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Artificial Thermal Decay: Influence of Mineralogy and Microstructure of Sandstone, Calcarenite and Marble

Andrea Aquino [1], Stefano Pagnotta [1], Marco Lezzerini [1]

[1] Department of Earth Sciences, University of Pisa, via S. Maria 53 - 56126, Pisa, Italy

andrea.aquino@phd.unipi.it

Abstract. Within a major framework of studies around artificial weathering and its effects on different lithotypes, in this work we study the effects of thermal stresses after artificial thermal decay on different types of stones used in historical buildings: a sandstone, a calcarenite and a marble. The sandstone belongs to the so called "Macigno" Formation and mainly outcrops along the northern Apennine (North Western Tuscany) and it has been widely used around Tuscany for building purposes (e.g., in Florence, Lucca, Pisa, Pistoia, etc.); the analysed calcarenite (Gravina) comes from the surrounding of Matera Town and has been deeply used for the construction of the ancient buildings of the town itself; and the marble comes from the Carrara marble district (Northern Tuscany), a highly used stone throughout the centuries as ornamental stone. All these types of stone for their physical and mechanical properties, and aesthetic appearance, have been extensively used as both ornamental stones and as construction materials. To reproduce a plausible effect of natural thermal decay of the stones due to day-to-night and season-to-season fluctuations, we subjected the samples to artificial thermal decay. We carried out different thermal cycles on the samples by using a stove at 150°C and a muffle furnace at 300°C and 450°C. We analysed the physical and mechanical properties before and after each cycle to compare and evaluate the effects of thermal stresses on the stones. Among the different analyses: mass and volume measurements, water absorption tests, mercury intrusion porosimetry, thin-section observations and determination of chromatic alterations through image analysis and Munsell charts method. It was then possible to evaluate the influence of both mineralogy and microstructures on thermal decay of the studied stones (variations in fabric and modifications on physical and mechanical properties).

1. Introduction

Within a major framework of studies around artificial weathering and its effects on different lithotypes, in this work we study the effects of thermal stresses after artificial thermal decay on different types of stones used in historical buildings: a sandstone, a calcarenite and a marble.

The sandstone belongs to the so called "Macigno" Formation (Upper Oligocene to Lower Miocene) and mainly outcrops along the northern Apennine (North-western Tuscany), from Pontremoli to Chianti, and even in some places in South-western Tuscany. This stone has been widely used, from prehistoric times until today, for ornamental and building purposes all around Tuscany (e.g., in Florence, Lucca, Pisa, Pistoia, etc.). In particular, the sandstone used in this work comes from Matraia, where it is still actively quarried. According to the existing scientific literature [1-10], the "Macigno" sandstones is generally made up of well consolidated, fine- to very coarse-grained, poorly to moderately sorted siliciclastic rocks consisting of sub-angular detrital grains of quartz, plagioclase, K-feldspar, chlorite

s.l., mica-like minerals (muscovite/illite and minor biotite), with minor amounts of rock fragments (< 10% by volume).

The analysed calcarenite (Gravina) comes from the surrounding of Matera (Basilicata, Italy) and has been widely used as a building stone both in Puglia and in the eastern Basilicata, up to the present day, thanks to its wide availability and easy workability. It is a well-known material especially thanks to it use in the construction of the so-called "Sassi di Matera", the old district of the city of Matera that represents one of the best-preserved rupestrian sites in southern Italy. As described by several authors [11-15], the Gravina Calcarenite is an extremely heterogeneous formation. It is a Pleistocene rock that overlies the Cretaceous Altamura Limestone. It is characterized by two main members that are recognized on the basis of the relative abundance of skeletal or lithoclastic grains [14].

