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EFFECTS OF THERMAL AGEING ON CALCARENITE FROM LIVORNO COAST (ITALY)

Abstract - A. AQUINO, S. PAGNOTTA, M. LEZZERINI, *Effects of thermal ageing on calcarenite from Livorno coast (Italy)*.

The “Panchina” stone widely outcrops along the South-western Tuscan coastline, from Italy. It is a highly porous calcarenitic rock characterized by grains with medium size, enriched in carbonate fragments of organic origin. Panchina stone is made up of abundant calcite and quartz, subordinate feldspars, and traces of phyllosilicates. The analysed samples are characterized by high porosity, highly variable water absorption by both capillarity and total immersion at atmospheric pressure. Thanks to the good physical and mechanical properties that characterize the stone, the “Panchina” calcarenite is easy to work and extensively used in the necropolis of the Gulf of Baratti since Etruscan times and, in medieval times, in various public and religious buildings in the city of Pisa. This work focuses on the effects of degradation produced by artificial thermal decay. The exposition of samples at increasing values of temperatures (110 °C, 200 °C and 300 °C) brings the samples to an increase in the amount of absorbed water (from 11.79 to 12.21 vol. % at 300 °C) and, therefore, to an increase in total porosity. This can bring to a higher circulation of fluids in the rock that can play a key role in its decay.

Key words - building materials, thermal decay, porosity, Tuscany

Riassunto - A. AQUINO, S. PAGNOTTA, M. LEZZERINI, *Effetti del degrado termico sulla calcarenite della costa livornese (Italia)*.

La pietra “Panchina” affiora ampiamente lungo la costa toscana sud-occidentale, in Italia. Si tratta di una roccia calcarenitica altamente porosa, caratterizzata da clasti di medie dimensioni, ricca in frammenti carbonatici di origine organica. La pietra “Panchina” è costituita da abbondante calcite e quarzo, subordinati feldspati e fillosilicati in tracce. I campioni analizzati sono caratterizzati da alta porosità, assorbimento d’acqua molto variabile sia per capillarità che per immersione totale a pressione atmosferica. Grazie alle buone proprietà fisiche e meccaniche che caratterizzano la pietra, la calcarenite “Panchina” è facilmente lavorabile e ampiamente utilizzata nelle necropoli del Golfo di Baratti fin dall’epoca etrusca e, in epoca medievale, in vari edifici pubblici e religiosi della città di Pisa. Questo lavoro si concentra sugli effetti del degrado prodotto dal trattamento termico artificiale. L’esposizione dei campioni a valori crescenti di temperatura (110 °C, 200 °C e 300 °C) porta i campioni a un aumento della quantità di acqua assorbita (da 11,79 a 12,21 vol. % a 300 °C) e, quindi, a un aumento della porosità totale. Questo può portare a una maggiore circolazione di fluidi nella roccia che può giocare un ruolo chiave nel suo decadimento.

Parole chiave - materiali da costruzione, degrado termico, porosità, Toscana

INTRODUCTION

Stone has always been the construction material par excellence thanks to its versatility, as well as its general durability for both external and internal applications, and its easy availability. The different types of rock, with their different physical-mechanical and aesthetic characteristics, have historically been used for a wide variety of purposes, both for construction and ornamentation. It is precisely their intrinsic characteristics that make them ideal building materials that are also at the root of the main problems linked to deterioration and the consequent need for protection and conservation (Brandi, 1963; Terrazzini, 1992; Lazzarini & Laurenzi Tabasso, 2010; Improta, 2012; Pereira *et al.*, 2015; Freire-Lista & Fort, 2019; Coombes & Viles, 2021; Freire-Lista, 2021).

This study is part of a wider research project aimed at studying the building stones and mortars used in monumental construction during the Italian Middle Ages, in Tuscany, in particular in the cities of Pisa and Livorno and their surroundings. Over the years, studies have been carried out at the Department of Earth Sciences of the University of Pisa on the various lithologies and mortars used in historical monumental building (Franzini *et al.*, 2001, 2007; Franzini & Lezzzerini, 2002; Lezzzerini *et al.*, 2014a, 2017; Ramacciotti *et al.*, 2015), but the “Panchina” stone is still a poorly studied lithotype (Sartori, 2004; Ciampalini *et al.*, 2006; Aquino *et al.*, 2020b). “Panchina” calcarenite is a highly porous stone with medium-sized grains and rich in organogenic carbonate fragments. This stone is extensively present in the south-western part of Tuscany, mainly along the Livorno coast. Used as a building material since Etruscan times, it was widespread during the Middle Ages until the second half of the 17th century. Today it is possible to see many ashlar of these stones in many buildings and in the ancient defensive walls of the Pisa’s city (Sartori, 2004; Lezzzerini, 2005), but its wide use in the past is also testified by its presence in the archaeological sites of Baratti and Luni, and in the ancient Roman remains of the Nerone Thermae.

