# **Influence of porosity on artificial deterioration of marble and limestone by heating**

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**Abstract** Testing of stone consolidants to be used on-site, as well as research on new consolidating products, requires suitable stone samples, with deteriorated but still uniform and controllable characteristics. Therefore, a new methodology to artificially deteriorate stone samples by heating, exploiting the anisotropic thermal deformation of calcite crystals, has recently been proposed. In this study, the heating effects on a variety of lithotypes was evaluated and the influence of porosity in determining the actual heating effectiveness was specifically investigated. One marble and four limestones, having comparable calcite amounts but very different porosity, were heated at 400 °C for 1 hour. A systematic comparison between porosity, pore size distribution, water absorption, sorptivity and ultrasonic pulse velocity of unheated and heated samples was performed. The results of the study show that the initial stone porosity plays a very important role, as the modifications in microstructural, physical and mechanical properties are way less pronounced for increasing porosity. Heating was thus confirmed as a very promising artificial deterioration method, whose effectiveness in producing alterations that suitably resemble those actually experienced in the field depends on the initial porosity of the stone to be treated.

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## **1 Introduction**

Porous building materials used in historical architecture, such as natural stones, bricks and mortars, are subject to environmental and anthropogenic deterioration processes, that cause modifications in original microstructural characteristics and physical-mechanical properties. Weathered stones usually exhibit an increase in porosity and water absorption, as well as a decrease in mechanical properties [\[1](#page-6-0)[–3](#page-6-1)]. Consequently, consolidating treatments and/or protective treatments are often applied (see, among others, [\[1](#page-6-0), [4–](#page-6-2)[10\]](#page-6-3)). Consolidating treatments are aimed at re-establishing the cohesion between grains, thus restoring mechanical properties of weathered stones, while protective treatments are aimed at increasing stone resistance to the aggressive action of water, e.g. by making the surface hydrophobic.

In the case of consolidating treatments, given the variety of natural stones used in historical architecture and the high number of available products (thermoplastic or thermosetting polymers, silicate consolidants, lime-based consolidants, etc.), preliminary tests should always be carried out before application on-site [[11,](#page-6-4) [12\]](#page-7-0). In this way, the effects of a consolidating treatment on a specific kind of stone can be evaluated, in terms of aesthetic, chemical and physical compatibility, efficacy in restoring mechanical properties, durability, etc. The most suitable treatment can then be selected. Moreover, also in the field of materials research applied to the development of novel stone consolidants, extensive preliminary tests must be carried out in order to properly evaluate all the effects of a novel treatment [[1,](#page-6-0) [2,](#page-6-5) [7,](#page-6-6) [10](#page-6-3), [14](#page-7-1)].

For performing systematic preliminary tests, naturally weathered stones, withdrawn from real buildings, are rarely available in sufficient quantity and with sufficiently regular characteristics. As a result, the need of using alternative samples comes out [[1,](#page-6-0) [2](#page-6-5), [10](#page-6-3), [13](#page-7-2)]. However, the possible

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use of unweathered quarry samples seems not so representative, since samples for testing of consolidants should exhibit uniform and reproducible characteristics and resemble naturally weathered stones, at the same time  $[1, 2, 7, 10, 14]$  $[1, 2, 7, 10, 14]$  $[1, 2, 7, 10, 14]$  $[1, 2, 7, 10, 14]$  $[1, 2, 7, 10, 14]$  $[1, 2, 7, 10, 14]$  $[1, 2, 7, 10, 14]$  $[1, 2, 7, 10, 14]$  $[1, 2, 7, 10, 14]$  $[1, 2, 7, 10, 14]$ . Naturally weathered stones are usually characterized by micro-cracks, grain detachment and modifications in pore size distribution that quarry samples do not exhibit [[11\]](#page-6-4).