The marble used in this work is a representative sample of the many varieties of marble quarried in the Apuan Alps marble district. Despite their aesthetical, chemical, and mineralogical homogeneity, marbles quarried from Apuan Alps basins exhibit a quite relevant variability in term of textural and structural features [16], due to different tectonic events that involved Apuan complex [17]. Numerous studies [18-23] have evidenced that such a diversity has a key role in hydric behaviour of marbles, determining a diverse response to decay processes. In particular, grain boundaries seem to have a relevant role in cracks opening and propagation, while grain size seems to have lower importance [24]. The marble samples are extremely pure in carbonate content (<98% pure $CaCO_3$), with few accessory phases (albite, quartz, pyrite, and phyllosilicate) and they present a granoblastic-heteroblastic texture. This marble has been highly used throughout the centuries as ornamental stone both in Tuscany and worldwide.

All these types of stone for their physical and mechanical properties, and aesthetic appearance, have been extensively used as both ornamental stones and as construction materials. To reproduce a plausible effect of natural thermal decay of the stones due to day-to-night and season-to-season fluctuations, we subjected the samples to artificial thermal decay. We carried out different thermal cycles on the samples by using a stove at 150°C and a muffle furnace at 300°C and 450°C. We analysed the physical and mechanical properties before and after each cycle to compare and evaluate the effects of thermal stresses on the stones. Among the different analyses: mass and volume measurements, water absorption tests, mercury intrusion porosimetry, thin-section observations and determination of chromatic alterations through image analysis and Munsell charts method. It was then possible to evaluate the influence of both mineralogy and microstructures on thermal decay of the studied stones (variations in fabric and modifications on physical and mechanical properties).

2. Materials and methods

Six samples of each lithotype, sandstone, calcarenite and marble, have been selected, for a total number of 18 samples. All the samples have cubic shape of 5x5x5 cm^3. For practical reasons, we have used two samples of each stone type to perform all the different stages of artificial weathering by means of heating cycles, and all samples have been measured before and after thermal treatment.

To determine the chemical composition, we completed a thorough chemical analysis through X-ray fluorescence for 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). The data collected have been elaborated using an in-group developed software and 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% [25-27]. We determined the volatile compounds content (mainly H_2O^+ and CO_2) by calcination (105-950°C) using a simultaneous TG-DSC thermo-microbalance Netzsch STA 449 C Jupiter according to the following operative conditions: ~25 mg fine grinded sample dust; thermal rate 10°C per minute; nitrogen flux 30 ml/min. To measure the correct amount of CO_2 present in each samples, we preferred using the gasomethric method perfected by Leone et al. [28].

Coupled to the chemical analysis we completed the mineralogical analysis by means of X-ray diffractometry (XRD) using a D2 Phaser by Bruke with Cu anticathode and filter Ni Detector 1D

Lynxeye at the University of Pisa and the software for acquisition Diffrac.suite and Diffrac.suite Eva software for interpretation of the data. The operating specifics were $\lambda = 1.5418$ Å, angle range 4-66° 2θ.

To check the variations occurred in each sample before and after heating treatment we performed the following analyses:

- petrographic analyses: transmitted light microscopic observation (Zeiss AXIO Scope.A1 microscope);

- physical properties of the stones like real (ϱ_r) and apparent (ϱ_a) density, water absorption coefficient by capillarity, water absorption at atmospheric pressure, total and open porosity have been determined following EN standards [29-31]. Real density (ϱ_r) has been determined using a gas pycnometer (ultra-pycnometer 1000 by Quantachrome Corporation) on 10g dried powder; apparent density has been determined by ratio between dry weight and volume of each sample. 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) [32]. Then the specimens were immersed in distilled water under vacuum for 24 hours and subsequently 24 hours more without vacuum; water absorption coefficient by capillarity has been determined on the same samples used for apparent density determination following [30]. Measurements taken after 1, 3, 5, 15, 30 minutes, 1h; determination of water absorption at atmospheric pressure has been carried out on the same samples. The total porosity has been calculated according to: P (vol. %) = 100 · (1− ϱ_a / ϱ_r).