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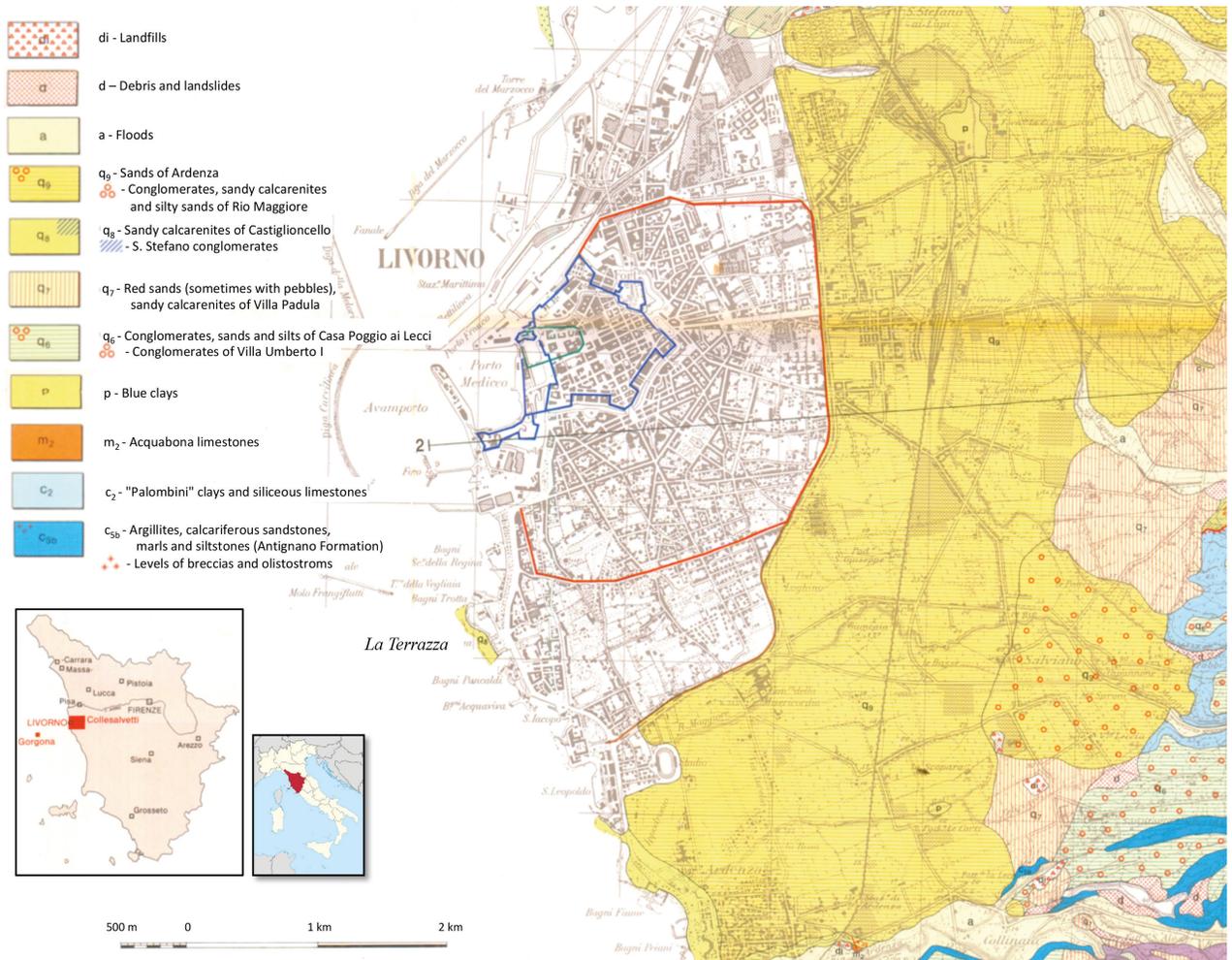


Figure 1. Geological map of the city of Livorno and its surroundings. “La Terrazza” represents the “typical” outcrop of the “Panchina” calcarenite (after Lazzarotto *et al.* 1987).

