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Thermal behavior of Carrara marble after consolidation by ammonium phosphate, ammonium oxalate and ethyl silicate

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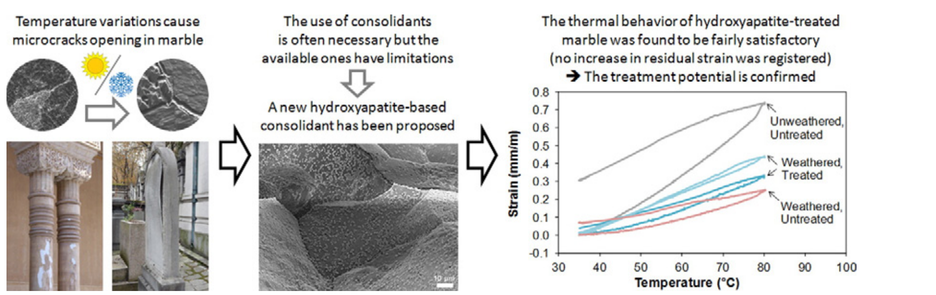
HIGHLIGHTS

- After consolidation by ammonium phosphate, Carrara marble subjected to thermal cycles exhibited no residual strain increase
- Also ammonium oxalate and ethyl silicate did not cause any increase in residual thermal strain
- All three treatments can be regarded as fairly compatible in terms of thermal behavior

GRAPHICAL ABSTRACT



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ABSTRACT

The response to thermal variations is the primary cause of marble deterioration in ancient and modern buildings. In this study, the thermal behavior of Carrara marble after consolidation by an innovative hydroxyapatite-based treatment was investigated in comparison with ammonium oxalate and ethyl silicate. Samples were subjected to heating-cooling cycles up to 80 °C. All the consolidating treatments were found to be fairly compatible, as in no case the residual strain after the thermal cycles was found to increase compared to the unweathered untreated marble. Anyway, the hydroxyapatite-treatment has the advantage of causing the highest increase in marble cohesion and the lowest residual strain, besides being more chromatically compatible and durable than the alternative commercial consolidants.

1. Introduction

Thermal excursions, such as day/night temperature variations and heating/cooling cycles due to exposure to solar radiation, are known to be the primary cause of deterioration of marble used for decorating historic buildings and for cladding modern façades. Thermal deterioration originates from the anisotropic thermal behavior of calcite crystals constituting marble [1]. Upon heating, calcite crystals expand parallel and contract perpendicular to the crystallographic c-axis, thus generating stress inside marble. When stress exceeds the cohesion among calcite grains, new (i.e. previously not existing) micro-cracks are formed at grain boundaries [1,2]. These newly developed micro-cracks progressively lead to two characteristic deterioration phenomena affecting marble: the so-called "sugaring" (i.e., grain detachment and loss) [3,4] and the bowing of thin slabs used as gravestones or cladding elements [5,6], as illustrated in Fig. 1. Sugaring and bowing are major issues threatening the durability of both historic monuments (e.g. the Cathedral of Florence and the Alhambra Palace in Granada) and modern buildings (e.g. the New York Public Library and the Finland Hall by Alvar

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Fig. 1. Examples of thermally induced degradation of marble. Left: Marble columns in the Courtyard of the Lions in the Alhambra of Granada (Spain, XIV century) exhibit severe granular disaggregation in the side directly exposed to solar radiation, while in the opposite sheltered side the same columns are substantially well preserved. Right: Thin slabs used as gravestones in the *Père Lachaise* Cemetery in Paris (France, XIX century) exhibit dramatic bowing and deformation.

Aalto in Helsinki) [3]. Besides causing the loss of important historic artifacts, these weathering phenomena also have significant economic consequences: for instance, the replacement of the bowed slabs used for cladding the Amoco Building in Chicago cost as much as $65 million [1]. In addition, thermally induced micro-cracks increase marble porosity and surface area, which results in increased marble susceptibility to dissolution in rain [7], black crust formation [8] and deterioration due to salt crystallization [9].

