

DEVELOPMENT OF HYDROXYAPATITE FILMS TO REDUCE THE DISSOLUTION RATE OF MARBLE

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Abstract

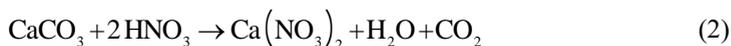
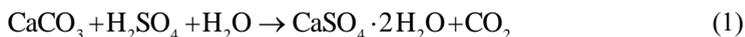
It has been demonstrated that treatment with a solution of diammonium hydrogen phosphate (DAP) provides effective consolidation of limestone by deposition of hydroxyapatite (HAP) (Sassoni et al. 2011a, 2011b). In this paper, the same reaction is used to protect marble from dissolution in acid. This is analogous to the use of oxalate films (Doherty et al. 2007), but HAP has a much lower solubility than oxalate and a dissolution rate that is four orders of magnitude slower than calcite (Naidu et al. 2011). By reacting DAP with marble in ambient conditions, porous HAP films with thicknesses between 5 and 20 microns are obtained within 1-7 days. The effect of surface roughness, precursor concentration, precursor choice, external cationic and anionic additions and pH on film growth and porosity are discussed. The performance of these films in acidic conditions, as well as the adhesion and mechanical strength of the films have been investigated. The DAP-treated stones offer significant protection over the untreated stones in acidic conditions.

Keywords: diammonium hydrogen phosphate, dissolution rate, porosity, film growth, pH, calcium phosphates

1. Introduction

Marble has been used extensively for centuries to create sculptures and monuments such as the Parthenon, the statue of David and the Taj Mahal. It is a metamorphic stone, composed of the mineral calcite, that is essentially non-porous and hence not susceptible to many weathering processes that plague limestone, such as damage from ice and salt crystallization. However it is a relatively soluble mineral, so the major threat to these precious monuments is attack by acid rain (Winkler 1997).

With the onset of industrialization, the concentration of sulphur dioxide and nitrogen oxides in air increased significantly. In the presence of rainwater, these pollutants form sulphuric acid, which reacts with calcite to make gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (1), and nitric acid, which reacts with calcite to make highly soluble $\text{Ca}(\text{NO}_3)_2$ (2):



The rates of these reactions increase with proton concentration and hence as the pH of rain decreases. In highly polluted areas, the pH of rain can be as low as 4.

Recently, research has been directed towards finding ways to chemically modify the surface of marble to reduce its dissolution in acid. One promising treatment, investigated by Matteini et al. (1994), was to form a calcium oxalate film on marble. However, tests showed that the oxalate layer had not formed uniformly on calcite (Doherty et al. 2007) and the treatment was not entirely effective. We believe that this could be due to the high solubility of calcium oxalate (not much lower than calcite) and the difference in crystal structure between calcite and calcium oxalate, which could inhibit nucleation on the substrate (Table 1).

The research on oxalate was the motivation for investigating the use of hydroxyapatite (HAP) as a surface-protective coating. Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is the main inorganic constituent of tooth enamel and bone (Johnsson et al. 1992). The advantage of using HAP over calcium oxalate is that HAP has a similar crystal structure and close lattice match to calcite (Table 1). This should favor nucleation of HAP on calcite, and might permit formation of a coherent layer of HAP on the surface of marble.

Table 1: Lattice parameters and solubility products of calcite, HAP and calcium oxalate (Nancollas et al. 1974; Lide 1999; Dorozhkin 2009; Brady 1996; Harouiya et al. 2007)

Mineral	a (Å)	b (Å)	c (Å)	K_{sp} (25°C)
Calcite (2x)	9.98	9.98	33.82	3×10^{-9}
Hydroxyapatite	9.43	9.42	6.88	3×10^{-59}
Calcium oxalate (2x)	12.58	29.16	20.32	2×10^{-9}

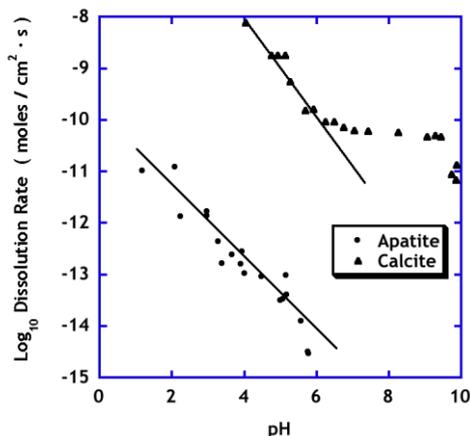


Figure 1. Dissolution data for calcite (Brady 1996) and apatite (Harouiya et al. 2007)

HAP has a much lower solubility (Table 1) and dissolution rate (Figure 1) than either calcite or calcium oxalate, thus having the ability to confer tens of years of protection in acidic environments, with a dense coating of only about 10 μm .