Because of their proximity to the sea, both the cities of Pisa and Livorno are constantly subjected to, and face problems related to, the presence of marine aerosol, which combined with wide temperature variations throughout the year can cause disintegration and loss of cohesion in the building materials used (Lazzarini & Laurenzi Tabasso, 2010; Ban *et al.*, 2016; Aquino *et al.*, 2020a), and in this case the “Panchina” stone (Aquino *et al.*, 2020a). Numerous studies have highlighted the importance of research into the behaviour of rocks as a result of temperature variations (Andriani & Walsh, 2010; Brotóns *et al.*, 2013; Freire-Lista *et al.*, 2016; Murru *et al.*, 2018; Shen *et al.*, 2019; Wang and Konietzky, 2019; Chen *et al.*, 2020; Rabat *et al.*, 2020; Wong *et al.*, 2020). In this work, we study the chemical, mineralogical and petrographic characteristics, together with the physical properties of the “Panchina” calcarenite as a construction material, in order to better understand the main effects of degradation caused by artificial thermal ageing on this rock.

GEOLOGICAL SETTING

The Panchina stone of the Livorno coast, in western Tuscany, is a lithotype that emerges mainly along the coast between Livorno and Rosignano Marittimo, reaching as far as the Gulf of Baratti (Rodolico, 1953; Franzini *et al.*, 2000; Lezzzerini, 2005; Aquino *et al.*, 2020b). The typical rocky outcrop is found within the city of Livorno and belongs to a morpho-sedimentary element known in literature as the “Terrazzo di Livorno” (Figs 1 and 2) (Malatesta, 1940, 1942; Barsotti *et al.*, 1974; Ciampalini *et al.*, 2006; Ciampalini and Forli, 2014), which also represents the substrate on which the city was built. The “Terrazzo di Livorno” was interpreted by these authors as a polycyclic marine terrace that developed from the fifth stage of marine isotopic stratigraphy (MIS 5), starting about 125,000 years ago (Barsotti *et al.*, 1974; Federici & Mazzanti, 1995).

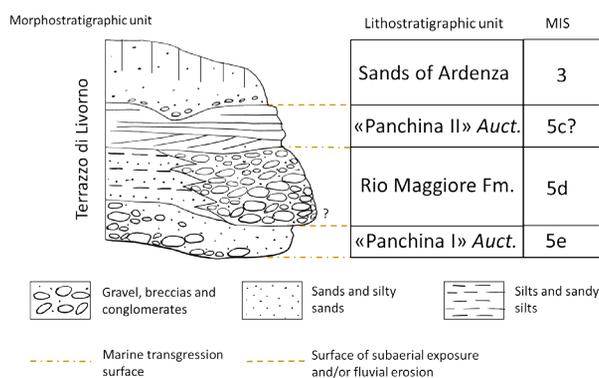


Figure 2. Diagram of the stratigraphic relationships between the lithostratigraphic units of the Terrazzo di Livorno described in the literature. Correlations with marine isotopic stages (MIS) are also shown. Modified after Ciampalini & Sammartino, 2007.

The following stratigraphic succession of this terrace can be recognized starting from the base up to the top (Fig. 2):

- Sandstone and conglomerates of coastal marine environment, which sometimes contain warm environment fauna (the so called “Panchina I”, or the “Calcareniti sabbiose di Castiglioncello” and the “Conglomerati di Bocca di Chioma”), MIS 5e (Malatesta, 1942; Barsotti *et al.*, 1974; Hearty *et al.*, 1986; Chen *et al.*, 1991; Federici & Mazzanti, 1995; Antonioli *et al.*, 1999; Zanchetta *et al.*, 2004).
- Silty clays, sometimes peaty, of a mainly continental environment, sometimes containing terrestrial malacofaunas and the remains of large mammals, which indicate a phase of climate deterioration, MIS 5d (Barsotti *et al.*, 1974; Lazzarotto *et al.*, 1990a; Federici & Mazzanti, 1995; Zanchetta *et al.*, 2006).
- Conglomerates in silty sandy matrix of river environment (“Conglomerati di Rio Maggiore”) that follow upward and in plausible heteropy to “Panchina I”.
- Sandstones from different environments, from coastal marine to aeolian (“Panchina II”, Lazzarotto *et al.*, 1990; Malatesta, 1942), of uncertain dating, but probably corresponding to MIS 5c (Antonioli *et al.*, 1999; Ciampalini *et al.*, 2006). This sequence refers to the “Calcareniti di Castiglioncello” (Lazzarotto *et al.*, 1990a).
- Continental sands and sandy silts, strongly reddened or brown or orange in colour (“Sabbie di Ardenza” by Lazzarotto *et al.*, 1990b); often inside them there are traces of Mousterian craftsmanship (Ciampalini & Sammartino, 2007; Malatesta, 1940), MIS 3 and 4 (Bossio *et al.*, 1981; Zanchetta *et al.*, 2006). The substratum of the rather varied Pleistocene deposits consists of Pliocene deposits

of the “Blue Clays” replaced to the west by sands and clays of the Lower Pleistocene of the Morrone Formation (Costantini *et al.*, 1993; Cauli & Bogi, 1997).

