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Optimizing the In Situ Deposition of Carbonate Hydroxyapatite for the Consolidation of Marble in Cultural Heritage Monuments

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Optimizing the In Situ Deposition of Carbonate Hydroxyapatite for the Consolidation of Marble in Cultural Heritage Monuments

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I. Extended Abstract

Strengthening the structure of marble is key to restoring its mechanical properties and contributing to the stability of stone monuments. Marble consolidation as a conservation technique has been attempted since the 1950's, initially using organic consolidants, i.e., acrylics, vinyl and silicone polymers, as well as epoxies [1,2]. These strategies, however, suffered from incompatibility, reversibility and low durability problems and were gradually replaced by the use of inorganic salts or bases with low water solubility. In recent years, the use of calcium hydroxide [3], calcium oxalate [4,5], and hydroxyapatite [6–8] has gained attention for the strengthening and stabilization of deteriorated or fragile marble surfaces. This method generally requires optimized deposition of the above materials in sub-micron or nano-sized particulate form, thus enabling their incorporation into the porous structure of marble, allowing (permitting) an efficient consolidation [9,10]

Hydroxyapatite (HAP), a calcium phosphate with the formula $Ca_{10}(PO_4)_6(OH)_2$, is known for its extremely low solubility (K_{sp} ~10^{-98}); in particular, its carbonate form, carbonate hydroxyapatite (c-HAP), $Ca_{10}(PO_4)_{6-y}$ $(CO_3)_y[(CO_3)_{x+(½)y}(OH)_{2-2x}]$ is commonly found in bones and teeth of vertebrates. The apatite family has been explored for various applications, including its potential for the conservation of marble and other calcareous materials. Marble, a calcareous metamorphic rock, is susceptible to deterioration over time due to environmental factors such as acid rain, pollutants, and biological activity.

The method entails depositing (involves the deposition of) the highly insoluble hydroxyapatite salt from aqueous solutions of diammonium phosphate (DAP). This is achieved by the interaction of diammonium phosphate (DAP) aqueous solutions on the surfaces of calcareous or marble objects of cultural heritage, providing a mechanism to reconnect and restore the cohesion lost in the porous marble substrate. Concurrently, the formation of a thin, sufficiently bonded layer on the surface acts protectively, retarding the decay process. This study evaluated the method's effectiveness combining infrared spectroscopy with SEM-EDX micro-analysis. The method was optimized by the addition of simulated body fluid (SBF), a cocktail of inorganic salts, showing particularly positive results in both immersion and surface application scenarios. Among the application methods tested, the dripping method presented satisfactory results on the monument, although immersion, if feasible, is considered ideal as the most efficient c-HAP formation was observed.

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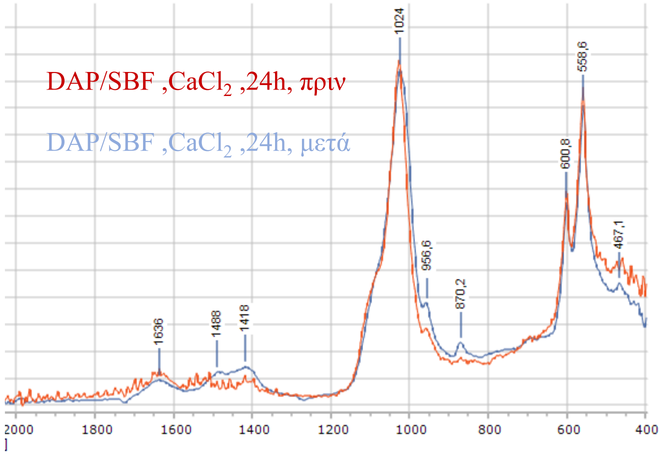

Figure 1. FTIR spectrum of the $CaCl_2$-enriched marble area after treatment with DAP, and SBF showing the formation of c-HAP

The HAP formation process requires the availability of calcium through the reaction of DAP with Ca ions, readily provided by the marble itself. This raises the concern of sacrificing some of the marble surface integrity for the consolidation process. At a first level, the formation of c-HAP, as shown by FTIR spectra (Figure 1), demonstrates that some of the calcium provided by the marble- still remains in the calcite form. An attempt was also made to further reduce this effect, by enriching the marble surface with $CaCl_2$ before applying the DAP solution.

The results of the method were highly encouraging, achieving significant hydroxyapatite formation and surface coverage along with satisfactory penetration and adhesion to the surface. Analysis of the FTIR spectra of the reaction products provided insights into the different phases of formation, shedding light on the chemical kinetics and the precise products being formed.

Although additional research is required, this method has shown great promise in terms of strengthening and stabilizing structures, offering compatibility due to its inorganic nature, and potentially providing long-term protection.

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