To re-establish cohesion between loose calcite grains, numerous organic and inorganic consolidating treatments have been proposed through the years [3,9–16]. In spite of the relatively abundant literature on consolidants effects on marble mechanical and sorption properties, a very limited number of studies investigated how consolidants affect marble thermal behavior [8,17]. Considering that marble response to temperature variations is the primary cause of its deterioration, the possible change in thermal behavior after consolidation is one of the most important aspects to evaluate the suitability of any possible consolidant for marble. In fact, in case the applied treatment was found to worsen marble thermal behavior, consolidation would result being counterproductive. For instance, this was the case of an organic consolidant based on polymethyl-methacrylate dissolved in xylenes, found to significantly increase marble residual strain after thermal cycles, thus potentially leading to accelerated deterioration [17].

The present study is aimed at evaluating the thermal behavior of weathered Carrara marble after consolidation with an innovative treatment based on hydroxyapatite. This treatment, originally proposed for limestone consolidation [18], is based on the formation of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) from the reaction between calcite grains and an aqueous solution of diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, DAP) [18,19]. The HAP-treatment has recently been investigated for consolidation of sugaring marble and very encouraging results have been obtained. Indeed, the HAP-treatment proved to restore weathered marble cohesion back to the condition before weathering, without significantly altering marble color [16]. The HAP-treatment outperformed traditional consolidants (such as ammonium oxalate and ethyl silicate), thus standing out as one of the most promising inorganic treatments for marble preservation [16]. In addition to the good consolidating ability, the HAP-treatment is also able to improve marble resistance to dissolution in rain, thanks to the very low solubility and slow dissolution rate of HAP, compared to calcite [19,20]. Considering its high potential, further development of the HAP-treatment for consolidation and protection of marble and limestone has been undertaken by several research groups [18–30] and the European Commission has recently funded the Marie Skłodowska-Curie project "HAP4MARBLE" [31], specifically aimed at multi-functionalizing the HAP-treatment for marble restoration and preventive conservation.

The issue of how HAP-consolidated marble responds to thermal stress has been preliminarily addressed by the Authors in a previous study [32]. An accelerated procedure, consisting in heating samples at 400 °C for 1 h, was adopted to cause thermal damage in consolidated marble, whose response was evaluated in terms of loss of consolidating efficacy [32]. Such heating procedure is effective in rapidly causing micro-cracks in marble (which can be exploited also for producing decayed samples suitable for testing of consolidants [33,34]), however it was found to be too extreme to evaluate the response that consolidated marble has in the field when subjected to natural thermal excursions (rarely exceeding a maximum temperature of ~80 °C [8]). Therefore, in the present study, conditions much closer to the real ones were adopted (heating-cooling cycles up to 80 °C), so that the actual thermal behavior of HAP-consolidated marble could be assessed. For comparison's sake, marble thermal behavior after treatment with ammonium oxalate and ethyl silicate (the two inorganic treatments most widely used nowadays in the practice of marble consolidation [35,36]) was evaluated as well. To the Authors' best knowledge, the present study is the first attempt to evaluate the thermal behavior of marble consolidated by HAP and ammonium oxalate, whereas one study on the thermal behavior of marble treated with ethyl silicate has been reported in the literature [17].

2. Materials and methods

2.1. Marble samples

A freshly quarried slab of White Carrara marble (supplied by Imbellone Michelangelo s.a.s., Italy) was used. From the slab, 12 prismatic samples ($30 \times 30 \times 20$ mm^3) were wet sawn. Two samples were left unweathered and untreated (samples labeled "UW-UT"), while samples to be consolidated by different treatments were subjected to preliminary artificial weathering. Indeed, as pointed out by several studies, testing consolidants on unweathered marble leads to unreliable results, because of its very low porosity and the consequent very low consolidant penetration into the unweathered substrate [10,16,32]. Hence, preliminary artificial weathering was performed by heating samples in oven at 400 °C for 1 h, according to a method previously developed by the Authors [33,34]. After heating at high temperature, marble samples exhibit formation of new micro-cracks, increase in open porosity and coarsening of pore radius very similar to those exhibited by naturally weathered marbles [3,16]. After artificial weathering, two samples were left untreated (samples labeled "W-UT"), while the remaining samples were subjected to different consolidating treatments (two samples per treatment), as described in the following.