plastic film was removed and the specimens were left drying at room temperature for other 24 hours with the poultice on top. The DAP poultice was then removed and the specimens were rinsed three times by poultice made with deionised water and dried at room temperature.

2.2. Methods

The crystalline phases of the Angera stone specimens before and after the consolidating treatments were investigated by X-ray powder diffraction (XRD) in Bragg–Brentano geometry with a Panalytical X'Pert PRO diffractometer, equipped with 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 samples were finely pulverised and spread on silicon zero background holders. The diffraction patterns were collected with a Cu Kα radiation source (λ ~ 1.54 Å), accelerating voltage 40 kV and electric current at the Cu anode of 40mA, in the 2 Theta angular range 4.5 – 65 ° with a stepsize of 0.17 °and time per step of 130 s.

A set of thermal treatments were carried out in order to fully explore the composition of the newly-formed calcium phosphates, which showed ambiguously interpretable X-ray diffraction patterns. For this reason, untreated and treated specimens were initially analysed at room temperature (rT); after that, the samples were heated at 400 °C, 600 °C and 900 °C, and re-analysed at rT after each heating process. The selection of the

temperature steps used to investigate the *T*-induced "parent-to-product" phase transformation is driven by literature data [9,16,31–36].

The micro-morphology of the specimens before and after the DAP treatments were investigated by zenithal observations using a JEOL 5910 LV scanning electron microscope (SEM) coupled with energy dispersive X-ray spectrometer (EDS) IXRF-2000 (0–20 keV) in high vacuum mode on carbon coated samples.

3. Results

3.1. Analysis of the newly-formed phases on Angera stone

Figure 1 shows the X-ray diffraction patterns of quarry Angera stone before and after the DAP consolidating treatment. The XRD pattern of the untreated substrate shows well-defined peaks of dolomite (main peak at 31.02° and secondary peaks at 24.13°, 33.61°, 35.33°, 37.42°, 41.18°, 44.96°,, 50.59°, and 51.11° of 2Theta, λ = Cu Kα) and weaker peaks of secondary minerals (quartz at 26.60° of 2Theta, phyllosilicates at 9.41° and 25.37°, feldspar at 26.96° and plagioclase at 27.48°).

The XRD patterns of Angera stone treated with 0.76 M and with 3.00 M DAP solution exhibit the formation of magnesium phosphates and calcium phosphates. In fact, the XRD peaks of struvite ($MgNH_4PO_4{\cdot}6H_2O$, peaks at 14.99°, 15.81°, 16.47°, 20.85°, 21.45°, 27.07° and 31.94°) and most likely apatite (peak at ~25.90 °) are revealed in mixture to the substrate phases.

The XRD peaks of struvite are sharp and well-resolved, indicating the formation of a well crystalline phase, whereas the peak of the possible apatite is extremely weak and broad, most likely due to a poorly-ordered structure. No other peaks ascribable to calcium phosphates are detectable in the XRD patterns, likely due to overlapping with the peaks of other phases or to their severe weak intensity. Several calcium phosphate phases have a peak at ~25.90 ° of 2Theta, as many of them are characterized by a similar crystalline structure (*e.g.,* hydroxyapatite; calcium-deficient hydroxyapatite and its partially-substituted forms; octacalcium phosphate; amorphous calcium phosphates, ACPs, $Ca_xH_y(PO_4)_z{\cdot}nH_2O$, with n=3–4.5 and 15-20% H_2O) [13,37–41]. The peaks of struvite are more intense in the XRD patterns of the specimens treated with the 3.00 M DAP, while the peak of the possible apatite is more visible in the 0.76 M ones.

The XRD pattern of the specimens treated with the 3.00 M DAP solution also shows evidence of residual traces of the reagent (DAP peaks at 17.55°, 17.94°, 23.56°, 26.43°, 27.70°, 28.41° and 29.16°) and of ammonium dihydrogen phosphate (ADP, $NH_4H_2PO_4$, at 16.63°), a by-product of the reaction; these two phases are still present within the specimens despite they were rinsed. No peaks of DAP and ADP are detected on the specimens treated with the 0.76 M DAP solution.

In order to further explore the microstructural-crystallographic feature of these poorly-ordered calcium phosphate phases, a sequence of investigations were carried out by electron backscatter diffraction (EBSD), FTIR and Raman spectroscopy. However, the outcomes of these supplementary techniques did not supply any further information and their results are not reported in this paper.

