COMPOSITIONAL, TEXTURAL, PETROPHYSICAL AND MECHANICAL CHARACTERIZATION OF THE CALCARENITE DI GRAVINA FROM THE MATERA AREA: CONNECTION WITH GEOLOGICAL FEATURES AND DEGRADATION PROCESSES

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INTRODUCTION

Stone monuments represent an important and diversified cultural heritage all over the world. Soft granular limestone has been used for constructions in Southern Italy in millennia, and even today is employed in structural elements and cladding, thanks to its availability and ease of use. However, due to its soft nature, weathering processes affect its durability and many old buildings show evidence of degradation. The Sassi of Matera (Southern Italy), is a UNESCO heritage site since 1992. It is a prehistoric rupestrian village, which represents an awesome example of a rock-cut settlement where architecture is intermingled with the geological and geomorphological features of the area (UNESCO list 1992). The Sassi and surrounding rupestrian settlements have a Palaeolithic age, as proven by the presence of archaeological remains of the Mousterian Industry (Middle Palaeolithic) (Azzaroli, 1968; Boenzi *et al*., 1971; Lo Porto, 1988). The first settlement evolved through time according to the architectural influences of different centuries and the slow evolution of the landscape. The Sassi of Matera have been dug and built in the right side of the Gravina valley, where the Calcarenite di Gravina has been widely used as a building and ornamental stone due to its large availability, good workability, lightness, and aesthetic appeal (Calia *et al*., 2015).

The Calcarenite di Gravina Formation (Lower Pleistocene) crops out extensively in the Apulia Foreland and onlaps the Cretaceous Calcare di Altamura Formation. It is characterized by continuous exposures of intrabasinal biocalcarenites and biocalcirudites (Iannone & Pieri, 1982). The formation has been subdivided in two informal members on the basis of its main composition (Pomar & Tropeano, 2001). The lower member is mainly lithoclastic, with limestone clasts derived from the erosion of the Cretaceous Altamura Formation, whereas the upper member of the Calcarenite di Gravina is predominantly bioclastic. Both bioclastic and lithoclastic calcarenite varieties outcrop in Matera and have been used over centuries as building materials. These materials are currently subjected to multiple degradation processes, caused by weathering and by the intrinsic properties of the calcarenite. Moreover, granular limestones are chemically homogeneous but might have a high variability in terms of texture and porosity that strongly affects the behaviour and the susceptibility to damage of building stones. Specifically, the presence of numerous very fine pores reduces the durability compared with calcarenites containing larger pores (Rescic *et al*., 2010). Other phenomena that can modify the pore networks are connected to dissolution processes of aragonitic component of rock (Espinosa-Marzal & Scherer, 2010), biological colonization (Miller *et al*., 2010), extreme temperature variations, wetting and drying cycles, and salt crystallization (Andriani & Germinario, 2014; Calia *et al*., 2015).

This study aims to understand the behaviour of the Calcarenite di Gravina and its typical degradation morphologies, providing information on the characterization of extremely heterogeneous carbonate rocks, on the diagenetic history and the degradation processes, in order to apply effective recovery and conservation strategies, to limit the damage of stone materials in the historical-architectural heritage in the Mediterranean area.

Two important aspects have been studied in this work: the first is the characterization of the Calcarenite di Gravina Formation, mainly carried out by macroscopic, microscopic and diagenetic analyses, followed by chemical and petrophysical characterizations of limestones. At first, a detailed geo-lithological survey was carried out to allow the recognition of the various facies used for the construction of the Sassi. Subsequently characterization of limestones, collected in the historical quarries of Matera, has been carried out, in order to identify the different facies used and to analyse the possible causes of degradation. Indeed, textural, petrophysical and mineralogical analyses have been performed in order to study of the intrinsic inhomogeneities of these rocks, which influence their degradation due to natural phenomena and human activities. This information can be used to properly arrange reconstructive recovery interventions in artworks or sites in Matera and all around the world.

As regard the inhomogeneities, bioturbation represents a major problem for the protection of the Sassi against degradation processes, because burrows produce differential cementation of the calcarenite. Consequently, one aim of this work is also to understand how the bioturbation controls texture, porosity, permeability and cementation of the calcarenite.

