MS10 – e-P11: Calcium phosphates crystallized on Carrara marble after phosphate-based consolidating treatment

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Diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$) solutions have been introduced in the conservation field as a new inorganic-mineral treatments to consolidate or protect decayed carbonatic stone materials of historical monuments [1].
The treatment forms calcium phosphates through a dissolution and re-crystallization reaction, which takes place between hydrogen phosphate groups of the reagent and calcium ions of calcite of the substrate. Calcium phosphates nucleate on calcite grains with a pseudomorphic replacement reaction, and form a crystal network able to restore the lost cohesion of the microstructure. Despite the high number of studies on the crystallization of calcium phosphates and their formation on the surface of carbonatic substrates, only a few studies explored the formation of calcium phosphate phases on marbles treated with DAP and using calcite of the substrate as unique source for calcium ions [2-4]. Previous studies revealed a non-stoichiometric reaction that lead to the formation of a mixture of phases, each one characterized by different Ca/P molar ratio, solubility and stability [4].
In this study, we carry out a non-destructive synchrotron radiation grazing incidence X-ray diffraction (SR-GIXRD) investigation on DAP-treated marbles to determine how the mineralogical composition of the stone substrate affects the crystallization of stable and metastable calcium phosphates. The analyses were performed on Carrara marble specimens treated by capillarity by 0.76 M DAP solutions. Our results indicate that the presence of compositional micro-heterogeneity of Carrara marble favours the formation of specific phases. In general, the composition and the localization of the phases directly depend on the availability of free Ca^{2+} ions. Dicalcium phosphate dihydrate, a calcium phosphate with a low Ca/P molar ratio, is formed on carbonatic phases with a low Ca content, such as dolomite grains and Mg-containing veins. Octacalcium phosphate (OCP, $Ca_8(HPO_4)_2{\cdot}5H_2O$) and poorly-crystalline partially-substituted hydroxyapatite (HAP, $Ca_5(PO_4)_3OH$) are the foremost newly-formed phases when the substrate is mainly composed by calcite.
This study shed light on 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 with an in depth evaluation of DAP consolidating processes [5].

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