Several alternative strategies have been hence investigated so far, for obtaining suitable samples for laboratory testing of stone consolidants:

- (1) the use of "simulated" calcareous stones, i.e. stone blocks obtained by repeatedly compacting calcium carbonate powder and particles, blended with water, until a cohesive sample is obtained [\[15](#page-7-3)]; notwithstanding the similitude in composition between thus obtained "simulated" stones and real limestones and marbles, from a microstructural point of view the absence of any cementing phase, bonding the carbonate grains, and the shape of the pore system seem to be representative only of a very extreme natural weathering condition;
- (2) the use of "artificial" stones, i.e. cementitious mortars designed to achieve suitable porosity values and cured before testing long enough to ensure complete hydration and carbonation [[16\]](#page-7-4); because of the presence of calcium silicate hydrates and calcium silicate aluminate hydrates, the ability of these "artificial" stones to actually resemble weathered natural stones needs further investigation;
- (3) the use of artificially weathered stones, which was proposed long ago [\[1](#page-6-0)]. Many methods for artificial deterioration of stone have been investigated so far, including freezing-thawing cycles, salt crystallization cycles, acid attack and mechanical pre-stress [[1,](#page-6-0) [13,](#page-7-2) [17](#page-7-5)[–21](#page-7-6)]. However, these methodologies exhibit some drawbacks, mainly related to hardly controllable and reproducible weathering effects, rupture of samples, excessive contamination by salts, differential decay between external and internal parts [\[2](#page-6-5), [13](#page-7-2), [16](#page-7-4), [20](#page-7-7)].

To overcome the above reported drawbacks, a promising new methodology for artificial deterioration of stone, based on heating samples at high temperature, has recently been proposed [[2,](#page-6-5) [7](#page-6-6)]. Alternatively, the use of a heating plate, on top of which stone samples are placed to induce differential thermal stress across the specimen, has been proposed as well [\[13](#page-7-2)]. The idea is exploiting the fact that calcite crystals deform anisotropically upon heating, expanding parallel and contracting perpendicular to crystallographic *z*axis [[22,](#page-7-8) [23\]](#page-7-9). Hence, when a calcitic stone is heated at high temperature (300–400 °C), stress arises and micro-cracks open at grain boundaries. This makes porosity and water absorption increase and mechanical properties (dynamic modulus, static modulus, compressive and tensile strength, resistance to abrasion) decrease  $[2, 7, 24]$  $[2, 7, 24]$  $[2, 7, 24]$  $[2, 7, 24]$  $[2, 7, 24]$  $[2, 7, 24]$  $[2, 7, 24]$ . Notably, by suitably choosing the heating conditions, the decay level of heated stone can be specifically tailored [[2,](#page-6-5) [7\]](#page-6-6). Artificial deterioration by heating has already been used in several studies aimed at investigating new stone consolidants [[7,](#page-6-6) [24–](#page-7-10)[26\]](#page-7-11).

However, stone porosity has emerged as a very important factor in determining the effectiveness of heating as an artificial weathering method [\[2](#page-6-5), [20\]](#page-7-7), therefore this study aims at elucidating the role of porosity, by means of a systematic comparison between heating effects on microstructural, physical and mechanical properties of five lithotypes (one marble and four limestones), with comparable amounts of calcite (91 wt% to 99 wt%) but very different porosity (0.5 % to 40 %).

In the case of marble, the role of several microstructural parameters on the damaging level induced by heating has actually been specifically investigated in several studies available in the literature, but for a different purpose. In fact, calcitic marbles are highly sensitive to environmental temperature fluctuations [\[27](#page-7-12), [28\]](#page-7-13) and phenomena such as the bowing of marble slabs used for cladding [[29](#page-7-14)[–31](#page-7-15)] and the socalled "sugaring marble" [[29\]](#page-7-14) have been ascribed by many authors to micro-cracks formation and grain decohesion that marble undergoes when it is subjected to differential thermal deformations. Observations from both real case studies and laboratory tests highlight a dependence of the degradation level on marble nature and quality [[29,](#page-7-14) [32,](#page-7-16) [33\]](#page-7-17). Mineralogical composition, grain size, grain boundaries linearity, grain shape preferred orientation, lattice preferred orientation, number of adjacent grains and initial number of micro-cracks have been found to be the most relevant parameters in determining marble susceptibility to damage by heating [\[23,](#page-7-9) [27–](#page-7-12)[31,](#page-7-15) [33–](#page-7-17)[35\]](#page-7-18).

