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# Artificial weathering of stone by heating

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ABSTRACT

Since the effectiveness of stone consolidants significantly depends on the weathering level of the stone samples on which they are tested, in this study the suitability of heating stone to high temperature, as an artificial weathering method to induce controllable microstructural, physical and mechanical alterations, was investigated. Three lithotypes with different characteristics were used: Giallo Terra di Siena (GS, a highly porous calcareous sandstone), Globigerina limestone (GL, a highly porous limestone) and Pietra Serena (PS, a porous quartzitic sandstone with low porosity). The lithotypes were characterized in terms of mineralogical composition, pore size distribution and water absorption, as well as dynamic modulus, static modulus, compressive and tensile strength. They were then heated for 1 hour, in different conditions: (i) dry samples were heated to 100, 200, 300 and 400 °C; (ii) water-saturated samples were heated to 200 °C; (iii) water-saturated samples were heated to 200 °C and, after cooling to room temperature, re-heated to 400 °C. After heating, all the lithotypes experienced an increase in open porosity and water absorption, as a consequence of the anisotropic thermal deformation of calcite crystals. Correspondingly, GS and GL exhibited an increasing reduction in mechanical properties for increasing heating temperature. PS, on the contrary, exhibited an increase in compressive and tensile strength, which was attributed to chemical-physical transformations undergone by secondary mineralogical fractions (clay minerals, etc.) at high temperature. All things considered, heating proved to be a fairly effective and reproducible method to cause artificial weathering in stone samples for the testing of consolidants. However, depending on the microstructural characteristics of the lithotypes, the effectiveness of heating may vary significantly, which requires a case-by-case adjustment of the most suitable heating procedure and the development of complementary methods for artificial weathering.



## 1. Introduction

Stones used in sculpture and architecture, as well as rocks in their original location, are exposed to environmental weathering, which is responsible for alterations in their microstructure (e.g. open porosity, pore size distribution, chemical-mineralogical composition of the phases, etc.), that, in turn, result in a modification of physical and mechanical properties.

The open porosity and effective porosity (i.e. the interconnected open porosity between two opposite sides of a specimen) generally increase as a consequence of weathering, responsible for the opening of new micro-cracks, the widening of existing micro-fractures and the dissolution of the most soluble fractions [1,2]. For instance, a sensible increase in effective porosity (+4% in the first 5 cm from the surface, compared to the underlying unweathered part) was detected in the case of a tuff-made stonework exposed to environmental weathering for 150 years [3]; more dramatic increases (up to 10 times) were found in the case of rocks weathered to various degrees [1,4]. Alongside the modification in porosity, pore size distribution is generally affected by weathering as well. On the one hand, the average pore size increases when dissolution of the most soluble fractions occurs, so that smaller pores are internally dissolved and/or collapsed, thus forming larger pores [1,5]; on the other hand, the average pore size decreases when clay minerals, formed through weathering, and/or crystallized soluble salts partially fill the pores, thus reducing the pore size [1]. As a consequence of the modification in open porosity and/or pore size distribution, also specific surface area is affected by weathering, generally increasing with increasing weathering degree [1]. Due to these modifications in the pore system, the physical properties of weathered stones are altered as well. In particular, water

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absorption, responsible for all the weathering mechanisms related to water (e.g., freeze–thaw cycles, crystallization of soluble salts, swelling of clays, etc.), was found to increase by up to 5 times in weathered stones, compared to unweathered ones [1]. Moreover, the increase in pore amount and size is responsible for significant decreases in mechanical properties of weathered stones. Ultrasonic pulse velocity and dynamic elastic modulus were reduced by about 40% in weathered rocks and stoneworks [3,4]. Moreover, weathered rocks exhibit a strong decrease in static elastic modulus (−30–60%), compressive strength (−30–80%) and tensile strength (−20–60%), in comparison with the same unweathered lithotypes [1,4].

To restore cohesion between grains and mechanical properties of weathered architectural stones, consolidating treatments are usually applied. The effectiveness of such consolidants significantly depends on the weathering level of the tested stone [6], so the actual performance of new consolidating materials should preferably be evaluated on weathered specimens. Nevertheless, environmentally weathered stone samples are rarely available in sufficient quantity and with suitably constant characteristics, hence the importance of developing methods for artificial weathering of stone, able to provide altered specimens with uniform and reproducible characteristics, is evident.