MATERIALS AND METHODS

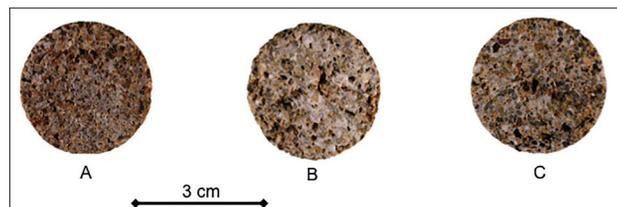


Figure 3. Macroscopic image of “Panchina” calcarenite samples.

The sampling campaign took place in many of the outcrops along the south-western coastline of Tuscany, where the calcarenite “Panchina” emerges, from Livorno to Baratti. The samples were then analysed starting with a chemical, mineralogical and petrographic characterization, followed by the determination of the physical properties. Three calcarenite blocks (A, B and C, Fig. 3) have been chosen among the collected ones, with the lowest values of porosity and the best preservation conditions, in agreement to what had been observed in our previous study (Aquino *et al.*, 2020b). Before proceeding with the determination of the physical properties of the rock, we cored the three calcarenite samples. From the three blocks of rock, we have obtained 12 cylinders of 30 mm in diameter and 40 mm in height, three cylinders for each block. On these cylinders, we have carried out all the determinations of the physical properties, before and after heat treatment, to be able to compare the effects of heat variations.

The determination of major and minor compounds (Na_2O , MgO , Al_2O_3 , SiO_2 , P_2O_5 , K_2O , CaO , TiO_2 , MnO , Fe_2O_3) has been obtained by means of X-ray fluorescence (Franzini *et al.*, 1975) using a new software recently developed (Tamponi *et al.*, 2020). The measurement uncertainty results between 4-7% by weight for concentrations < 1%, between 2-4% for concentrations between 1 and 10% and around 1% for concentrations > 10% (Lezzerini *et al.*, 2013, 2014b).

The mineralogical analyses were carried out through both X-ray diffractometry (XRD), using a Bruker D2 Phaser X-ray diffraction (XRD) instrument, Cu K_α radiation, $\lambda = 1.5418 \text{ \AA}$, angle range $4-66^\circ 2\theta$, operating at 0.020 deg step displacement and 65.6 s step time; and petrographic analyses: transmitted light microscopic observation of thin sections (Zeiss Axioplan microscope).

The physical properties of the stones (real density (ρ_r) and apparent density (ρ_a), water absorption by capillarity, water absorption at atmospheric pressure, total and open porosity, and saturation index) have been determined following EN standards (EN 1925, 1999; EN 13755, 2009; EN 1936, 2010).

In detail, ρ_r has been determined using a gas pycnometer (ultrapycnometer 1000 by Quantachrome Corporation) (EN 1936, 2010), and ρ_a has been determined by ratio between dry mass and volume of each specimen. The specimens were placed in a stove at 60 °C until the dry weight was reached, (i.e., when the difference between two successive weighing at an interval of 24 h is not greater than 0.1 % of the mass of the specimen itself).

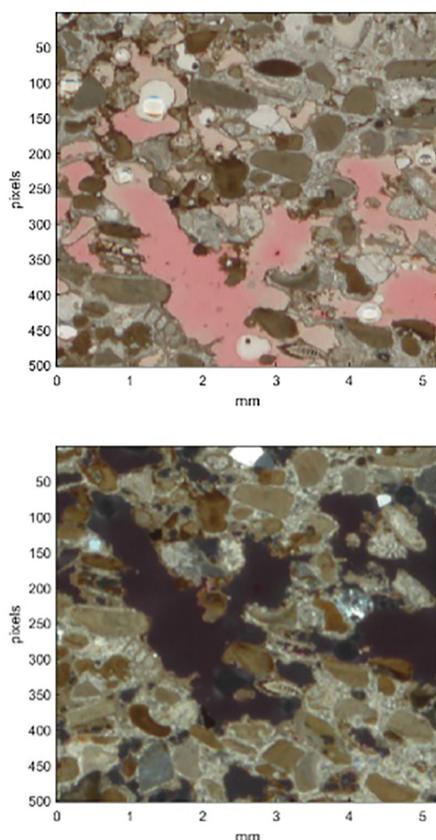


Figure 4. Optical microscopy images in transmitted light at parallel (top) and crossed Nicols (bottom) of a sample of “Panchina” calcarenite from Livorno. It is possible to see the presence of the remains of some of the organisms that make up the structure of this stone.