However, in the above mentioned studies—regarding exclusively calcitic and, in a few cases, dolomitic marbles porosity was not specifically taken into account. In fact, in marbles porosity usually reaches very low values (0 to 1 %), without a dramatic variability between marble types. Moreover, experimental studies on the modification of marble microstructure upon heating were usually designed to reproduce thermal variations that may be experienced in the field, therefore the maximum heating temperature rarely exceeded 100 °C [[27,](#page-7-12) [33,](#page-7-17) [36,](#page-7-19) [37\]](#page-7-20).

Differently, the present study is aimed at investigating the effects of heating at *high* temperature (400 °C) on a *variety* of carbonate stones (one marble and four limestones with increasing porosity). In this way, the influence of stone porosity on the actual damaging produced by heating, with the aim of obtaining artificially deteriorated samples suitable for testing of consolidants, can be assessed.

#### **2 Materials and methods**

### 2.1 Stones

Several different carbonate stones, which are the lithotypes most widely used in historical architecture and most frequently needing consolidation [[38\]](#page-7-21), were used. Five lithotypes, used in historical architecture in Italy and Malta [\[39](#page-7-22)], were selected with the aim of achieving a high variability in porosity, but at the same time a little variability in carbonate content: (i) Carrara marble (M1), a calcitic marble with very low porosity, composed of medium to fine calcitic grains and very low amounts of impurities; (ii) *Pietra di Trani* (L1), a limestone with very low porosity; (iii) *Crema Luna* (L2), a limestone with medium porosity; (iv) *Pietra di Vicenza* (L3), a limestone with high porosity, mainly composed of fossils and shells, bonded by calcareous cement; (v) *Globigerina* limestone (L4), a limestone with very high porosity, mainly composed of calcite crystals and fossils, bonded by calcareous cement. All the stones were supplied by Roncato s.r.l. (Italy), with the exception of *Globigerina* limestone, supplied by Xelini Skip Hire and High-Up Service (Malta).

# 2.2 Heating

Stone samples were exposed to 400 °C for 1 hour in an oven, according to the methodology proposed in [[2\]](#page-6-5). Additionally, stone samples were subjected to re-heating for a second time in the same conditions as above, to evaluate the additional effects of heating on already altered samples.

### 2.3 Stone characterization

The mineralogical composition of the stones was determined by powder X-ray diffraction (XRD) using a Philips Diffractometer PW 1840 (operating at 40 kV/20 mA; Cu Ka radiation with k = 1.54184 Å; scan range  $2\theta = 5{\text -}80^{\circ}$ ; step size  $2\theta = 0.020^{\circ}$ ; scan speed  $2\theta$ /s = 0.020; Philips Analytical PCPDF Diffraction Software and PDF-2 Reference Database). The calcium carbonate content  $(CaCO<sub>3</sub> wt\%)$ was determined on duplicate samples by the Dietrich– Frühling method (based on the measurement of the CO<sub>2</sub> volume released by reacting the powdered sample with HCl).

The total open porosity (*OP*), the average pore radius  $(r_{av})$  and the pore size distribution were determined by mercury intrusion porosimetry (MIP) using a Fisons Macropore Unit 120 and a Porosimeter 2000 Carlo Erba. For each stone type, four samples were obtained by hammering from different parts of the stone slabs and were used for MIP measurements.

The rate of water sorption by capillarity (sorptivity) and the absorption coefficient (*AC*) were measured according to EN 15801 [\[40](#page-7-23)] using  $30 \times 30 \times 10$  mm<sup>3</sup> samples, the squared

<span id="page-2-0"></span>**Table 1** Microstructural characteristics of the lithotypes.  $CaCO<sub>3</sub>$  = calcium carbonate content;  $OP =$  open porosity;  $r_{av} =$  average pore radius. CaCO<sub>3</sub> values are averages for 2 samples while  $OP$  and  $r_{av}$ values are averages for 4 samples (standard deviations in brackets)

	$CaCO3$ [wt. %]	$OP$ [%]	$r_{\rm av}$ [µm]		
M1	99.3 $(\pm 0.6)$	$0.5 (\pm 0.2)$	$0.097 \ (\pm 0.036)$		
L1	98.5 $(\pm 0.5)$	$1.1 (\pm 0.7)$	$0.011 (\pm 0.004)$		
L2	97.9 $(\pm 0.8)$	$7.7 (\pm 0.7)$	$0.114 \ (\pm 0.015)$		
L <sub>3</sub>	$91.7 \ (\pm 0.8)$	$24.9 \ (\pm 3.9)$	$0.866 \ (\pm 0.140)$		
L4	91.4 $(\pm 1.6)$	40.8 $(\pm 2.2)$	1.933 $(\pm 0.284)$		

face being put in contact with water. The water absorption by capillarity (*WA*<sub>24</sub>) was determined on the same samples as the total amount of water penetrated after 24 hours, in the same conditions as the sorptivity test.