In particular: i) for EBSD, it was not possible to obtain the XRD patterns of the investigated area due to the poorly crystalline nature of the phases, their nanometric size and the boundary effects, deriving from the alteration during the sample preparation of the interface between the new phases and the substrate; ii) for Raman spectroscopy, phosphate phases have a weak Raman scatter, especially when submicrometric and/or poorly ordered, and in mixture with carbonates (phases characterized by a very high Raman cross section); iii) as for FTIR data, the superimposition of the characteristic stretching and bending PO_4 vibrational bands of both the phosphate phases prevented their unambiguous identification.

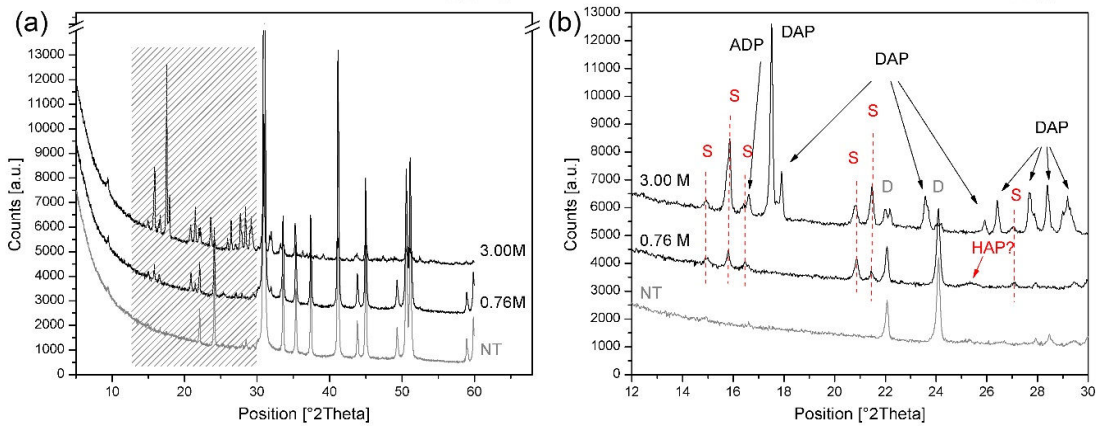

Figure 1. (**a**) XRD patterns of untreated Angera stone (NT) and Angera stone treated by poultice with a 0.76 M (0.760M) and 3.00 M (3.00M) DAP solutions. (**b**) Detail in the range 12-30 ° showing the phase variations occurred after the consolidation. D = dolomite, S = struvite, HAP? = possible hydroxyapatite, DAP = diammonium hydrogen phosphate, ADP = ammonium dihydrogen phosphate.

3.2. Micro-morphological investigations of the stone surface

The micro-morphology of untreated Angera stone, showing the well-shaped rhombohedral crystals habit of dolomite is appreciable in Figure 2a, while that of the reacted dolomite is shown in Figures 2b and 2c. After the DAP treatments, the stone surface shows the presence of a newly-formed coating characterized by a pseudo-amorphous aspect. This coating is prevalently adherent to the stone matrix together with the crystallization of spherical particles agglomerates. Both of them cover the characteristic morphological features of the lithotype.

In the case of the specimens treated with the 0.76 M DAP solution, the newly-formed phases appear as a pseudo-amorphous thin film (thickness ~ 0.6 µm) that covers the micritic dolomite (Figure 2b, left). On the film profiles, an incipient formation of spherical particles in an elongated arrangement has been detected. On dolomite rhombohedral grains (dolomite crystal size ~ 15-20 µm),a shell of spherical crystallites having a bigger size is distinguishable (Figure 2b, right).

In the case of the specimens treated by DAP 3.00 M, the profiles of the dolomite crystals appear affected by pronounced corrosion marks, with the consequent crystal nucleation of spherical structures combined to form elongated chain individuals (detail of Figure 2c).

Phosphorous is detected by EDS microanalysis in correspondence of the crystals overgrown on the substrate and morphologically different from the dolomite grains of the substrate. By measuring these newly-formed phases, calcium, magnesium and phosphorous are always present, even though the ratio of their elemental abundance varies.