The second aspect of this work includes a new approach based on image analysis and visual inspection of ashlars in order to introduce smart methods for surveying, monitoring and providing diagnoses for the decay of the Sassi buildings through mapping of degradation and creation of a qualitative-quantitative classification of mechanical degradation. This classification might be useful during restoration works, providing also information on the priorities that should be taken into account during the planning phase.

WORKFLOW AND METHODS

The first part of the study consisted in the illustration of a detailed geological survey of the area, that was realized on the basis of the field observations, focusing on the hardness, grain size, large bioclasts and lithoclasts, and cementation. This study was followed by a study of the calcarenite microfacies through the analysis of 120 thin section using optical microscope (OM), modal analysis by point counting and multivariate analysis via cluster analysis to identify and quantify the main components of each lithofacies. Microfacies quantification was carried out by point counting on 70 thin sections taken from 120 samples.

Cementation typologies were studied in detail using scanning electron microscope (SEM) and cathodoluminescence (CL) analyses. Porosity was identified and quantified using several techniques, such as point counting, image analysis, water absorption tests and Computed Tomography (CT)-scans. Diagenetic implications were also considered in the evolution of porosity and cementation of different lithofacies in connection with the amount of bioclasts and lithoclasts, the depositional environment, and the diagenesis of rocks.

Chemical and mineral composition of the studied lithofacies were determined using X-ray fluorescence (XRF), calcimetric analysis and X-ray diffraction (XRD) on the bulk samples. Petrophysical characterization was carried out focusing mostly on the behaviour of the rocks with regard to water. Specifically, water absorption by capillarity, water absorption by total porosity, real and apparent density, open and total porosity, relative permeability and uniaxial compressive strength were measured to obtain a complete petrophysical characterization of the identified lithofacies.

A bioturbated calcarenite level, outcropping in the Parco Scultura- Cava Paradiso in La Palomba (Matera Northern area), was selected as case study. Large samples including fossil traces and surrounding rocks were analysed by means of OM, SEM, and micro-CT. Macroscopic and microscopic descriptions, modal and cluster analyses were performed based on point counting of 50 images taken from large thin sections (7.5 cm^2) to characterize trhe texture and the composition of the bioturbated calcarenite. In addition, SEM observations were carried out to describe the cements and CT scans to visualize the internal structure and the connected porosity of the samples. Facies analyses were carried out at the GeoZentrum Nordbayern - Friedrich-Alexander University, Erlangen-Nürnberg (Germany) and at the Basilicata University; physical and mechanical limestones characterization was performed at the Applied Mineralogy Laboratory of the Pisa University and at the IBAM-CNR in Lecce.

Finally, a complete census of degradation morphologies in the Sassi was carried out on 250 façades, considering the main typology of calcarenite used as building stone. Statistical evaluation highlighted that the main degradation is connected to the mechanical loss of material. A qualitative and quantitative classification of loss of material degradation is here proposed as a practical tool to evaluate the state of conservation of the buildings. In this context, Structure from Motion (SfM) photogrammetric methods were applied to measure the volume of lost materials.

RESULTS

Field analysis and facies description

The Calcarenite were subdivided into six lithofacies on the basis of field and microfacies analyses. These lithofacies were described on the basis of the field observation, grain size, texture, colour, relative percentage of components determined by cluster analysis performed on the quantitative data obtained by point counting analyses. Bioclast, lithoclast, voids, cement and matrix were counted as well as the main bioclasts (echinoderm, red algae, bentic and planctonic foraminifera, mollusc shell, unidentified calcitic shell fragments, bryozoan, ditrupa tubiphytes). The six lithofacies are (Fig. 1): 1) Basal bioclastic calcarenite (BBC); 2) Lithoclastic calcirudite-microconglomerate (LCM); 3) Lithoclastic calcarenite (LC); 4) Large bivalve bioclastic calcarenite (LBC); 5) Rhodolith bioclastic calcarenite (RBC); 6) Fine bioclastic calcarenite (FBC).