The ultrasonic pulse velocity (*UPV*) was measured by transmission method on  $30 \times 30 \times 10$  mm<sup>3</sup> samples, using a Matest instrument with 55 kHz transducers. A rubber couplant was used between the transducers and the sample, a constant load of 100 N being applied onto the transducers, to ensure a good measurement repeatability.

For evaluating the alterations induced by heating, microstructural, physical and mechanical properties of unheated and heated stones were compared. To prevent the possible stone variability from complicating the evaluation of the heating effects, for each lithotype MIP was performed on unheated and heated samples, collected one right next to the other, while *AC*, *WA*<sup>24</sup> and *UPV* measurements were performed on the same sample, before and after heating.

## **3 Results and discussion**

### 3.1 Untreated materials

The microstructural characteristics of the lithotypes are reported in Table [1](#page-2-0) and Fig. [1](#page-3-0), while the physical-mechanical properties are summarized in Table [2.](#page-4-0)

M1 is a marble characterized by a very high calcium carbonate content and a very dense microstructure, in agreement with values reported in the literature for Carrara marble [[32\]](#page-7-16). Due to its very low porosity, M1 also exhibits very low water absorption and sorptivity, as well as a high *UPV*, in agreement with values reported in the literature for freshly quarried calcitic marbles [\[27](#page-7-12)] and, in general, for unweathered marbles [[41\]](#page-7-24).

L1 and L2 are limestones with high calcium carbonate content and low to medium porosity. Correspondingly, L1 exhibits low water absorption and very slow sorptivity, due to its very small average pore radius, while L2 has higher water absorption and sorptivity. Both stones exhibit quite high *UPV* values.

<span id="page-3-0"></span>**Fig. 1** Pore size distribution and ultrasonic pulse velocity of the five lithotypes, before heating and after the first and the second heating (the *y*-axis of the MIP graphs has a different scale for different lithotypes to allow a better readability)



<span id="page-4-0"></span>**Table 2** Microstructural modifications of the lithotypes after heating.  $OP =$  open porosity;  $r_{av} =$  average pore radius;  $OP r > 1 \mu m =$  porosity in the range of pore radius coarser than 1  $\mu$ m; *OP* 0*.*1 < *r* < 1  $\mu$ m = porosity in the range of pore radius between 0.1 and 1 µm; *OP* 0*.*01 *<*

 $r < 0.1 \mu m$  = porosity in the range of pore radius between 0.01 and 0.1  $\mu$ m; *OP r* < 0.01  $\mu$ m = porosity in the range of pore radius smaller than  $0.01 \text{ um}$ 

	OP [%]	$r_{\rm av}$ [µm]	$[\%]$	$[\%]$	$OP r > 1 \text{ µm}$ $OP 0.1 < r < 1 \text{ µm}$ $OP 0.01 < r < 0.1 \text{ µm}$ $[\%]$	$OPr < 0.01$ µm [%]	AC $\left[\frac{\text{(mg/cm}^2)}{\sqrt{s}}\right]$	$WA_{24}$ $UPV$ $[wt\%]$	[km/s]
M1	0.5	0.097	0.1	0.1	0.3	0.0	0.05	0.1	6.0
$M1-400-I$	1.8	0.836	0.5	1.2	0.2	0.0	0.34	0.4	1.9
$M1-400-II$	2.1	0.847	0.6	1.3	0.2	0.0		-	1.7
L1	1.6	0.013	0.2	0.0	0.7	0.7	0.03	0.2	7.4
$L1-400-I$	2.4	0.020	0.3	0.0	1.8	0.3	0.11	0.3	5.6
$L1-400-II$	2.6	0.019	0.2	0.0	1.9	0.5	$\qquad \qquad -$	$\overline{\phantom{a}}$	5.3
L2	7.9	0.110	0.7	3.6	3.6	0.0	0.57	2.1	6.0
$L2-400-I$	8.9	0.122	0.9	4.2	3.7	0.1	0.95	2.3	4.5
$L2-400-II$	9.0	0.121	1.0	4.2	3.7	0.2	-	-	4.1
L3	26.6	0.857	12.4	10.4	3.4	0.4	6.22	8.6	3.4
$L3-400-I$	30.8	0.981	15.3	11.7	3.4	0.5	6.76	9.2	2.7
$L3-400-II$	30.0	1.029	15.2	11.3	3.2	0.4	-	-	2.4
L4	38.7	1.957	26.2	9.3	3.0	0.2	14.4	14.6	3.0
$L4-400-I$	36.7	2.009	25.3	9.3	2.1	0.1	14.8	16.1	2.7
$L4-400-II$	35.4	1.930	23.9	8.8	2.5	0.1			2.6