The SEM investigations suggest the presence of two different phosphates phases, a magnesium and a calcium phosphate which exhibit differences in morphology and particle size (Figure 2b and c). These phases (struvite and a possible apatite, as suggested by the XRD data) do not show their typical orthorhombic and rose-like morphologies [9,42]. However, on the basis of the XRD results and on literature data about the mutual influence of Ca^{2+} and Mg^{2+} ions on the size and habit of hydroxyapatite and struvite, it is possible to hypothesize the following correlation: i) the pseudo-amorphous aspect of the coating could be ascribed to nano-sized agglomerates of Ca-phosphate spherical particles; ii) the spherical particles (consistently in the range of 10–50 nm; dimension slightly affected by the treatment concentration) often characterized by an aggregate prismatic aspect (Figure 2c, right) could be correlated to the formation of magnesium phosphate nuclei.

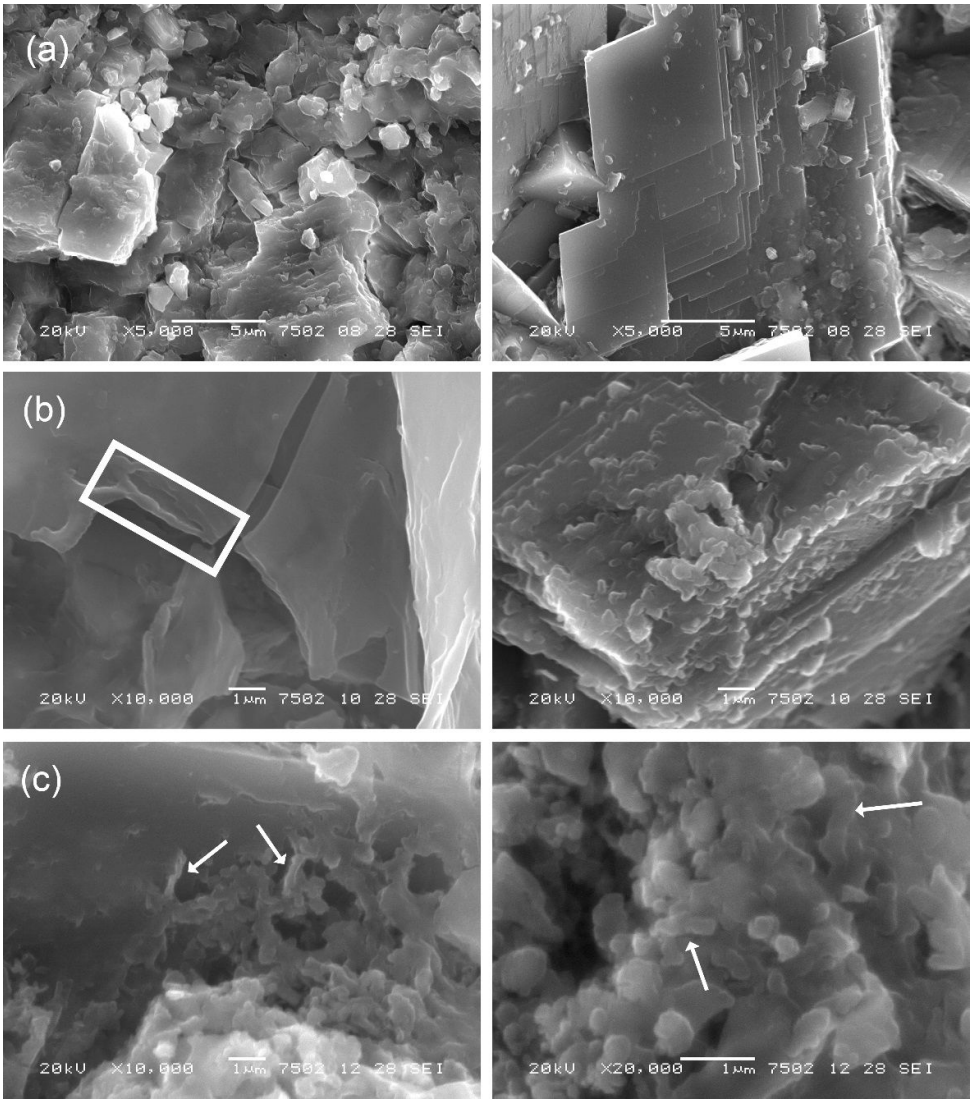

Figure 2. SEM images of Angera stone.(**a**) untreated substrate, showing micritic dolomite on the left and bigger grains of well-shaped rhombohedral dolomite on the right; (**b**) treated lithotype after the poultice with a 0.76 M DAP solution. On the left, pseudo-amorphous coating formed on micritic dolomite and incipient formation of spherical structures in an elongated arrangement (white rectangle); on the right, big dolomitic crystal with the overgrowth of crystal agglomerates in spherical structures, some of them having prismatic elongations; (**c**) treated Angera stone after the poultice with a 3.00 M DAP solution, showing detail of spherical crystallites and their aggregation in chains - elongated arrangement (arrows).