After oven drying the specimens were immersed in distilled water following EN 1936, (2010). The volume of the specimens was measured by means of a hydrostatic balance on water-saturated samples (Franzini & Lezzerini, 2003).

The water absorption by capillarity has been determined on the same specimens used for ρ_a determination following (EN 1925, 1999). Measurements were taken after 1, 3, 5, 15, 30, 60, 120, 180, 240, 300, 360, 420, 480, 1440, 2880, 4320, 5760 minutes; total porosity has been calculated using the following formula:

$$P \text{ (vol. \%)} = 100 \cdot (1 - \rho_a / \rho_r).$$

Degradation of samples by means of thermal shock. Three different thermal degradation tests using 12 cylindrical specimens. Before performing the thermal degradation, each specimen was brought to constant weight and subjected to water absorption cycles both by capillarity and by total immersion, for at least 14 days. After sample preparation, the following tests were carried out: a - heating to 110 °C using 12 samples, three for each of the 3 samples, with the aid of an oven; b - heating to 200 °C using a muffle furnace; c - heating to 300 °C using a muffle furnace.

After each test, all samples were thermally shocked by putting them under current deionized water, at room temperature, for at least three minutes, then air dried for ca. 30 minutes.

RESULTS AND DISCUSSION

The three stone samples have been firstly observed by naked eye and described as follow (Fig. 3): sample A, is yellowish-white composed by fine sand and high porosity, showing a minor state of decay; while both sample B and C, are reddish white, composed by fine-medium sand and high porosity, showing a low-medium state of decay. Fig. 4 shows two pictures of thin sections in transmitted light at parallel and crossed Nicols in which it is possible to appreciate the microtexture and mineralogical composition of the samples studied, including microfossils.

The analysed samples of “Panchina” stone are composed mainly of calcite and quartz, with some feldspar and phyllosilicates in traces. The colour of the analysed samples varies from yellowish-white to reddish-brown. The “Panchina” stone is a calcarenite with a grain size ranging from silt to coarse sand and a porosity that varies from low to very high, and a variable external alteration from absent to advanced. It is a granular sedimentary rock composed mainly of carbonate fragments (35-90 vol. %, size from 100 μm to 500 μm), quartz (10-40 vol. %, size from 200 μm to 500 μm) and feldspars (5 vol. %, size from 300 μm to 500 μm) and bioclasts (5-20 vol. %, size from 200 μm to 500 μm), mainly brachiopods. Some carbonate cement (15 vol. %) is present. The “Panchina” stone samples studied in this work is classifiable as “calcarenite” according to Folk (1959). The results of the microscopic anal-