Echinoderm fragments are always the most abundant skeletal component, whereas different abundances of mollusk shells, planktic foraminifera and rodholiths were taken into account for the identification of the four mainly bioclastic calcarenite facies. The mainly lithoclastic calcarenite was subdivided into two facies on the basis of grain size.

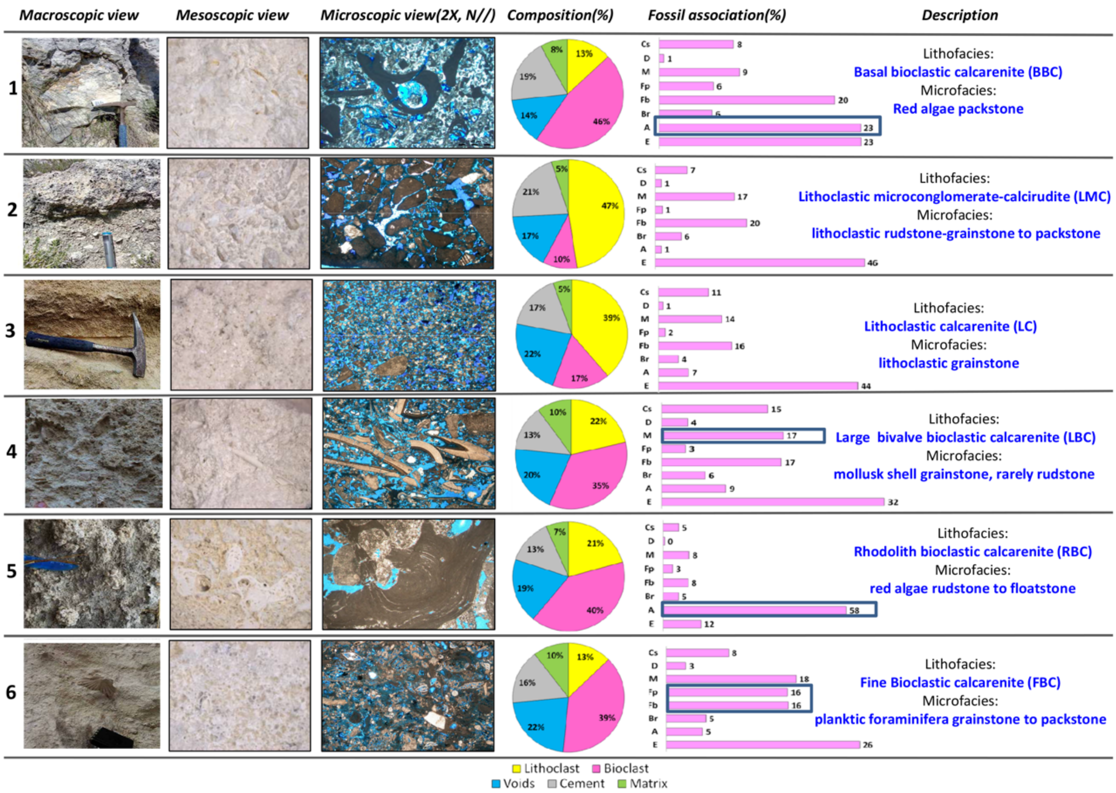

Fig. 1 - Summary of the six calcarenite lithofacies and microfacies identified on the basis of field and OM observation as well as quantitative measurement made by point counting of the main components (cake diagram) and of the bioclast types (bar histogram). Bioclast are: echinoderm (E), red algae (A), benthic foraminifera (Fb) planktonic foraminifera (Fp), mollusc shells (M), unidentified calcitic shell fragments (Cs), bryozoan (Br), ditrupa tubiphytes (D).

Interpretation of the depositional environment

The distribution of the six lithofacies was reported in a geolithological map of Matera and its surroundings, at 1:5.000 scale (Fig. 2). The inferred relationships between the lithofacies recognized on the basis of field observation carried out in four key areas (the Monumental quarry in La Vaglia, Parco Scultura - Paradiso quarry, La Palomba quarry and the active Petragallo quarry) are shown in a cross-section of the quarries area, located in the Northern sector of Matera (Fig. 3).