There has been extensive investigation of HAP synthesis in the biomedical field, using extreme conditions including high pressures and temperatures and complicated techniques (Osaka et al. 1991; Brendel et al. 1992; Yoshimura et al. 1994). However, we have found that

HAP can be synthesized from mild wet chemical routes, and our aim is to investigate the feasibility of forming a low-solubility, dense film of HAP on calcite using non-toxic aqueous precursors at ambient temperature and pressure.

The performance of HAP has already been proven in restoring the strength of weathered limestone (Sassoni et al. 2011a, 2011b). Other workers have also investigated the use of HAP as a consolidant (Yang et al. 2011; Liu et al. 2011; Matteini et al. 2011). In this paper, we discuss its use as a surface-protective layer for marble to reduce its dissolution in acid. This treatment offers the following advantages: (a) noticeable retar-

dition of the stone's dissolution rate in acidic conditions, (b) simple, non-toxic and ambient chemistry involved and (c) visually unaltered appearance of the stone.

2. Experimental Procedure

Diammonium hydrogen phosphate (DAP) was used as solution precursor for the reaction to form HAP. The reaction between calcite and DAP is essentially a dissolution/precipitation process and is expected to proceed via the following mechanism (Kamiya et al. 2004):



2.1 Wet chemical synthesis

DAP was obtained from Sigma-Aldrich ($\geq 99.0\%$, CAS No. 7783-28-0). Carrara marble samples were obtained from Pasvalco (Closter, NJ, USA). The marble samples were cut using a diamond saw. Cubes of marble with dimensions 0.5 x 0.5 x 0.5 cm were placed in 250 ml beakers and reacted with DAP solutions via wet precipitation. Each cube was left in a sealed beaker with 100 ml of solution for a set time period, then removed, washed with demineralized water and left to dry at room temperature for 24 hours, before film characterization and testing were conducted.

2.2 Effect of changing variables (temperature, time, concentration)

To prepare dense coatings for acid resistance, the variables explored were reaction temperature (20-105 °C), phosphate concentration (1 mM to 2 M) and reaction time (1 hour to 7 days). The source of phosphate was also varied. Using 1 M ammonium dihydrogen phosphate resulted in soluble brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) films, which will be discussed in a later publication. All of the results reported here were obtained with DAP.

2.3 Ionic additions

In the experiments described in section 2.1, the underlying substrate was the calcium source for film growth. This is counter-productive, as the purpose of the reaction is substrate protection, not substrate removal. The continuous removal of calcium ions from the stone is believed to create channels through the film, from the substrate to the film-solution interface, thus creating permanent porosity (Kasioptas et al. 2008). To suppress this dissolution and increase film density, cationic (1 mM CaCl_2) and anionic (15, 50 and 150 μM $(\text{NH}_4)_2\text{CO}_3$) additions were investigated. The calcium and carbonate salt solutions were added to stirred DAP very slowly to avoid precipitation in solution. The cubes were reacted as detailed in section 2.1.

2.4 Characterization

An environmental scanning electron microscope (ESEM) (FEI Quanta-200 FEG) was employed to observe microstructural changes on the sample surface. The instrument is capable of producing high-resolution images in gaseous environments, which rendered sample pre-coating unnecessary. Energy dispersive X-ray spectroscopy (EDX) in the ESEM was used to detect the phosphorous in films. It was also used to confirm absence of unreacted DAP or ammonium salt in the film. To determine film thickness and assess porosity, cross-sectional profiling was performed on cubes coated with epoxy and polished with alumina (down to 1 μm grit on an Allied Multi Prep Polisher) to expose

the cross-section. These were then examined under the ESEM and elemental profiling was conducted using EDX. X-ray diffraction (XRD) (Bruker D8 Discover X-Ray Diffractometer) was employed to identify the crystalline phases present in the films, as it distinguishes between HAP and other calcium phosphate phases.