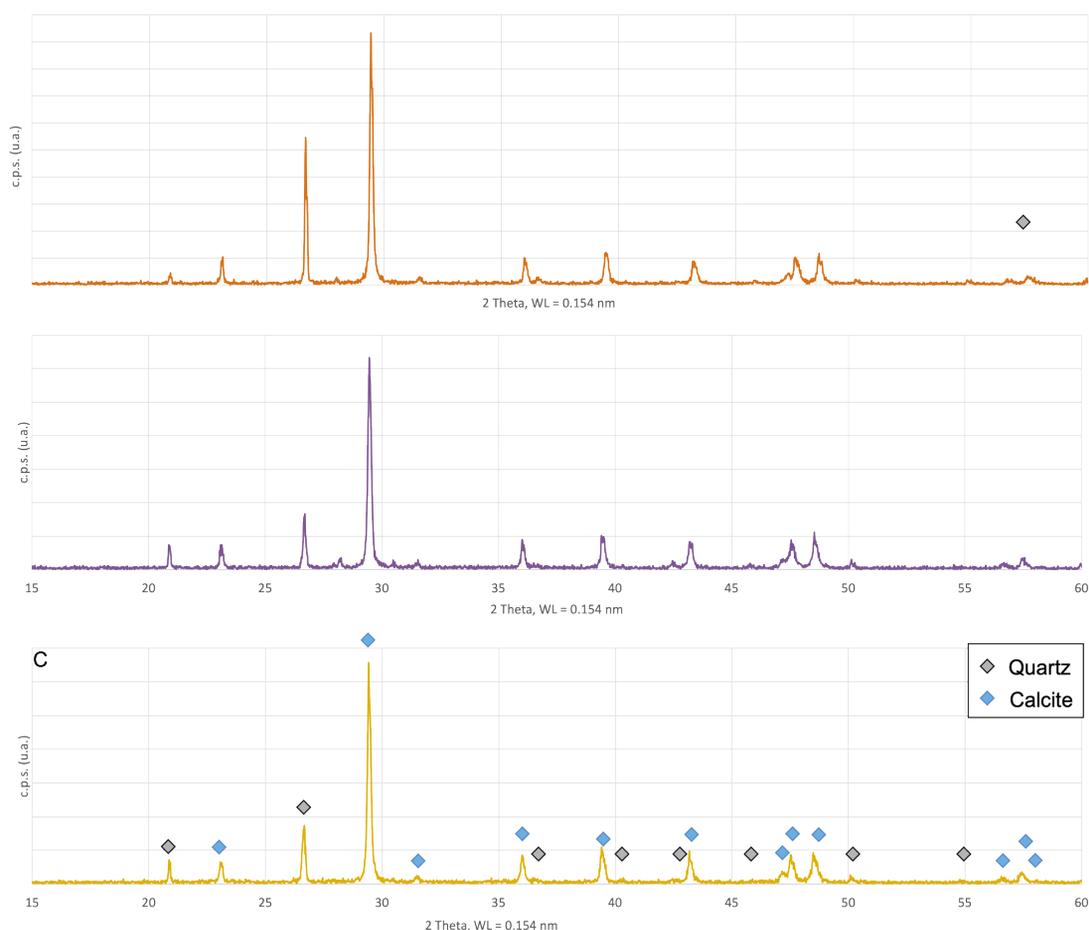


Figure 5. Diffractograms (XRD) of the three “Panchina” stone samples A, B and C. Panchina is mainly composed of calcite and quartz, followed by some feldspars and phyllosilicates in traces..

ysis in transmitted light agree with those shown by the powder analysis in X-ray diffractometry (Fig. 4), where the presence of quartz and calcite is evident.

In Tab. 1, we report the average values of the chemical analysis by X-ray fluorescence for the present work, compared with those of the previous literature. The main components of the “Panchina” calcarenite, excluding the Loss on Ignition (LOI) values, which are essentially due to the CO_2 content, are represented by CaO, with an average value of 27.27 wt.%, and SiO_2 with an average value of 42.46 wt.%. It is clear that, compared with the previous literature, there is a substantial difference in the composition of the stone. In the samples examined in this work, there are higher values of SiO_2 at the expense of CaO content than shown in previous work. Both feldspars and phyllosilicates are also present, but only in trace amounts, in agreement with the literature and X-ray diffractometry data.

The results of the analyses of the physical properties are reported in Tabs 2 and 3, before and after thermal

degradation. In the non-degraded samples, ρ_a varies from 2.28 to 2.37 g/cm^3 in agreement with the total porosity values, ranging from 12.65 to 15.82 vol.%. The water absorption varies from 4.99 to 6.52 wt.%, and from 11.37 to 15.73 vol.%, with a saturation index that varies from 72 to 95. The values of the water absorption by capillarity varies from 30.56 to 68.44 $\text{g/m}^2\text{s}^{0.5}$ (68.44 $\text{g/m}^2\text{s}^{0.5}$ sample A, 30.56 $\text{g/m}^2\text{s}^{0.5}$ sample B, and 35.70 $\text{g/m}^2\text{s}^{0.5}$ sample C).

Tabs 2 and 3 show the physical property values before and after heat treatment. The values of ρ_a show a slight increase after heat treatment, increasing with the temperature applied, minimum for sample A degraded at 110 °C ($+0.01 \text{ g/cm}^3 \pm 0.01$) and maximum for sample C degraded at 300 °C ($0.04 \text{ g/cm}^3 \pm 0.02$). The values of the absorption coefficient C1 show a decrease after thermal treatment for sample A, from 68.44 g/cm^3 to 68.25 g/cm^3 , while both sample B and sample C show an increase in the value of C1: sample B from 30.56 $\text{g/cm}^3 \pm 2.58$ to 31.84 $\text{g/cm}^3 \pm 3.28$; sample C from 35.70 $\text{g/cm}^3 \pm 1.98$ to 45.01 $\text{g/cm}^3 \pm 13.31$.

It is also interesting to note the increase in the standard deviation recorded in the samples after thermal treatment. As far as water absorption is concerned, both percentage by weight and volume, a general increase in the absorbed water content is recorded in both cases for each sample treated at different temperatures as the temperature applied increases.