The artificial thermal decay of the samples was performed by heating in stove and muffle. We subjected the samples, two for each lithotype, to three separate tests at different temperatures so to reproduce different stages of decay, low, medium and high: 150°C, 300°C and 450°C. Before performing the thermal degradation, each specimen was brought to constant weight and subjected to a water absorption cycle both by capillarity and by total immersion for at least 7 days. After the sample preparation the tests were carried out as follows using 6 specimens, two for each of the 3 stones: a – heating at 150°C, with the help of a stove; b - heating at 300°C using with the aid of a muffle; c - heating at 450°C with the help of a muffle.

At the end of each of the three different degradation tests, all 18 specimens were again subjected to a water absorption cycle to evaluate whether the degradation somehow determined the alteration of the samples under study.

3. Results and discussion

The data from XRD show that the main components for Macigno sandstone are primarily Quartz, plagioclase, k-feldpar followed by phyllosilicate and calcite, in agreement with the existing literature [7]. Carrara marble is extremely pure with a content of CaCO3 > 98%, and traces of quartz and pyrite as shown by both XRD and gasomethric analyses. Gravina Calcarenite is mainly composed of Calcite as primary phase (> 95 wt. %) as confirmed by both XRD and gasomethric analyses.

Table 1 reports the average chemical composition for the three analysed lithotypes. Macigno sandstone, is mainly composed of SiO_2 (mean 63.9% ± 0.549), Al_2O_3 (12.64% ± 0.495) and subsequent CaO (4.537% ± 1.038), MgO (4.86% ± 1.145), K_2O (2.53% ± 0.06). Carrara marble, is mainly composed of CaO (mean 53.13% ± 0.02), and traces (< 1%) of Al_2O_3, MgO, Na_2O.

Table 1. Chemical compositions (wt. %) of the sandstone and marble analysed samples. $Fe_2O_{3\,T}$= total iron expressed as Fe_2O_3.

Sample	L.O.I.	Na₂O	MgO	Al₂O₃	SiO₂	P₂O₅	K₂O	CaO	TiO₂	MnO	Fe₂O₃ T
Sandstone											
mean	4.96	2.16	4.86	12.64	63.90	0.12	2.53	4.54	0.44	0.06	3.77
St.Dev.	*0.55*	*0.09*	*1.15*	*0.50*	*2.01*	*0.01*	*0.06*	*1.04*	*0.03*	*0.01*	*0.05*
Marble	43.45	0.02	0.81	0.14	1.77	0.08	0	53.66	0.01	0	0.06
mean	43.3	0.015	0.945	0.135	1.38	0.07	0	54.13	0.03	0	0.005
St.Dev.	*0.035*	*0.005*	*0.035*	*0.005*	*0*	*0*	*0*	*0.02*	*0.01*	*0*	*0.005*

Table 2 shows the physical properties for the three analysed lithotypes. It is possible to notice the differences in total porosity and water absorption values for each stone.

Table 2. Main physical properties of the analised lithotypes: Macigno sandstones from Matraia, Gravina calcarenite from Matera and Carrara marble from Apuan Alps.

Commercial name	Pietra di Matraia*				Pietra di Gravina					Marmo Statuario			
Geological formation	Macigno sandstone				Gravina calcarenite					Apuan marble			
Petrographic name	Arenitic arkoses				Calcarenite					Marble			
Quarry	Matraia				La Palomba					Ravaccione			
City/Province	Capannori/Lucca				Matera					Carrara			
Country	Italy				Italy					Italy			
Physical properties	**n.**	**min.**	**max.**	**mean**	**s**	**n**	**min.**	**max.**	**mean**	**s**	**n.**	**min.**	**max.**	**mean**	**s**
Real density (kg/m³)	6	2700	2720	2710	10	6	2710	2710	2710	-	6	2710	2710	2710	-
Apparent density (kg/m³)	6	2669	2685	2676	4	6	1517	1703	1565	56	6	2700	2710	2703	5
Total porosity (vol. %)	6	0.9	1.5	1.3	0.1	6	37.16	44.02	42.24	2.06	6	0.46	0.57	0.50	0.04
Water absorption at atmospheric pressure (wt. %)	6	0.26	0.34	0.29	0.02	6	17.79	24.21	22.72	2.0	6	0.17	0.21	0.18	0.01