2.5 Acid resistance

As the reaction between stone and acid proceeds, dissolved hydrogen ions in solution are taken up to form water, so the pH increases. This increase was monitored for bare and HAP-coated samples of marble. Rectangular samples of 2 x 1 x 0.5 cm were cut and reacted as outlined in sections 2.1-2.3, then placed in 250 ml stirred beakers containing 200 ml HNO₃ with starting pH 3.5. These were reacted for 10 hours, the time required for the HNO₃ to reach neutral pH when reacting with bare calcite. Continuous monitoring of pH was conducted using CyberComm Professional data-logging software.

3. Results

3.1 Effect of temperature, time, and concentration

Samples treated at 105 °C, 60 °C and room temperature (RT) followed a similar sequence of nucleation, growth and coarsening, with the reaction rate decreasing as temperature decreased. Reaction at 105 °C resulted in a coherent coating with full substrate coverage within a few hours; while samples reacted at RT took a day or more. At RT, the reaction rate increased with DAP concentrations (1 mM to 2 M). Nucleation occurred at scattered points on the stone and the coating spread out from those points to cover the entire substrate. The coatings appeared porous and the crystal morphologies were needle-like, with eventual coarsening to smoothen and completely cover the underlying substrate, as shown in Figure 2. At 0.5 M to 2 M, dense films formed between 1 and 7 days, while at lower concentrations (0.1 M and below), it took a few weeks to a month for complete surface coverage.

EDX analysis confirmed that the films contained phosphorous (Figure 3). Peaks indicating presence of precursor solution and contaminants were not detected. XRD confirmed HAP was obtained (Figure 4). No peaks for soluble metastable phases were observed.

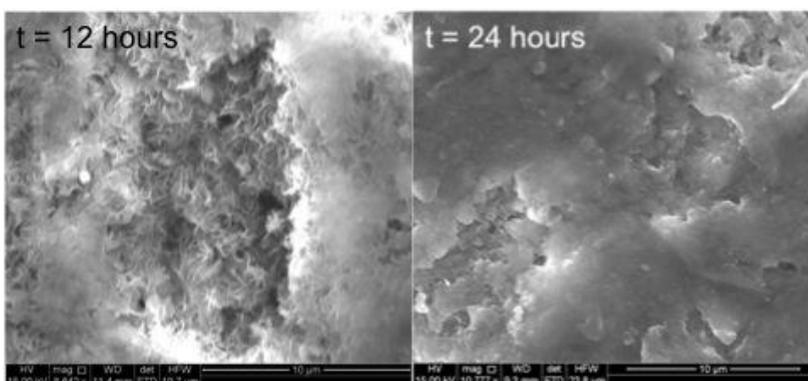


Figure 2. 1 M DAP reaction for two time periods (mag. bar: 10 µm) showing structural evolution of the film.

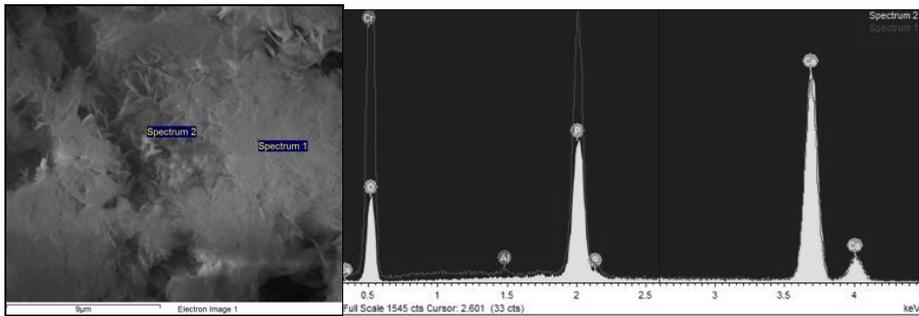


Figure 3. EDX peaks (right) for calcite reacted in 1 M DAP for 24 hours (left)

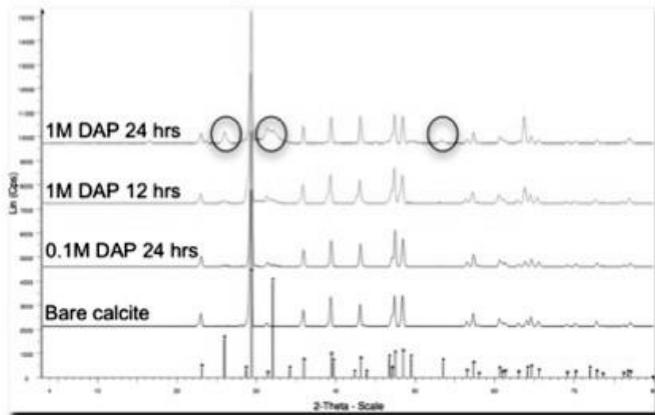


Figure 4. XRD peaks for bare calcite and DAP-treated calcite with different variables

3.2 Ionic additions

Addition of 1 mM CaCl_2 to 1 M DAP increased the rate of reaction and resulted in complete surface coverage within 24 hours of reaction. EDX analysis confirmed the presence of phosphorous and a very small amount of chloride (which may be incorporated into the HAP crystal).