In particular, at 110 °C there is an increase in water content from 6.52 wt. % ± 0.06 to 6.65 wt. % ± 0.09 , at 200 °C it varies from 4.99 wt. % ± 0.05 to 5.07 wt. % ± 0.07 and at 300 °C there is the maximum increase, from 4.99 wt. % ± 0.25 to 5.16 wt. % ± 0.28 . Similar variations are recorded for the percentage water absorption values by volume. The total porosity values of the studied calcarenite samples generally show an increase with increasing temperature, with the exception of the samples treated at 110 °C, which show a slight decrease in porosity, but still well within the values of the standard deviation. In general, what has been observed for the increase in absorbed water content is confirmed by the values of the Saturation Index, which increases with increasing temperature.

Fig. 6 shows the mean capillary absorption curves of samples A, B and C before heat treatment (dotted line) and after heat treatment (solid line) at 110 °C, 200 °C and 300 °C. As can be seen in the figure, the heat treatment leads to an increase in the water content absorbed by the treated samples. This increase in absorbed water is greater as the treatment temperature is increased. Samples treated at 110 °C show the least variation in water absorption. The absorption curves of the samples treated at 200 °C show a slight increase compared to the previous ones, while the curves of the samples treated at 300 °C show a marked change in the water content absorbed by the samples treated at this temperature.

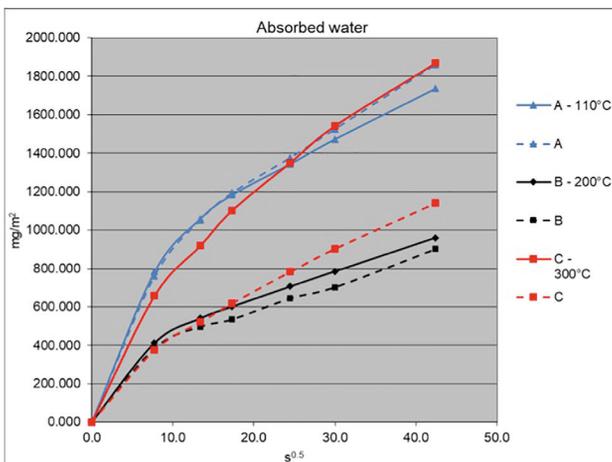


Figure 6. Mean water absorption curves of samples A, B and C. Continuous lines represent degraded samples (110 °C sample A, 200 °C sample B, 300 °C sample C) and dotted lines represent samples before thermal degradation.

Clearly, subjecting the “Panchina” calcarenite to thermal treatment induces in the stone structural changes that lead it to absorb a greater amount of water than the “sound” sample, comparable to the increase in porosity of the sample studied. These changes in the content of absorbed water and total porosity as a result of thermal treatment are phenomena already observed in the literature for marble (Royer-Carfagni, 1999; Siegesmund *et al.*, 2000; Cantisani *et al.*, 2009; Franzoni *et al.*, 2013; Ban *et al.*, 2016; Murru *et al.*, 2018) the emphasis lies on reproducing this key-deterioration effect in every lithotype. An additional effect to be studied for porous limestone is the formation of a gradient of compactness within the specimen, mimicking a crust on loose substratum. The ageing progress was evaluated by the methods of determining changes in ultrasound velocity and water absorption coefficient by capillarity. At critical stages the micro defects created are analysed by polarizing light and scanning electron microscopy on petrographic thin sections and mercury intrusion porosimetry. The methodologies for artificial ageing are as following: 1., in which the thermo-induced changes in porosity and micro textures that develop are due to differential expansion of calcite crystals within the marble subjected to heat treatment (Rosenholtz & Smith, 1949; Battaglia *et al.*, 1993; Leiss & Weiss, 2000) the anisotropic thermal dilatation was calculated from texture analyses of four exemplary samples from the Carrara area in Italy and compared to experimentally measured dilatation coefficients. The thermal dilatation as determined in the experiment is controlled by an intrinsic part (anisotropic single crystal properties and texture. Similarly, it is conceivable that the changes in total porosity of the studied calcarenite samples result from the differential deformation of the calcite crystals contained in the samples. This differential expansion of calcite is likely to lead to the formation of new micro-fractures and the widening of existing ones.

CONCLUSIONS

Monumental stone heritage is an important economic resource to be protected over time. In order to allow proper planning of conservation and restoration policies for stone cultural heritage, it is important to have a thorough knowledge of the materials used and their behaviour. In this work, the effects of thermal heating on samples of calcarenite, “Panchina” stone of Italian origin (Tuscany) were investigated. For this study, the mineralogical and petrographic characteristics as well as the physical properties of this rock were investigated. The physical parameters were measured according to international standard norms. The evaluation of the effects of ageing by thermal heating was carried out by exploiting water absorption by capillarity. The stone studied can be classified as calcarenite, with a fine to

Table 1. Chemical compositions (wt. %) of the analysed samples of “Panchina” stone.