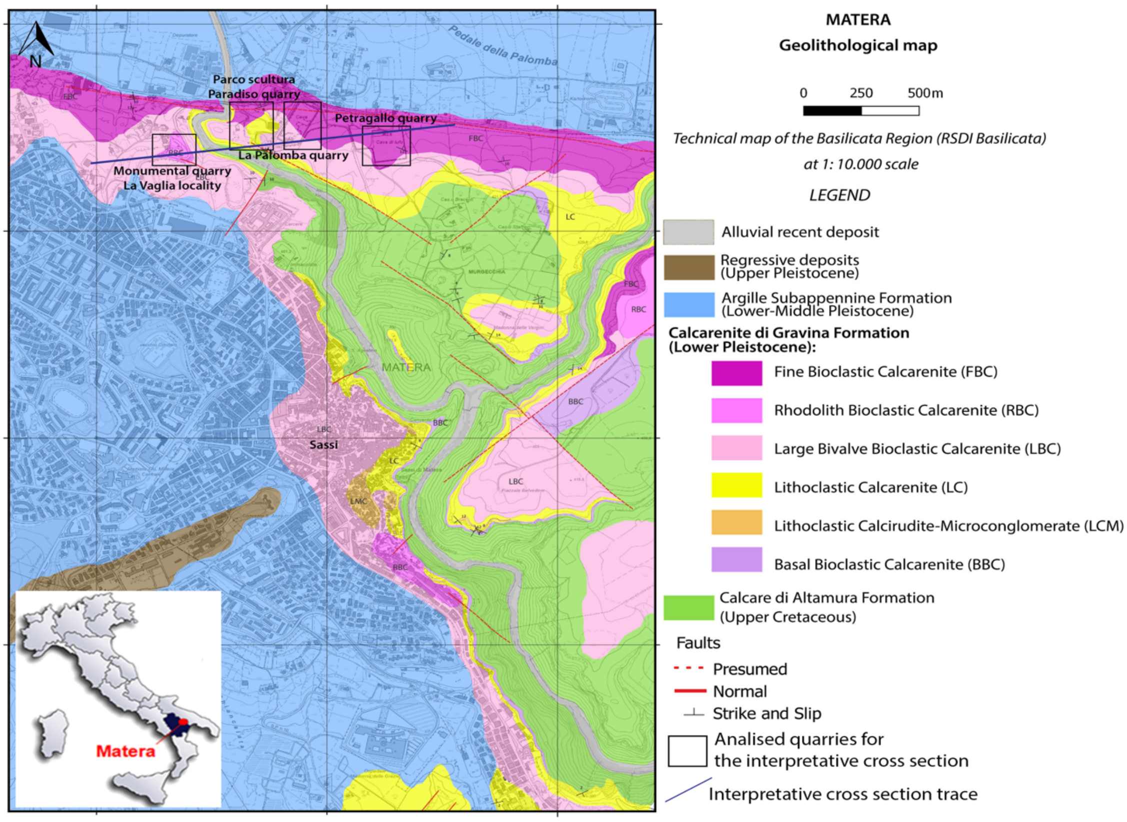

Fig. 2 - Geolithological map based on the technical map of the Basilicata Region (RSDI Basilicata) at 1: 5.000 scale.