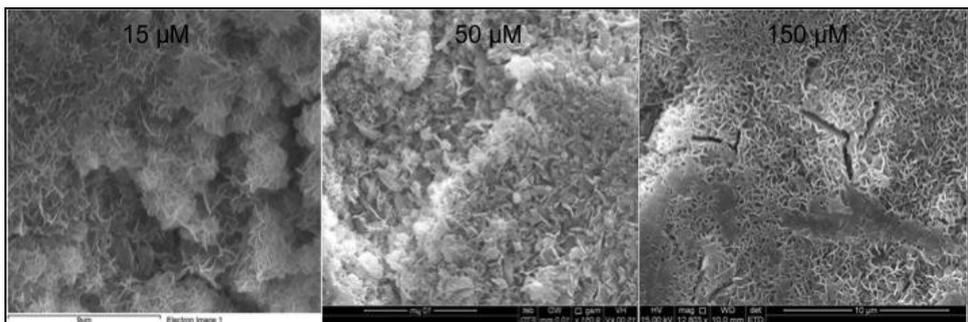


Figure 5. Effect of 15, 50, 150 μM $(\text{NH}_4)_2\text{CO}_3$ with 1 M DAP + 1 mM CaCl_2 after 24 hours (mag. bar:10 μm)

Additions of 15, 50 or 150 μM of $(\text{NH}_4)_2\text{CO}_3$ to 1 mM CaCl_2 and 1 M DAP (24 hours) revealed a similar level of coverage as the 1M DAP + 1 mM CaCl_2 reaction, but slightly different film morphology, compared to layers made from 1M DAP + 1 mM CaCl_2 and 1 M DAP alone (Figure 5).

Cross-sectional analyses of the films with calcium (Figure 6) and carbonate additions revealed seemingly dense profiles of approximately a 10- μm thickness after 24 hours reaction. X-ray analysis revealed HAP formation and no soluble metastable calcium phosphate phase.

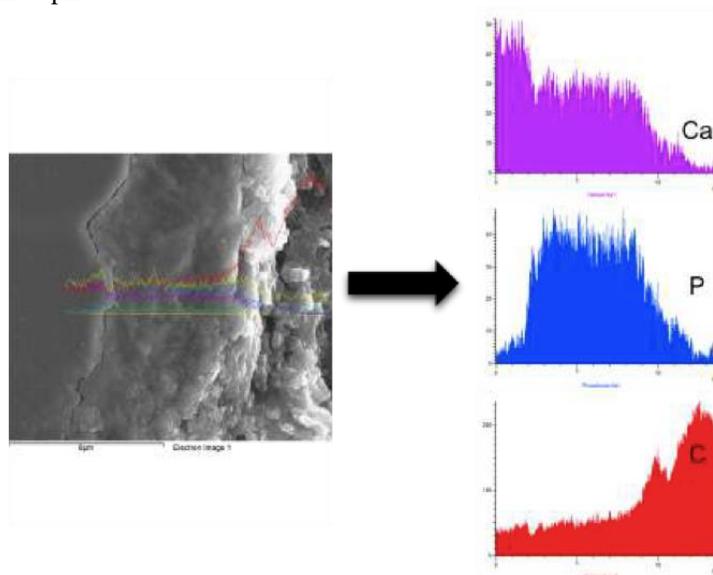


Figure 6. Cross-sectional images and elemental profiles of stone reacted with DAP + CaCl_2 . Profiles show calcium (top), phosphorous (middle), carbon (bottom) counts across the film.

3.3 Acid resistance

The time-dependence of the pH was measured for bare calcite and samples treated in 1M DAP, 1M DAP + 1mM CaCl_2 , 1M DAP + 1mM CaCl_2 + 150 μM $(\text{NH}_4)_2\text{CO}_3$ and 2 M DAP and the results are displayed in Figure 7. Treated samples displayed slower pH increases with time, indicating slower acid attack. After 10 hours, the pH of all samples approached 7 and the rate of change became very slow.