*data from Lezzerini et al., 2008

In this work we used water absorption by capillarity as method to relate the variations of the water absorption speed compared to different degradation states. Figures 1, 3, 5 show the different curves for water absorption by capillarity of the analysed samples with different degradations, while figures 2, 4 and 6 show the differences in water absorption for each sample. At the beginning of the tests the curves show a steeper slope, while after some time, depending on the lithotype, they are less steep, asymptotically aiming to a constant value. This means that over time the absorption rate slows down, and the filling of the residual porosity becomes slower. The dotted lines in the graphs represent degraded samples. The water absorption curves by capillarity for heating at 150 °C and 350 °C already show a considerable difference compared to unweathered samples. Samples degraded at 450 °C show the highest rate of water absorption. The macigno sandstone (Figure 1-2) presents generally the lowest values of absorbed water, among all the sudied lithotypes. When subjected to thermal degradation by heating in stove and muffle it shows a high variability in its water absorption values from 150°C to 450°C, increasing from low to high temperature.

Gravina calcarenite (Figure 3-4) presents the highest values of water absorption both before and after thermal degradation. Probably due to its already high values in water absorption, it shows lower values of absorbed water increase compared to the other two stones.

Carrara marble (Figure 5-6) shows very low values of absorbed water when unweathered (continuous line) but experience the highest gradient difference of absorbed water due to the effect of thermal degradation. It is interesting to see how the sample behave after heating at 300°C, displaying a minor amount of water absorbed compared to the heating at lower (150°C) and higher (450°C) temperature.
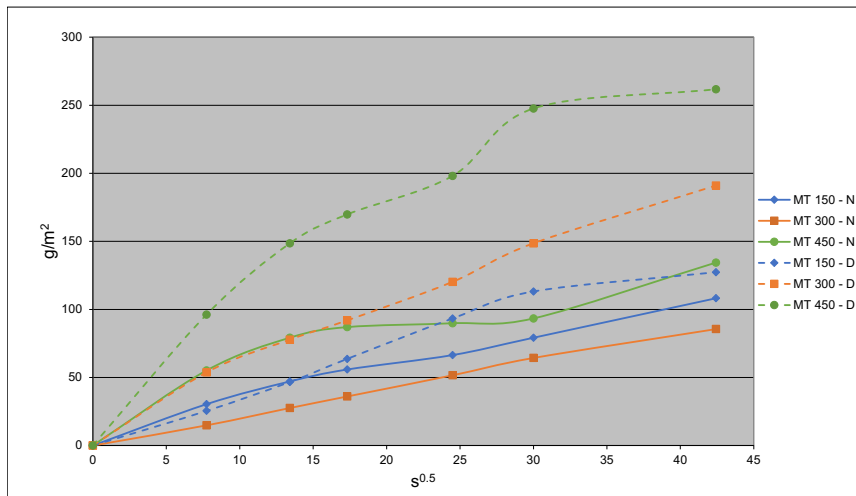
Figure 1. Water absorption by capillarity curves for sample MT, Matraia sandstone, degraded at 150°C, 300°C and 450°C. *N=before heating (continuous line), D= after heating (dotted line).*
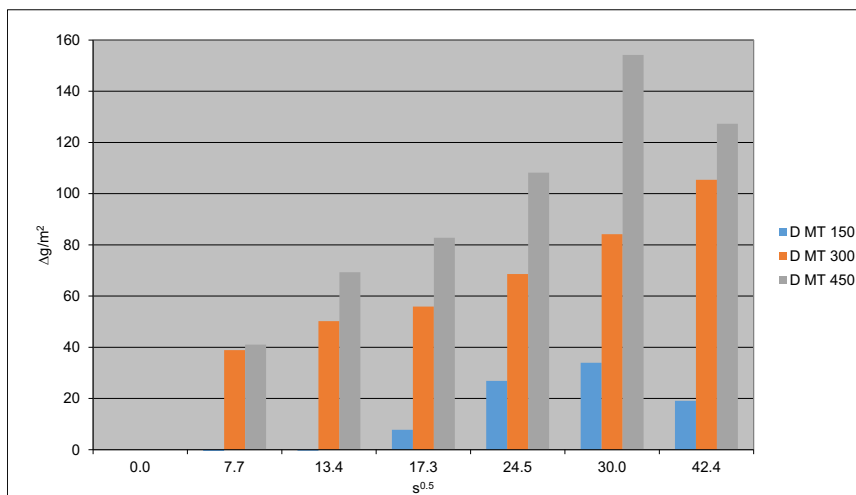