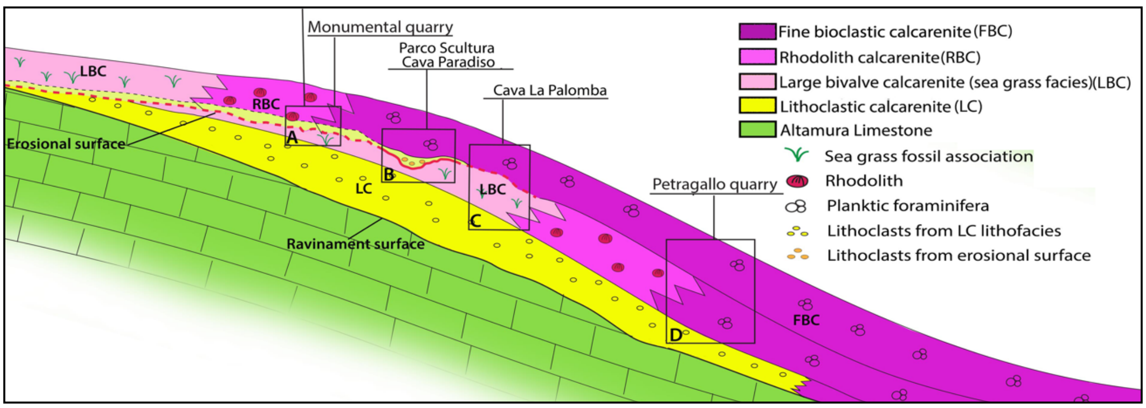

Fig. 3 - Interpretative cross section of the Matera old quarries area (La Palomba and La Vaglia). Not in scale.

The quarries area is characterized by the presence of four of the six recognized lithofacies. The base consists of the lithoclastic calcarenite (LC lithofacies), followed upwards by the bioclastic calcarenite (LBC, RBC and LBC lithofacies). The basal level is represented by a medium to fine sand sized LC lithofacies, always well sorted and homogeneous. The lithoclastic facies derives from the erosion of the exposed Altamura limestone during a partial emersion of the palaeo-island of Matera and initial transgression after a regression stage. During continued transgression, the submersion of the palaeo-island produced the classical deposition of a carbonate ramp/fan that, from the nearshore to the offshore and from shallow to deep water settings, consists of the seagrass facies (LBC lithofacies), rhodolith bioclastic facies (RBC lithofacies) and planktic foraminifera facies (FBC lithofacies). This facies association was deposited during the whole period of a marine transgression, followed by an important regression, testified by the erosional surface documented in the Parco Scultura - Paradiso quarry. Moreover, the regression is testified by the stratigraphy of La Vaglia, between the monumental quarry and the Northern Matera area. In this latter area, the lithoclastic calcarenite is present between the RBC lithofacies (above) and the LBC (below). This particular stacking sequence is possible only if the bioclastic calcarenite was deposited during two different transgressive cycles separated by a regression, as outlined by the lithoclastic level. Moreover, the CL study of diagenetic processes showed multiple episodes of small variations in oxygenation conditions associated to changes in the diagenetic environment thus testifying the end of the marine diagenesis during final regression.

Mineralogical and petrophysical characterization

XRD analyses showed roughly the same mineralogical composition for all lithofacies. Calcite ($CaCO_3$) is the main mineralogical phase (> 95 wt.%), as confirmed by calcimetric analysis, indicating a content of calcium carbonate varying from 95 to 99%. Small amount of quartz, feldspars and phyllosilicates are also present. In fact, CaO is the most abundant chemical component of the rocks, and the contents of MgO, SiO_2, Al_2O_3, Na_2O, K_2O, Fe_2O_3 are below 5 wt.%.

At a first glance, the petrophysical data (Table 1) reflect primary differences during deposition and early cementation of the carbonate rocks.

Table 1 - Summary of petrophysical mean data performed on representative samples of the 6 Calcarenite di Gravina lithofacies.

Lithofacies	Apparent density [g/cm^3]	Open porosity [vol%]	Total porosity [vol%]	Water absorption at atmospheric pressure [wt.%]	Water absorption coefficient by capillarity [g/m^{2}s$^{0.5}$]	Permeability [mD]	Ultrasonic measurement	
							Vp [m/s]	Vp [Km/s]
BC	1.98	23.54	27.00	14.61	449.72	4.31	0.00	30.9
MCL	1.97	23.37	27.34	12.00	442.65	659.97	0.66	27.2
LC	1.57	35.5	42.2	22.7	608.00	15492.30	2394.45	239
LBC	1.45	36.1	42.80	23.40	677.00	26548.46	2108.32	2.11
RBC	1.99	21.40	26.69	11.02	153.73	5548.37	4476.93	4.48
FBC	1.40	40.71	48.48	29.24	926.53	47411.92	-	-