	LOI	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃
Mean	22.09	0.81	0.97	3.95	42.46	0.05	0.45	27.27	0.18	0.06	1.91
<i>St. Dev.</i>	±0.26	±0.03	±0.01	±0.09	±0.13	±0.00	±0.02	±0.36	±0.01	±0.00	±0.02
Mean*	33.69	0.14	0.28	1.29	21.5	0.07	0.35	42.15	0.24	0.29	0.45
<i>St. Dev.*</i>	±3.45	±0.07	±0.05	±0.30	±7.57	±0.03	±0.05	±4.36	±0.05	±0.08	±0.07

LOI = Loss on Ignition at 980 °C; Fe₂O₃ = total iron expressed as Fe₂O₃; *Data from Aquino *et al.* 2020.

Table 2. Main physical properties of the analysed samples of “Panchina” stone.

Campione	ρ_r (g/cm ³)	ρ_a (g/cm ³)	C ₁ (g/m ² s ^{0.5})	w. Abs. (wt. %)	w. Abs (vol. %)	Total porosity (vol. %)	Saturation Index
A mean	2.71	2.28	68.44	6.52	14.90	15.73	95
<i>St. Dev.</i>	±0.01	±0.02	±1.11	±0.06	±0.11	±0.09	±1
B mean	2.71	2.28	30.56	4.99	11.37	15.82	72
<i>St. Dev.</i>	±0.01	±0.01	±2.58	±0.05	±0.12	±0.17	±1
C mean	2.71	2.37	35.70	4.99	11.79	12.65	93
<i>St. Dev.</i>	±0.01	±0.02	±1.98	±0.25	±0.48	±0.83	±3

ρ_r = real density; ρ_a = apparent density; C₁ = water absorption coefficient by capillarity; w. abs. = water absorption.

Table 3. Main physical properties of the analysed samples of “Panchina” stone after thermal degradation.

Campione	ρ_r (g/cm ³)	ρ_a (g/cm ³)	C ₁ (g/m ² s ^{0.5})	w. Abs. (wt. %)	w. Abs (vol. %)	Total porosity (vol. %)	Saturation Index
A mean (110 °C)	2.71	2.29	68.25	6.65	15.20	15.70	97
<i>St. Dev.</i>	±0.01	±0.01	±1.07	±0.09	±0.19	±0.10	±1
B mean (200 °C)	2.71	2.31	31.84	5.07	11.57	15.83	73
<i>St. Dev.</i>	±0.01	±0.01	±3.28	±0.07	±0.15	±0.17	±1
C mean (300 °C)	2.71	2.41	45.01	5.16	12.21	12.72	97
<i>St. Dev.</i>	±0.01	±0.02	±13.31	±0.28	±0.56	±0.83	±2

ρ_r = real density; ρ_a = apparent density; C₁ = water absorption coefficient by capillarity; w. abs. = water absorption.

medium grain size and high porosity, rich in calcite (35-90 vol. %) and quartz (10-40 vol. %) and subordina-ly feldspars (\approx 5 vol. %).

An increase in the values of the physical characteristics, and above all of the capillarity coefficient, can be seen after heating at 200 °C in furnace; this increase becomes more marked with heating up to 300 °C, so it can certainly be said that, unlike the other degradations, a cycle at 300 °C leads to a change in the amount of water absorbed correlated with a modest increase in the apparent volume, and to the formation of open porosity. Exposure of samples to increasing temperatures leads to an increase in the amount of water absorbed and thus to an increase in the total porosity, which can be attributed to the differential deformation of the calcite crystals. This may lead to increased fluid circulation in the rock, which may play a key role in its decay. Heating cycles

produce degradation of the rock studied, but as seen above it does not seem possible to attribute the degradation effects normally observed on the “Panchina” stone exclusively to thermal degradation. In this respect, one aspect to be verified in the future is certainly the effect of complete thermal cycles on samples with increasing calcite content, freezing and subsequent thawing cycles and the influence of salts and acid attacks.

AUTHOR CONTRIBUTIONS

Conceptualization, A.A and M.L.; methodology, A.A. and S.P.; validation, A.A., S.P., and M.L.; formal analysis, A.A and M.L.; investigation, A.A.; resources, M.L.; data curation, A.A.; writing—original draft preparation, A.A.; writing—review and editing, S.P. and M.L.; visualization, A.A.; supervision, M.L. All authors have read and agreed to the published version of the manuscript.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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