L3 and L4 are limestones mainly containing calcium carbonate, as well as some secondary phases. In the case of L4, a small amount of quartz was detected by XRD and the presence of small amounts of clays (not detected by XRD) might be possible as well in this kind of stone [[2\]](#page-6-5). L3 and L4 are characterized by highly porous microstructure, with coarse pores. Accordingly, both stones have high water absorption and sorptivity. Because of the highly porous microstructure, both stones exhibit low *UPV* values.

In summary, all the lithotypes exhibit similar calcium carbonate contents (91.4 to 99.3 wt%) but, at the same time, they significantly differ in terms of pore size distribution and porosity (0.5 to 40.8 %). Correspondingly, a significant variety is found among the stones in terms of water absorption, sorptivity and *UPV* (Table [2](#page-4-0)).

### 3.2 Heating

### *3.2.1 First heating*

Artificial deterioration by heating caused significant modifications in microstructural, physical and mechanical properties of the lithotypes, as reported in Table [2](#page-4-0) and Fig. [1.](#page-3-0)

In the case of M1, a significant increase in porosity (from  $0.5\%$  to  $1.8\%$ ) and a shift of the pore size distribution towards larger pores (*r*av increasing from 0.097 µm to 0.836 µm) were found. Such alterations are owing to the opening of new micro-cracks at grain boundaries, as a consequence of the anisotropic deformation of calcite crystals upon heating [[22,](#page-7-8) [23](#page-7-9)]. Consistently with the increase in porosity and the coarsening of the average pore size, after heating M1 also experienced a definite increase in water absorption ( $\triangle WA_{24} = +300\%$ ) and sorptivity ( $\triangle AC =$ +580 %). As a consequence of micro-cracks formation and propagation, the *UPV* was drastically reduced, passing from 6.0 km/s before heating to 1.9 km/s after heating. According to the classification of marble damage based on velocityporosity correlation, as proposed by several authors and reported in [[41\]](#page-7-24), after heating M1 passed from the "unweathered" condition  $(UPV > 5 \text{ km/s})$  to the "danger of breakdown" condition  $(1.5 < UPV < 2$  km/s).

The above described alterations in the pore system and in physical-mechanical properties closely resemble those experienced in the field by marble subjected to natural thermal weathering. For instance, in the case of Carrara marble slabs used for cladding, a porosity increase from 0.45 % (unweathered marble) to 2.00 % (weathered marble, exhibiting a high level of bowing) was found [\[32](#page-7-16)]. In the same study, the maximum pore radius was reported to increase from around 0.1  $\mu$ m (unweathered marble) to around 1  $\mu$ m (weathered marble, exhibiting strong bowing) [[32\]](#page-7-16). Also in the case of *UPV*, the results found for M1 ( $\triangle UPV$  = −68 %) are in good agreement with values reported in the literature for calcitic marbles subjected to thermal degradation by repeated heating-cooling cycles at temperature simulating natural conditions ( $\Delta UPV = -65$  % after 50 cycles between  $-15$  °C and  $+80$  °C [\[33](#page-7-17)],  $\Delta UPV = -55$  % after 10 cycles between  $+20$  °C and  $+90$  °C [\[27](#page-7-12)]).