In particular, the real density value is 2.71 ± 0.01 g/cm^3 for all analysed samples corresponding to that of calcite, according to mineralogical analysis. Based these data, three most suitable building stones were distinguished. Specifically, lithoclastic calcarenite (LC) and large bivalve calcarenite (LBC) lithofacies are similar in petrophysical properties, even though displaying different compositions. However, differences in the typology of clasts (bioclasts and lithoclasts) are fundamental in the evaluation of the behaviour regarding water absorption and weathering processes. The third typology is the fine bioclastic calcarenite (FBC), defined as the best calcarenite in terms of workability. It displayed different characteristics compared to the other lithofacies, mainly related to its extreme variability in porosity and cementation. Consequently, the fine bioclastic calcarenite showed wide variations in density, water absorption and degradation. This variability is due to its intense bioturbation, which strongly influences the petrophysical properties. With regards to the remaining three types of lithofacies, basal calcarenite (BC) has never been used as building stone as it is very hard and not easily workable; on the other hands, rodholith (RBC) and calcirudite and microconglomerate (MCL) lithofacies have been rarely used, mainly as ornamental stone. In fact, these latter lithofacies is extremely heterogeneous and therefore is hardly used in constructions, highlighting the importance of sorting in the selection of building stones.

Bioturbation contribution to degradation

The most distal, fine-grained bioclastic calcarenite (FBC) is characterized by large bioturbation traces. By using ichnological analysis, trace fossils were identified as Thalassinoides and Ophiomorpha, connected to the burrowing action of decapod crustacean Callianassidae (Fig. 4). Optical microscope and SEM observations showed a close connection between sediment sorting and cementation. In the well-sorted area, thin isopachous layers of microgranular cement around and inside bioclasts occur, whereas in moderately-sorted gravels, where pore space is larger, well developed syntaxial cement and granular rim around bio- and lithoclasts were observed. Moreover, it was clearly observed a gradient of cementation from the external lining of the burrows to the internal part of the trace fossil. Diagenetic processes allowed for selective cementation inside the trace fossils.

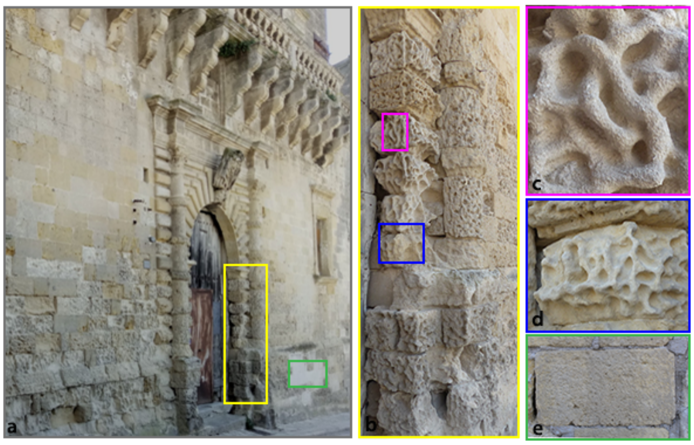

Fig. 4 - a) Degradation of the Calcarenite di Gravina on Palazzo Santoro, Matera; b), c), d) detail of the fossil traces deriving from the bioturbation after weathering activity (differential erosion).

Based on thin sections and cluster analysis of point-counting results it was possible to distinguish different sub-facies that were organized in 4 groups on the basis of their position and characteristics: Internal portion (H1); lining of the burrows (H2); storage chamber infill (H3); area surrounding the burrows (S1) (Fig. 5).

The well-cemented portions are represented by the actively filled sub-facies that correspond to the cemented lining of the burrows, that appears as a well cemented crust, and to the storage chamber, where large syntaxial crystals grow.