4. Discussion

4.1 Effect of different variables (temperature, time, concentration)

The reaction rate increased with temperature, as expected. At room temperature, for 1 M and 2 M DAP, 24 hours of reaction time was sufficient for complete coverage of substrate, while at lower concentrations (1-500 mM), it took 7 days to 1 month for complete coverage. A phosphorus peak in EDX indicates the presence of a calcium phosphate phase. No nitrogen peaks were observed, which excludes deposition of ammonium carbonate salts and unreacted DAP. XRD confirmed HAP and some octacalcium phosphate, which are both desirable, due to their extremely low solubilities (Johnsson et al.

1992). None of the more soluble calcium phosphate phases, including brushite, were detected in XRD analyses.

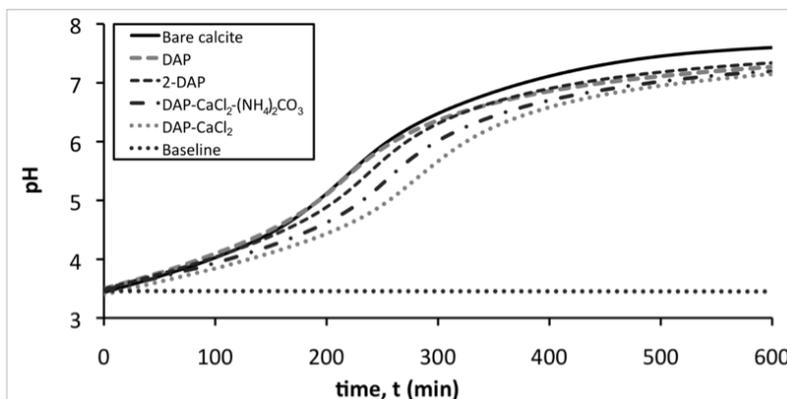


Figure 7. Acid attack comparison of three samples at pH (initial) = 3.5. The time for the pH of the solution to rise from 3.5 to 4 is about 3 times as long for the samples treated with DAP.

4.2 Ionic additions

Calcium chloride salt addition enhanced the overall coverage and smoothing (resulting in lower surface area). Cross-sectional profiles showed dense layers close to the substrate, but flowery structures at the growth site (*i.e.*, the film-solution interface). The film thickness after 24 hours of reaction was $\sim 10 \mu\text{m}$, which if the film were dense, would confer years of protection against acid attack in an environment of pH 4. The effect of ammonium carbonate was more ambiguous. Although SEM images revealed greater and faster coverage with the carbonate addition, there was less smoothing (and higher surface area) in the 1 M DAP + 1 mM CaCl_2 + 150 μM $(\text{NH}_4)_2\text{CO}_3$ compared to 1 M DAP + 1 mM CaCl_2 . The visual appearance of films with carbonate salt additions was similar to that of films with only calcium salt additions, in terms of thickness and structure near the substrate and at the film-liquid interface. Nevertheless, preliminary tests indicate improved acid protection from the coatings made with carbonate additions; further tests of this effect are underway.

4.3 Acid resistance

The rate of change of the pH was slower for samples coated with HAP than for the bare stone. Given the extremely high surface areas of the films available for acid attack, particularly at the growth surface, one would expect the pH of the film to rise very quickly; however, the rate was lower than for the bare stone, which had a significantly lower surface area. If the surface areas of the films were lower (*i.e.*, if they were free of needle-like structures) and in the absence of porosity, the pH increase would likely be much lower than what was observed. Hence from these preliminary results, HAP films, particularly those synthesized from mixtures of DAP and CaCl_2 , appear to have provided some enhancement of acid resistance. These tests are very conservative, given that the most aggressive pH found in field conditions is ~ 4 , so substantially greater protection is expected at more realistic levels of acidity.

5. Conclusions

Dense HAP coatings can be grown on marble substrate in as little as 24 hours, using aqueous solutions of DAP. The rate of reaction is increased and the porosity of the films is decreased by the addition of calcium and carbonate salts. Films tested in the lab have demonstrated acid resistance in highly acid environments, and are expected to show even greater protection under less aggressive acidity and with reduced surface area. The films have also demonstrated good strength and adhesion to the calcite substrate (which will be discussed in a future publication).