Figure 2. Differences of absorbed water for Macigno sandstone sample after thermal degradation at different temperatures.
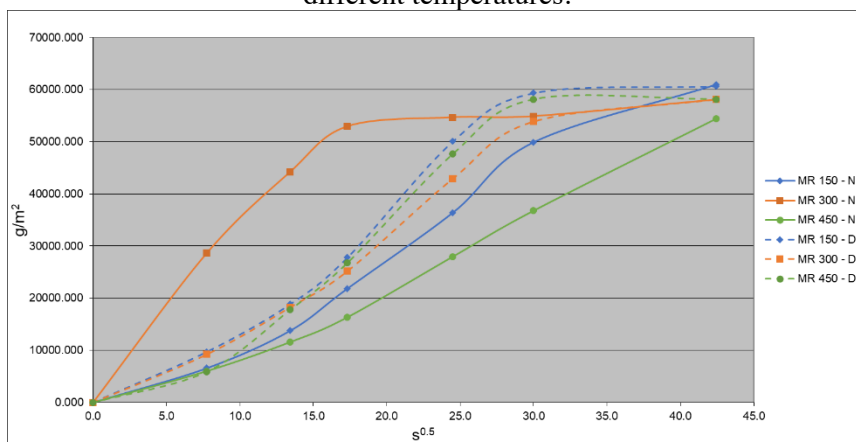

Figure 3. Water absorption by capillarity curves for sample MR, Gravina calcarenite, degraded at 150°C, 300°C and 450°C. N=before heating (continuous line), D= after heating (dotted line).
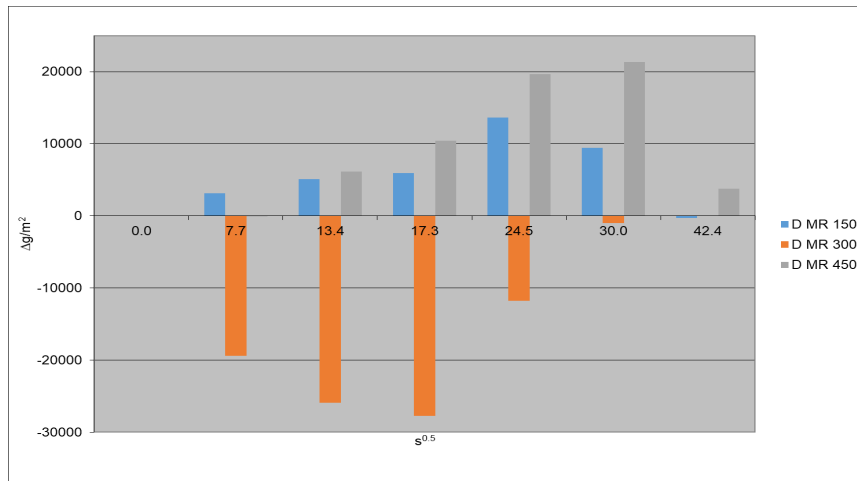
Figure 4. Differences of absorbed water for Gravina calcarenite sample after thermal degradation at different temperatures.
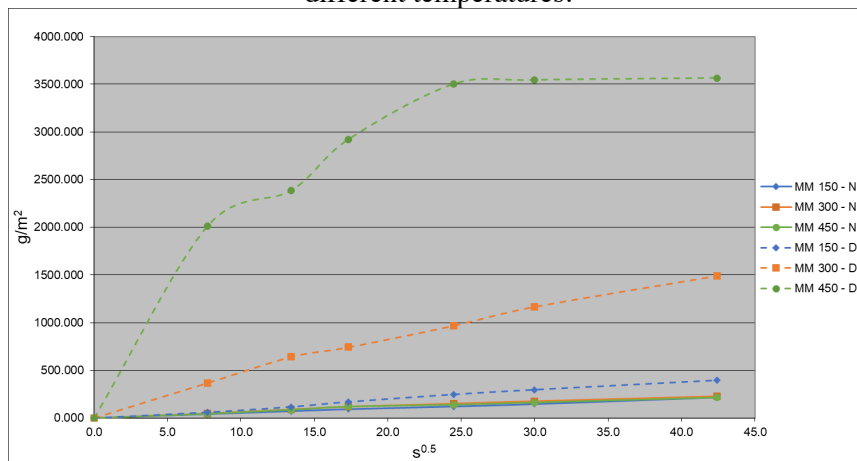