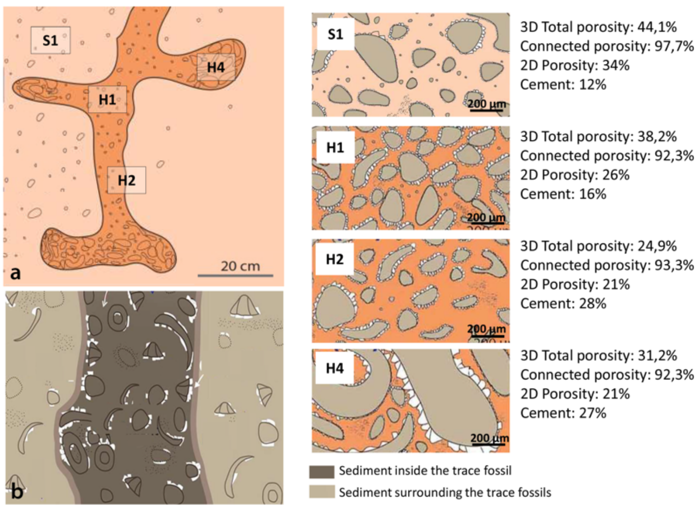

Fig. 5 - Selective cementation of fine bioclastic calcarenite (FBC). a) schematic view of callianassidae burrows with localization of the analysed samples: S1 is the fossil trace surrounding sediment, H1 is the internal infilling of burrow, H2 is the lining of burrows and actually, the external crust, H4 is the storage chamber actively filled by callianassidae. b) Gradient of cementation (in white) with respect to the burrows and the surrounding. On the right are reported the porosity results performed by point counting and micro CT-scan.

From the observation of the facies inside the fossil traces, a gradual progressive cementation from the lining to the internal parts of the fossil trace is outlined. Facies outside of the fossil traces are moderately to well sorted and porosity is the highest.

Moreover, porosity was measured by means of several methods: image analysis, point counting (2d porosity), ct-scan (3D connected porosity) (Fig. 5a). These measurements showed that differences in porosity were noticeable reduced in most cemented areas (Fig. 5b). Indeed, the presence of a cementation gradient inside the trace fossil is explained considering the contribution of different factors: *i*) geochemical environments allowing the $CaCO_3$ precipitation inside the burrows starting from the lining to the internal area thanks to the microbial actions, *ii*) water circulation and *iii*) relative oxygenation of fluids. Dissolution of aragonitic component represents the principal source of $CaCO_3$. Variation in cementation and porosity are very low but they are capable of generating noticeable differences in the resistance to weathering due to differential erosion. This constitutes a fundamental problem in the protection against degradation.

Degradation analysis and classification

The degradation state of the Sassi of Matera was established in three steps: 1) decay mapping and observations on 250 façades with a different conservation state, from well preserved to deeply damaged, in various localities of the studied site, by studying the areal distribution of decay, in relation to exposition and visible interventions of renovation ; 2) qualitative decay evaluation in connection with lithological features; 3) quantitative classification of the natural mechanical loss of materials through the use of photogrammetric techniques.

The detailed analysis of degradation on the 250 buildings showed which morphologies develop on either bioclastic or lithoclastic calcarenites. Morphologies derived from mechanical loss of materials were mostly observed and linked to differential erosion and alveolization of calcarenites showing bioturbation processes.

The application of the SfM method on ashlars with different degrees of loss of material allowed their 3D reconstruction, and differences between the zero ashlars and the damaged ashlars allowed the identification of 5 classes of degradation, which can be compared with the decay stages. The result of this analysis was summarized in Fig. 6, where the calculated volume of loss of material for each class was expressed as a volume range derived by the SfM. The results of SfM analysis evidenced that bioclastic and lithoclastic calcarenites were characterized by different percentages of loss of material patterns. The main differences were observed for differential erosion (about 20% of difference between lithoclastic and bioclastic calcarenite). This phenomenon was more intense in the bioclastic calcarenite, as a consequence of its textural features. Roughening was more frequent in the lithoclastic calcarenite, where grain size is coarser than in the bioclastic ones, favouring the development of this decay pattern. The different susceptibility of the two calcarenite varieties to the degradation processes determines relevant differences in the degradation degree quantified by SfM method. The SfM photogrammetric technique was used to provide an economical, portable and simple method for obtaining high-resolution models with