3.3. Evidence of HAP formation by thermal treatments

Thermal treatments are an acknowledged tool to investigate the nature of calcium phosphate phases showing at room conditions (rT) hardly distinguishable X-ray diffraction patterns [31], by promoting *T*-induced phase transitions.

More specifically, heating of: i) poorly-crystalline stoichiometric HAP generates crystalline stoichiometric HAP; ii) partially-substituted HAP (*e.g.,* carbonated-hydroxyapatite) produced crystalline HAP in mixture with β-tricalcium phosphate (β-TCP, β-$Ca_3(PO_4)_2$), and with β-TCP predominant vs HAP; iii) OCP do not generates HAP, but only β-TCP in mixture with β-calcium pyrophosphate (β-CPP, $Ca_2P_2O_7$) [9,31].

Figure 3 shows the parent-to-product phase transformations occurred in Angera stone treated with the 0.76 M DAP solutions. Identical results are obtained on the specimens treated with the 3.00 M one. Thermal treatments were carried out also on untreated Angera stone for comparison and the principal XRD patterns are provided as well.

The heating at 400 °C induces the first phase variation, namely the total disappearance of the XRD peaks of struvite, due to the collapse of struvite into amorphous magnesium phosphate phases. Previous studies describe that heating induces a chain decomposition, involving the initial formation of amorphous magnesium hydrogen phosphate hydrate ($MgHPO_4 \cdot 3H_2O$ [36]), followed by its transformation into amorphous anhydrous magnesium hydrogen phosphate ($MgHPO_4$ [32,35,36]). In this study, it was not possible to discriminate between the two amorphous products, thus they are referred to a generic amorphous magnesium phosphate phases.

The heating at 600 °C acts on poorly-crystalline calcium phosphates, as the weak broad peak at ~25.90 ° of 2 Theta becomes more pronounced. The principal phase transformation occurs after heating at 900 °C, where dolomite of the substrate is decomposed into magnesium oxide (MgO, peaks at 42.92° and 62.30°) and lime (CaO, peaks at 32.27°, 37.48° and 53.97°; phase transformation probably occurred between 600-820 °C [33,34]) and the peaks of calcium phosphates become more defined. More precisely, the growth of sharp, well-defined peaks at 2 Theta of 25.90° (d_{002}), 31.77° (d_{211}), 32.96°(d_{300}) and 34.08° (d_{202}) unambiguously identify crystalline HAP as heating by-product. Only the very weak peak at 28.09° could be attributed to β-TCP.

Magnesium oxide and lime, the calcinations by-products of dolomite, are active components that might interact with the calcium phosphates at high temperature, resulting in a further calcium source. However, even if the occurrence of this phenomenon cannot be *a priori* excluded, there is no evidence of other high-temperature calcium phosphate phases nor of high-temperature magnesium phosphates formed by the reaction of active oxides with amorphous phosphates.

These results demonstrate that apatite formed after DAP treatments is poorly-crystalline but mainly stoichiometric. The formation of minor fraction of β-TCP indicates that a partially-substituted nonstoichiometric apatite and OCP are formed as well by the DAP treatment, but with poorly-crystalline stoichiometric HAP predominant versus these phases.

No phase variations are observed for silicates and phyllosilicates of the Angera stone matrix.