Extensive experimental studies on artificial weathering of stone have been performed with the aim of reproducing and accelerating environmental weathering processes occurring in the field, i.e. dissolution in clean and acid rain and formation and dissolution of soluble salts, owing to pollutant dry deposition (see review in [7]). These studies, performed on different types of stone (mainly carbonate stones), involved a wide range of environmental conditions, in terms of temperature, relative humidity, presence of atmospheric gaseous pollutants (such as $SO_2$, $NO_x$, $O_3$) and particulate matter, as well as presence of acidic solutions (such as $H_2SO_4$, $HNO_3$, $H_2CO_3$, HCl) (see, among others, [8–16]). However, those experimental investigations generally aimed at evaluating the rate of stone surface recession (determined by measuring stone weight loss and/or the amount of $Ca^{2+}$ ions dissolved from the stone). Therefore, they provide little guidance regarding the effects of the artificially induced decay on stone microstructure and physical-mechanical properties that would be of use in producing weathered stone samples for testing of consolidants.

A more promising method for obtaining artificially damaged stone specimens could be to adopt some methods described in international standards for assessing stone resistance to various weathering mechanisms (such as aging by $SO_2$ action [17], salt crystallization [18], freeze–thaw [19] or thermal shock [20]). Such methods can be used to intentionally induce damage in the stone [2,21,22]; however, these methods exhibit some drawbacks:

(i) the duration of the weathering procedures: according to the cited European Standards, a prolonged exposure period is required for determining the resistance to $SO_2$ (21 days, [17]), salt crystallization (up to 15 cycles [18]), freeze–thaw (up to 168 cycles [19]) and thermal shock (up to 20 cycles, unless failure happens earlier [20]). Accordingly, in the cited studies 5–32 cycles of salt crystallization [2,22], 50–75 cycles of freeze–thaw [2,21] and 32–50 cycles of thermal shock [21,22] were repeated to achieve significant weathering;

(ii) the conditions of stone samples at the end of the weathering procedure: artificial weathering by freeze–thaw, salt crystallization and thermal shock is hardly controllable and capable of being modulated to a desired weathering level, so that weathered samples often exhibit intense cracking and huge material loss [2,22]. In addition, samples subjected to salt crystallization are usually contaminated by high amounts of salts. Such opening of cracks, detachment of parts and contamination by salts, although being somehow representative of decay conditions that may be experienced in the field, complicate the evaluation of consolidant performance (in terms of chemical reactivity, ability to bond grains, etc.).

Therefore, in this study, as an alternative artificial weathering method, the effectiveness of heating stone to high temperature for obtaining damaged specimens with uniform and reproducible characteristics, but still uncontaminated by salts, was investigated. Heating was selected as a promising damaging method because:

(i) crystals of calcite, present in most architectural stones, such as limestones, marbles and calcareous sandstones, are known to undergo a marked anisotropic thermal expansion, expanding parallel and contracting perpendicular to crystallographic *c*-axis (respectively, about 0.19% and 0.04% for a thermal variation from 20 to 100 °C) [23,24]; such anisotropic deformations are responsible for stress that can lead to the opening of micro-cracks at grain boundaries. As a matter of fact, grain decohesion and intergranular cracking owing to natural heating–cooling cycles have been recognized as a main cause of weathering processes that typically affect marbles, e.g. bowing and sugaring [24–28];

(ii) crystals of different minerals, which may be present in heterogeneous stones such as granite and sandstone, have different thermal expansion coefficients and hence undergo different deformations, which may result in additional micro-cracks [29];

(iii) the possible presence of water inside the pores, when stone is heated to high temperature, may be responsible of further damaging, as a consequence of the pressure exerted on pore walls [30] and of the chemical reaction between water and Si—O bonds on the surface of the newly formed micro-cracks [31].

Given the frequent problems of thermal weathering of marbles, many experimental studies have been carried out to analyze the effects of heating–cooling cycles on marble porosity and/or mechanical properties (see for instance [24,30,32,33]). However, these studies were basically aimed at imitating the thermal variations in the field, hence they generally involved heating–cooling cycles with a relatively low maximum temperature (rarely exceeding 100 °C). The effects of heating stone samples to higher temperatures – not representative of realistic thermal excursions, but useful to induce more dramatic alterations in stone microstructure – have been considered only in few cases and only for marble and granite [29,32].

The effect of heating as an artificial weathering method for stone was investigated for the first time in a previous study [6], where Indiana limestone (a medium porous limestone) was heated at 100, 200, 300, 400 and 500 °C for 1, 4 and 16 h. For the heated samples, a decrease in dynamic elastic modulus linearly proportional to the heating temperature was found. Samples heated to 300 °C for 1 h exhibited a decrease of −43.4% in dynamic modulus and of −27.1% in tensile strength. Heating duration longer than 1 hour proved to have no further effect on the dynamic modulus reduction.

In this study, for three lithotypes with different microstructural characteristics, the effectiveness of heating to high temperature (up to 400 °C) to induce controllable microstructural, physical and mechanical alterations, has been systematically investigated. In particular, the effects of heating have been evaluated in terms of modifications in porosity and pore size distribution, water absorption and sorptivity, dynamic and static modulus, compressive and tensile strength.