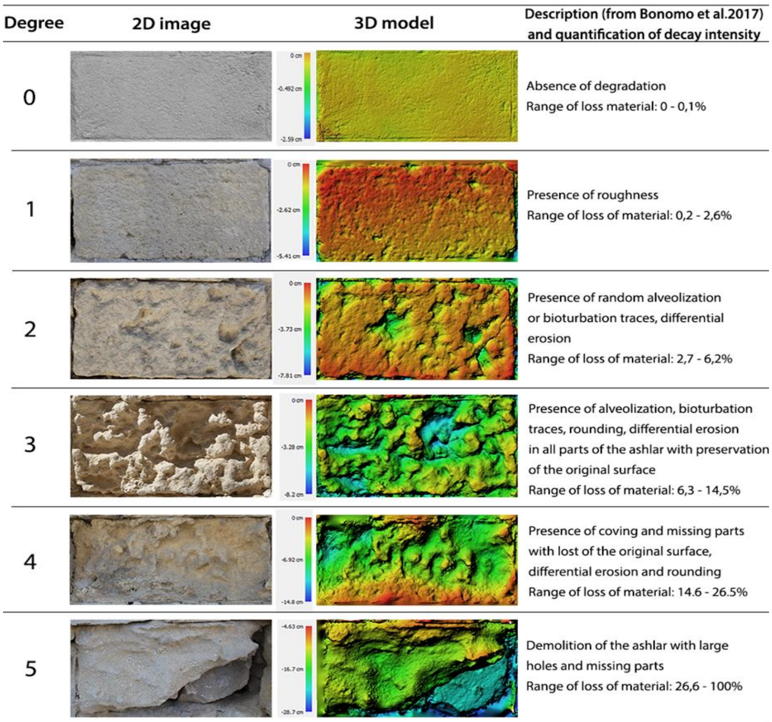

Fig. 6 - Qualitative and quantitative classification of loss material in soft limestones, from not altered to degraded calcarenite ashlars, with surface image and related 3D model obtained with photogrammetric analysis.

detailed accuracy of the amount of erosion suffered by buildings. Through the overlap of the models it was possible to calculate the volume of lost material.

The qualitative and quantitative methods to estimate the loss of material was applied to a case study in Matera, *i.e.*, Palazzo Santoro, which allowed to verify that the proposed classification represents a powerful tool that can be used to estimate the survival time of buildings, to establish a schedule for renovation actions and to manage the effective conservation of stone heritage.

CONCLUSIONS

This study is aimed at analysing the Gravina Calcarenite, considering in particular the use of granular limestone as building stone and the related degradation processes with particular emphasis on the preservation of the UNESCO site of the Sassi of Matera. Field, petrographical and microtextural analyses of the Calcarenite di Gravina Formation allowed the identification and characterization of six lithofacies at macro and micro scale (microfacies) that were reported in a geolithological map and interpreted in a cross section explaining the architecture of the calcarenite body. The characterization of microfacies highlighted how the intrinsic composition of rocks in terms of sorting, typology of clasts, cementation and porosity influences the behaviour of rocks in relation with natural and anthropic degradation processes. From a chemical and mineralogical point of view, all lithofacies are pure carbonates with percentages of calcium carbonate of up to 95%. Petrophysical characterization of the six lithofacies confirmed differences in compositional features. The Sassi buildings were mainly constructed using the large bivalve calcarenite, lithoclastic calcarenite and fine bioclastic calcarenite. The last one is extremely heterogeneous despite its apparent homogeneous aspect on a fresh cut, because of its intense bioturbation, which also generates selective cementation of the rocks. In this regard, trace fossils are identified mainly as produced by Callianassidae decapods crustacean. These traces were analysed to understand the important role exerted by selective cementation in producing the pore network of rocks. Finally, a detailed analysis of degradation showed that morphologies related to mechanical loss of materials were mostly observed and linked to differential erosion and alveolization of calcarenites. A new qualitative and quantitative classification of mechanical loss of material including five degradation stages was proposed through the application of the SfM photogrammetric technique providing an economical, portable and simple method to obtain high-resolution models with a detailed estimate of the amount of erosion suffered by buildings.

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