Acknowledgements

The authors would like to thank Lafarge, NCPTT and the Kress Foundation for financial support provided. We would also like to thank PRISM for the use of its Imaging and Analysis Center instrumentation and in particular Dr. Nan Yao and Mr. Jerry Poirier for their technical assistance. We also acknowledge Prof. Robert Cava (Department of Chemistry, Princeton University) and Dr. George Wheeler (Columbia University) for valuable technical discussions.

References

- Brady, P.V. 1996. "Surface-controlled dissolution and growth of minerals", Ch. 4 in *Physics and Chemistry of Mineral Surfaces*, ed. P.V. Brady (CRC Press, Boca Raton, FL).
- Brendel T., Engel A., Rossel C. 1992. "Hydroxyapatite coatings by a polymeric route." *Journal of Materials Science: Materials in Medicine* 3(3): 175-179.
- Doherty B., Pamplona M., Miliani C. et al. 2007. "Durability of the artificial calcium oxalate protective on two Florentine monuments", *J Cult Herit* (8): 186-192.
- Dorozhkin S.V. 2009. "Calcium orthophosphates in nature, biology and medicine", *Materials* (2): 399-498.
- Harouiya, N., Chairat, C. et al. 2007. "The dissolution kinetics and apparent solubility of natural apatite in closed reactors at temperatures from 5 to 50 °C and pH from 1 to 6", *Chemical Geology* (244): 554–568.
- Johnsson, M.S.A., Nancollas G.H. 1992. "The Role of Brushite and Octacalcium Phosphate in Apatite Formation." *Critical Reviews in Oral Biology & Medicine* 3(1): 61-82.
- Kamiya M., Hatta J., Shimada E. et al. 2004. "AFM analysis of initial stage of reaction between calcite and phosphate." *Materials Science and Engineering B* 111 (2-3): 226-231.
- Kasioptas A., Perdikouri C., Putnis C.V. et al. 2008. "Pseudomorphic replacement of single calcium carbonate crystals by polycrystalline apatite", *Mineralogical Magazine*, 72 (1): 77–80.
- Lide D.R. (Ed. 1999): *CRC Handbook of Chemistry and Physics*, The Chemical Rubber Co.
- Liu Q., Zhang B. 2011. "Synthesis and characterization of a novel biomaterial for the conservation of historic stone buildings and sculptures", *Materials Science Forum* (675-677): 317-320.
- Matteini M., Moles A., Giovannoni S. 1994. "Calcium oxalate as a protective mineral system for wall paintings: methodology and analyses", *Proc. 3rd Int. Symp. Conservation of Monuments in the Mediterranean Basin, Venice, S.B.A.S. Venezia*: 155–

161.

- Matteini M., Rescic S., Fratini F. et al. 2011. "Ammonium Phosphates as Consolidating Agents for Carbonatic Stone Materials Used in Architecture and Cultural Heritage: Preliminary Research", *Int. J. Architectural Heritage: Conservation, Analysis, and Restoration*, 5 (6): 717-736.
- Naidu S., Sassoni E. Scherer, G.W. (2011): "New Treatment for Corrosion-Resistant Coatings for Marble and Consolidation of Limestone", *Jardins de Pierres* (SFIIC, Champs-sur-Marne, France): 289-294.
- Nancollas G.H., Gardner G.L. 1974. "The kinetics and crystal growth of calcium oxalate monohydrate", *J. Crystal Growth* (21): 267-276.
- Osaka A., Miura Y. et al. (1991): "Calcium apatite prepared from calcium hydroxide and orthophosphoric acid." *J Mater Sci: Mater Med.* (2): 51–5.
- Sassoni E., Naidu S., Scherer G.W. 2011a. "The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones", *J Cult Herit* (12): 346–355.
- Sassoni E., Naidu S., Scherer G.W. (2011b): "Preliminary Results of the Use of Hydroxyapatite as a Consolidant for Carbonate Stones", *Materials Issues in Art and Archaeology IX*, Vol. 1319, Eds. P.B. Vandiver, W. Li, J. L. Ruvalcaba Sil, C.L. Reedy, L.D. Frame (Materials Research Society) ISBN-13: 9781605112961: 189-195.
- Winkler E.M. 1997. "Stone in Architecture", 3rd. ed. Springer, Berlin.
- Yang F., Zhang B., Liu Y. et al. 2011. "Biomimic conservation of weathered calcareous stones by apatite", *New J. Chem.* (25): 887–892.
- Yoshimura M., Suda H., Okamoto K. et al. 1994. "Hydrothermal synthesis of biocompatible whiskers." *Journal of Materials Science* 29 (13): 3399-3402.