Figure 5. Water absorption by capillarity curves for sample MM, Marble, degraded at 150°C, 300°C and 450°C. N=before heating (continuous line), D= after heating (dotted line).
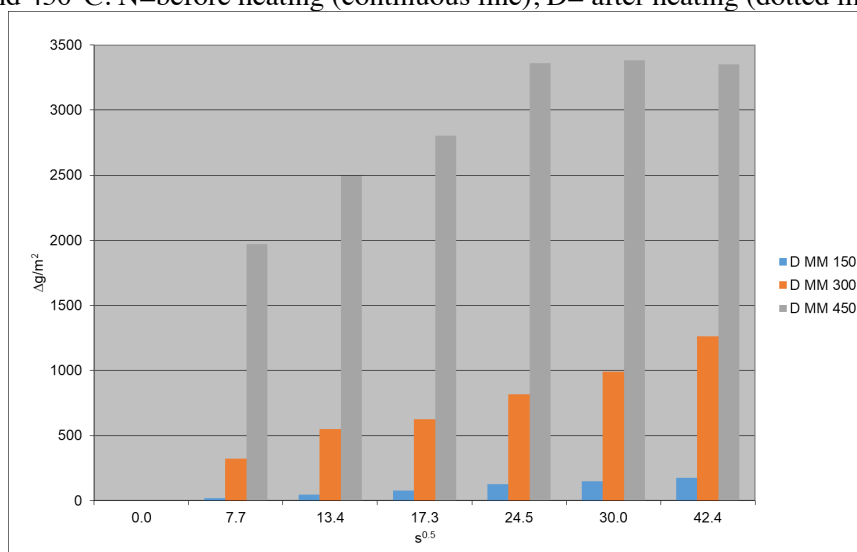

Figure 6. Differences of absorbed water for Carrara marble sample after thermal degradation at different temperatures.

4. Conclusions

This study gives a better understanding of some of the aspects related to the assessment of the physical characteristics of the water circulation inside a rock mass, in connection with the thermal decay to which stones like the studied ones can be subjected to during their life as building materials. Although between the three lithotypes, Gravina calcarenite is the most subjected to water circulation, due to its high amount of water absorbed in normal conditions, it seems to be the less affected by heating treatments in terms of decay of its physical properties. It seems in fact to become slightly less responsive to water absorption in the first stages of imbibition. Carrara marble, on the other hand, has suffered the major effects of thermal degradation with the increase of the temperature, experiencing in the samples heated at 450°C the highest values of water absorbed compared to the unweathered sample. Macigno sandstone presents mean values between Marble and Calcarenite but still suffers a discrete amount of thermal decay due to high temperature heating. We can therefore say that Gravina calcarenite is less likely to be damaged by heating at high temperatures thanks to its high porosity that do not allow the stone to create new porosity over a certain amount. Marble, as also known from literature, is greatly affected by thermal degradation at high temperatures. Macigno sandstone proved itself to be a good building material resisting sufficiently well to thermal degradation.

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