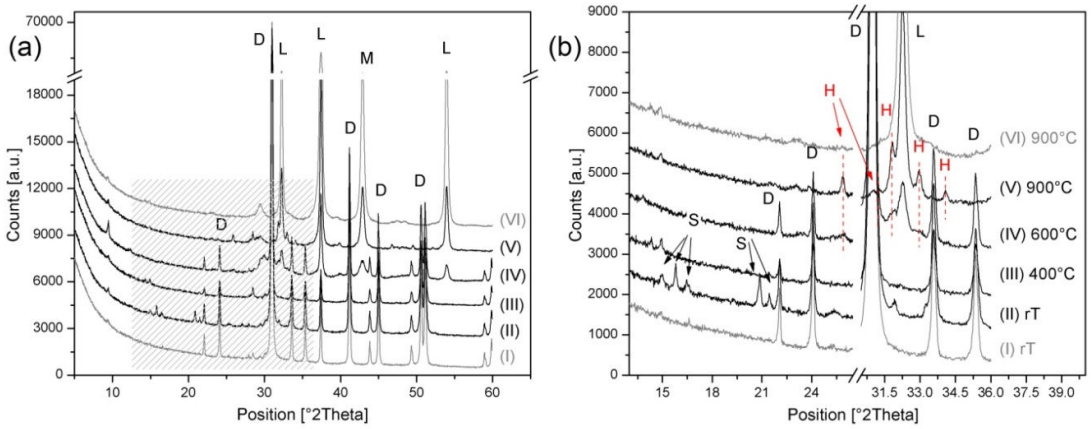

Figure 3. (**a**) XRD patterns of untreated (grey patterns) and treated (black patterns) Angera stone at room temperature (rT) and after heating at 400 °C, 600 °C and 900 °C. (**b**) zoom of (a) showing the phase transformation occurred with heating. D = dolomite, L = lime, M = MgO, S = struvite, H = hydroxyapatite.

4. Discussion

The DAP reaction with the Angera stone involves the partial dissolution of the dolomite grains, with the release of calcium and magnesium ions from the stone substrate. It is followed by the interaction of these bivalent ions with the reagent ions, with the consequent nucleation and growth of newly-formed phosphate phases. This dissolution - recrystallization process is topotactic and forms magnesium phosphates and calcium phosphates: (struvite and hydroxyapatite, respectively) arranged in a coating on dolomite grains. The micro-morphology of this coating, which resembles almost the features of polymeric products used for the conservation, is actually quite different from the crystalline *shell* observed on calcite-based lithotypes [9,10], even where the reaction occurred in presence of Mg-containing veins [9,16,17]. The crystallization of these phases is not merely a superficial film, but it is a binding network which connects different dolomite grains.

The crystallization of the newly-formed phosphates is influenced by the microstructure and the composition of the lithotype. In particular, the microstructure of the substrate acts on the micro-morphology of the new phases. In fact, the newly-formed phosphates are well shaped when they grow on dolomite in large crystals, while on micritic dolomite the phosphates mainly develop tiny crystals with irregular morphologies.

Mg-phosphates are crystalline, as demonstrated by the sharp well-defined XRD peaks of struvite. On the contrary, the apatite is formed as poorly ordered partially-substituted crystals. It is worth underlying that hydroxyapatite formed after DAP treatments by using only calcium ions of the substrate is never highly crystalline, even when the reaction occurs on calcium carbonate stones. However, the DAP reaction on dolomite of Angera stone is particularly non-stoichiometric, and the formed apatite is so poorly ordered that its identification before heating is assumed only by a weak broad XRD peak. It is conceivable that Mg^{2+} ions destabilizes the crystalline structure and growth sequence of apatite, that shows a morphology characterized by an amorphous-spherical aspect similar to that reported by Ren *et al*. [43]. In any case, the thermal treatments shed light on the nature of this phase and, for clarity's sake, the poorly ordered calcium phosphate phase formed after the DAP treatment will be labelled as HAP in the following discussion.

The HAP X-ray diffraction peak is more intense in the specimens treated with the DAP 0.76 M, while struvite peaks are more evident in the specimens treated with the DAP 3.00 M, even though it is only a semi-quantitative evaluation. The higher is the DAP molarity, the higher is the ion dissolution from the substrate; consequently, the more pronounced is the formation of struvite and the more poorly crystalline is HAP. Regarding to the DAP molarity, the "coating-like" morphology is more evident in the specimens treated with the DAP 0.76 M, whereas the rounded morphology in elongated chains is prevalent on the specimens treated with the DAP 3.00 M. Considering these features, it is conceivable to hypothesize that these morphological and compositional differences depends on the reaction variables, first of all the pH and the ionic strength. Moreover, dolomite is less reactive than calcite to DAP solutions [20], thus the reaction kinetic may be different as well.

The minimum solubility of struvite is documented in the pH range 9-11 [42], while HAP crystallize in aqueous solutions at pH >8.5-9 [14].