Considering the very good agreement between modifications induced by heating M1 at 400 °C for 1 hour and those reported in the literature for naturally weathered marble [[32\]](#page-7-16) and for marble subjected to repeated thermal cycles [[27,](#page-7-12) [33](#page-7-17)], heating appears as a very suitable method for artificial deterioration of marble.

In the case of the other lithotypes, in spite of the almost identical calcium carbonate content, significantly different modifications in porosity and pore size distribution were produced. In particular, the magnitude of the alterations induced by heating proved to progressively decrease for increasing porosity of the heated lithotype.

Indeed, in the case of L1, having a porosity 2–3 times higher than M[1](#page-2-0) (Tables 1 and [2](#page-4-0)), less pronounced modifications were found:  $\Delta OP = +46 \%$ ,  $\Delta WA_{24} = +50 \%$ ,  $\Delta UPV = -24$  $\Delta UPV = -24$  $\Delta UPV = -24$  % (Table 2). The overall heating effect is hence more limited in the case of L1, compared to M1, because the larger volume of voids allows some calcite crystal deformation, without inducing stress and consequent formation of new micro-cracks in the stone.

This explanation finds confirmation in the results obtained for the other limestones, as the heating effects decrease for increasing open porosity. Indeed, in the case of L2 ( $OP = 7.7$  %), even smaller modifications in stone properties were found after heating:  $\Delta OP = +13\%$ ,  $\Delta WA_{24} =$ +10 % and  $\Delta UPV = -25$  % (Table [2\)](#page-4-0). Similarly, L3 and L4 ( $OP = 24.9$  % and 40.8 %, respectively) underwent quite limited alterations in microstructural, physical and mechanical properties (Table [2\)](#page-4-0). In particular, in the case of L4, no significant variation in pore size distribution was detected by MIP (Fig. [1\)](#page-3-0), the difference between unheated and heated samples being within the variability of the stone. Nonetheless, heating caused a ∼10 % decrease in *UPV*, as well as a slight increase in water absorption and sorptivity, which were measured on the same samples before and after heating and which, therefore, can be considered as fully comparable and reliable (Table [2\)](#page-4-0). Such modification in physicalmechanical properties, even if no significant alteration in pore size distribution was observed by MIP, can be ascribed to the opening of cracks at the nano-scale (beyond the MIP sensitivity, i.e. below 0.035  $\mu$ m). This is in agreement with previous results found for *Globigerina* limestone, where specific surface area measured by BET method was found to increase after heating at 400 °C, which was attributed to the opening of nano-cracks [[20\]](#page-7-7).

While in the case of Carrara marble a direct comparison between microstructural modifications caused by heating with those induced by natural weathering in the field was possible, in the case of limestones L1-L4 such a direct comparison is rather difficult, as literature data on the environmental weathering of these specific lithotypes are lacking. However, the effects of natural weathering on a limestone with almost the same calcite content and porosity as L1  $(CaCO<sub>3</sub> > 95 \text{ wt}\%$ , effective porosity = 1.0 %) have been reported in the literature  $[42]$  $[42]$ . For this limestone, the effective porosity was found to steadily increase with increasing weathering degree (from 1.0 % up to 2.8 %), while water absorption was found to correspondingly increase from 0.3 to 1.5 wt%  $[42]$  $[42]$ . As the increase in porosity was mainly due to dissolution, a general enlargement of pores occurred. In particular, for moderate weathering, new pores with diameter smaller than 0.1 µm opened, while for more weathered samples pores with diameter up to 1 µm developed [\[42](#page-7-25)]. The above described microstructural modifications, undergone in the field by a limestone with characteristics similar to those of L1, actually fairly resemble those experienced by L1 after heating, in terms of both alterations in porosity and pore size distribution. Therefore, the capability of heating to produce microstructural modifications similar to those produced in the field by natural weathering seems confirmed.

For a specific investigation of the effects of natural weathering on limestone L1–L4, as well as M1, the authors have undertaken an experimental campaign of field exposure of the five lithotypes in controlled environmental conditions. In this way, modifications in porosity, pore size distribution and water absorption induced by natural weathering will be estimated and possibly correlated to the initial microstructural characteristics of the stones. Such work is currently in progress.