At the beginning of the reaction the pH is 8.8, which is close to the ideal crystallization pH for both the phases. Actually, even though it is not possible to measure the evolution of pH on grain boundaries, it is reasonable that pH decreases as long as the reaction evolves, due to the: i) dissociation of the reagent into PO_4^{3-} and H^+ ions [9,44], ii) nucleation of HAP which consumes OH^- ions [41]; iii) precipitation of struvite which subtract NH_4^+ ions [36].

Furthermore, close to dolomite boundaries where the dissolution-recrystallization process is ongoing, Ca^{2+} and Mg^{2+} ions compete for PO_4^{3-} groups to nucleate calcium phosphates or magnesium phosphates. In the microscale variations of the pH and of the ionic strength at the grain boundaries, carbonate and bicarbonate ions are reasonably involved as well [45].

The prediction of struvite/apatite crystallization is particularly challenging when this reaction occurs on dolomite stone. A combination of conditions governed by thermodynamics of solid-liquid equilibrium, kinetics of reaction, pH of the solution from which struvite and hydroxyapatite may precipitate, super saturation and presence of foreign ions influence their nucleation and crystallisation process.

In particular, the influence of foreign ions on struvite/hydroxyapatite nucleation and their crystallisation is a crucial issue because of Ca and Mg are at the same time "impurities" in that solution from which the two Mg/Ca phosphate phases may precipitate. This mutual interference affects the growth rate, which in turn inhibits the increase of crystal size [36].

This complex ionic equilibrium, with pH fluctuations toward not ideal reaction conditions, generates two effects. The first one is a clear inhibiting effect of Mg^{2+} ions on the crystallinity, morphology and crystal size of HAP, which nucleates as a poorly-crystalline phase and with a pseudo-amorphous coating aspect or in agglomerated structures (depending on the employed DAP molarity). A partial intra-crystalline Mg^{2+} *vs.* Ca^{2+} substitution, as ab initio simulated by [43], is also possible. Referring to previous findings, this phenomenon should induce a slight variation of the unit-cell constants. In the case of HAP formed after the DAP treatment on dolomite, the possible generation of a Mg-HAP is not clearly documented, as it is most likely a very minor phase.

The second aspects is the interference of Ca^{2+} ions in the crystallization of struvite, which occurred in sub-micrometric nuclei of crystals, more than well structured micrometric prismatic crystallites. The possible presence of ions substitutions in struvite is also highly likely size [36].

Focusing on conservation evaluations, the newly-formed crystalline phases nucleate in a coating on dolomite grains by forming a covering which provides new functional properties to the substrate.

Irrespective by their composition, the newly-formed phases nucleate on the dolomite grain surface and among dolomite grains, hence their crystallization provide a clear bonding action on the stone microstructure. Further experiments are scheduled in order to explore the quantitative ratio of the two phases and their arrangement within the stone pores.

5. Conclusions

The DAP reaction with polycrystalline dolomite of the Angera stone determines an interaction among calcium and magnesium ions, which compete each other to form phosphate phases. The variation of the solution pH and of the ionic strength during the DAP reaction with dolomite generate a complex crystallization processes of the phosphate phases, which are formed as Mg-phosphates and Ca-phosphates crystals with morphologies different from those commonly described in literature. The mutual interference of the ions involved in reaction (NH^{4+}, Mg^{2+}, PO_4^{3-}, Ca^{2+}, CO_3^{2-}, HCO_3^{-}) determines an irregular crystal growth pattern with respect to the primary nucleation process. The consequence is a clear effect in the crystallization of the new phases (struvite and hydroxyapatite) in terms of crystal size, micro-morphology, composition and crystallinity.

In particular, the Mg^{2+} ions presence destabilizes the hydroxyapatite well-ordered structure, causing a structural variation that inhibits the growth of well-shaped crystals and, on the contrary, promotes the formation of an amorphous coating on the dolomite grains. The higher is the DAP molarity, the higher is the Mg molar fraction in the solution and then the lower is the crystallinity of the formed calcium phosphate. In any case, heating treatments demonstrated that the newly-formed apatite is poorly crystalline but mainly stoichiometric, thus with a Ca/P molar ratio quite close to the ideal one (1.67).

On the other hand, the struvite formation is affected by the presence of free calcium ions as well, and the descending effects are observed in the crystal morphology and crystal size.

Regarding the effects induced by the DAP treatment on the Angera lithotype, it is important to consider that the new phases formed on the dolomite grains create a crystalline network that likely improves the cohesion of the lithotype.

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