### *3.2.2 Second heating*

A further confirmation of the role of porosity in determining the damaging effectiveness of heating was obtained by reheating stone samples for a second time. According to the hypothesis that heating is less effective when stone porosity increases, samples that have already been subjected to artificial deterioration by heating are expected to undergo less pronounced alterations, compared to samples heated for the first time. In fact, after the first heating, an increase in porosity and micro-cracks occurs, so that, when the stone is re-heated, more voids and cracks are available to accommodate calcite crystal deformation.

This hypothesis was confirmed after carrying out the second heating: for all the five lithotypes, the modifications in porosity, pore size distribution and *UPV* were indeed much less pronounced after the second heating, compared to the first one (Table [2](#page-4-0) and Fig. [1\)](#page-3-0). In particular, while in the case of M1 and L1, which still have rather low porosity after heating for the first time, a distinguishable modification in pore size distribution can be observed, in the case of L2, L3 and L4, the effect of re-heating becomes way less pronounced (Fig. [1](#page-3-0)). For all the lithotypes, a small further decrease in *UPV* was found after the second heating: while for the less porous stones this can be ascribed to the additional opening of micro-cracks that can be observed in Fig. [1,](#page-3-0) in the case of the more porous stones the further modifications in stone microstructure seem to have occurred beyond the MIP sensitivity, as previously discussed in the case of L4.

The fact that new micro-cracks, opened after the first heating, allow some calcite crystals deformation during subsequent heating, thus reducing its impact on stone properties, also explains some experimental results reported in the literature. Unweathered marble samples, subjected to artificial deterioration by repeated thermal cycles over a heating plate (reaching a maximum temperature of 300  $^{\circ}$ C), were found to undergo the highest degradation (in terms of increase in water absorption) after the first cycle, while the second cycle brought no significant increase to marble damaging [[13\]](#page-7-2). Similarly, in the case of marble slabs, that had been thermally weathered after years of field exposure and that were then removed and subjected to 40 thermal cycles in laboratory conditions (reaching a maximum temperature of  $+80$  °C), the slabs with the highest level of initial bowing (and hence of initial microstructural alteration) exhibited the lowest further bowing increase, and vice versa [\[32](#page-7-16)].

## **4 Conclusions**

Based on the results obtained in the present study, the following conclusions can be derived:

- (1) In the case of Carrara marble, by heating at 400 °C for 1 hour, modifications in porosity, pore size distribution and *UPV*, closely resembling those experienced in the field by naturally weathered marble, were obtained. Similarly, also physical-microstructural alterations undergone by L1 after heating were found to fairly resemble those of a limestone with similar characteristics, subjected to natural weathering to various degrees.
- (2) Heating effects proved to change significantly, depending on the initial porosity and pore size distribution of the heated stone. In fact, for increasing initial porosity, less pronounced modifications in microstructural, physical and mechanical properties were found. This was explained considering that, in a more porous stone, more voids and cracks are available for calcite crystals to deform upon heating, without causing stress and consequent cracks formation inside the stone.
- (3) The reduction of heating effectiveness for increasing initial porosity was confirmed by re-heating the stone samples for a second time. As micro-cracks opened after the first heating, resulting in a porosity increase, reheating proved to cause very limited additional effects,

thus confirming the decisive role of initial porosity in determining the heating effectiveness.

All things considered, heating is confirmed as a very promising method for obtaining artificially weathered specimens to be used for testing of stone consolidants. However, depending on the initial characteristics of the stone, heating might lead to modifications in stone microstructure that resemble those experienced by naturally weathered samples in a more or less close manner. Indeed, in the case of Carrara marble, heating caused an increase in porosity and a shift towards larger pores that fairly reproduce those found in the case of slabs that have been exposed to daily and seasonal thermal excursions for years. However, in the case of *Globigerina* limestone, after heating a decrease in mechanical properties was found, which certainly resembles the mechanical deterioration occurring in the field, but such degradation was mainly owing to cracks that opened at the nano-scale, which not necessarily resembles microstructural degradation in the field. Therefore, preliminarily tests on the lithotypes to be subjected to artificial deterioration by heating should always be carried out, in order to assess the heating capability of simulating actual natural weathering.

#### <span id="page-6-5"></span><span id="page-6-2"></span><span id="page-6-1"></span><span id="page-6-0"></span>**References**

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