CALCARENITE DI GRAVINA FORMATION A ROW MATERIAL FOR THE LIME PRODUCTION

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Abstract – **Sassi di Matera represent one of the best preserved rupestrian settlements and the oldest town in the world. It is UNESCO site since 1992 thanks to its cultural history and its harmonious development within its ecosystem. Sassi are completely built with a soft granular limestone, the Pleistocene Calcarenite di Gravina Formation, characterised by good workability. The stone, however, can be an extremely heterogeneous building material depending on the composition of the particles and their characteristics. Six lithofacies corresponding to sub-typologies of building stones have been characterized from a chemical and mineralogical point of view. The Calcarenite di Gravina was in the past, and still is used also for the production of mortars.**

The aim of this study is to identify and describe the Calcarenite di Gravina as a raw material for the production of lime to be use for preserving the stones of Matera. Mineralogical and chemical results show that, despite the differences in sorting, typologies of bioclasts, cementation and porosity, they have mostly similar compositions. This confirms the good quality of Calcarenite di Gravina for the production of aerial lime.

Key words: lime, building stone, soft limestone, Calcarenite di Gravina, tufina.

I. INTRODUCTION

Natural and cultural heritages represent an inestimable value for a country as witnesses for its historical, cultural and technological development. In this context, local stone materials have been used for construction and decoration and particularly for sculptures, monuments and buildings. The Sassi of Matera represents one of the most important rock civilization habitats [1]. It shows historical reconstructions, full of evocative details that fascinate artists, historians, architects and scientists that focus their studies on the building stones with all their different aspects. Sassi of Matera is totally built and excavated in the soft limestone outcropping there, the Pleistocene Calcarenite di Gravina Formation (Fig.1).

Bonomo et al. [2] focused on the interrelationships between primary lithology (facies, microfacies) and degradation processes to help in the preservation of the whole Sassi district. At this regard, six typologies of calcarenites are described macroscopically in the Matera area. Moreover, the interrelationships between petrophysical properties and primary stratigraphic, sedimentological and diagenetical features have been highlighted [3].

Calcarenite di Gravina is the preferential building stone in the Apulia region (Southern Italy) for its workability, availability and aesthetic appeal. Indeed rupestrian settlement were from the Palaeolithic age of the Mousterian Industry [4-6]. During time in this area several villages and then, cites were developed, totally built in the same soft calcarenite. The best example of rupestrian settlement is the Matera old district, the Sassi, the best preserved rock-cut urbanistic center in the southern Italy. Here, the constructive techniques were similar during time, including the use of, the Calcarenite di Gravina, which was used for buildings and ornamental elements [7-9]. Specifically masonry wall blocks were bound together by lime mortar containing fragments of the same stone used for the wall itself. The selective use of calcarenites as good quality building stones over historical times clearly indicates that their properties were well known in the past. The most compact and hardest varieties were used for basis stones while the less dense varieties were used preferentially for the construction for the walls

Fig. 1. Panoramic view of the Sassi of Matera (Southern Italy)totally built inside and within the Calcarenite di Gravina soft limeston, outcropping in situ.

themselves [10-12]. The technique in the construction of walls is defined as "sparse" arrangement of the *tuff* blocks, to give greater thickness and the gaps are filled with soil to balance the thrust of the vaults. The technique is characterized by the contact between the stones, with the use of small quantity of mortar. The mortar is made mainly with waste material deriving from the quarry cutting of the ashlars. It was reused to produce cementitious mortars called tufina, useful for covering the surface of the buildings and confer, therefore, a homogeneous colour to the dwelling.

Several studies have been carried out in ancient buildings with different methodologies [15-17]. Pagnotta et al [18] proposed a fast method for obtaining a quantitative elemental mapping of highly inhomogeneous samples by μ-LIBS maps for quantification of cluster prototypes, verifying on heterogeneous materials such historical lime mortars. Other authors [19, 20] focused on the use of a scanning electron microscope equipped with a microanalytical system for characterising ancient mortars. They presented a techniques that allow to determine the binder and aggregate compositions (including volatile components) from microprobe data collected on the binder, and chemical, mineralogical, petrographical and physical data collected on the mortar bulk sample.

Aims of this work is to characterize from chemical point of view the local calcarenite used for ancient and modern constructions during time.

II. CHARACTERIZATION OF BUILDING STONES IN MATERA

The Gravina calcarenite has already been subject of many studies [8, 13,14], which can be considered as basis for more detailed sedimentological, petrophysical and mechanical analyses. The complex vertical and lateral interfingering of different facies types in sedimentary bodies of various sizes and different intensity of early and late lithification reflects the palaeogeographic morphology of the underlying substratum and sedimentary environments [11]. Specifically Bonomo et al 2018 macroscopically subdivided the Calcarenite di Gravina Formation into four mainly lithotypes. From base to top these are: (1) the Basal Calcarenite, (2) microconglomerate layers, (3) the lithoclastic calcarenite, and (4) the bioclastic calcarenite. Furthermore, the bioclastic calcarenite is subdivided into: (4a) calcarenite with large bivalve (4b) calcarenite with rhodoliths. The Basal Calcarenite is a grey, thin-bedded (0,5 to 5 meters thick beds), well cemented unit directly on the top of Altamura limestone. It consists of white calcarenite and locally calcirudite with red algae, pectinids, ostracods, serpulids and echinoids. The lithoclastic calcarenite, calcirudites and microconglomerate layers are composed of Cretaceous limestone pebbles, granules, sand and locally boulders. They are different for their grain size but are similar in composition. Indeed they consist of a prismoidal unit prograding toward south-west onlapping

the Cretaceous limestone [21]. Wedges made up of carbonate boulders have been deposited at the toe of palaeocliff in an infralittoral setting [22].

Bioturbated medium- to fine-grained bioclastic calcarenites represent the transition from offshore to slope deposits. Common fossils include mollusc shells, benthic and planktic foraminifera , rhodoliths, branching and encrusting bryozoans, solitary corals, well-preserved brachiopods and irregular echinids. Scattered pebbles are often bored by sponges or encrusted by red algae. Significant bioturbation is consistent with an offshore sedimentation in a deeper area of the photic zone [21] and represent the main cause in the reworking of the sediments [9]. Bioclastic calcarenites are located on the top of the prism-shaped body [21,22]. This is subdivided in a bioclastic calcarenite with mollusk shells, and a bioclastic calcarenite with rhodoliths. The latter is quite similar to the other calcarenites in terms of composition but is mainly characterized by hard rhodoliths with a whitish and granular matrix in between.

III. MATERIALS AND METHODS

Ten samples of Calcarenite di Gravina Formation have been selected from the quarrying area located to the North of Matera. From each sample (Fig. 2), petrographical and petrophysical analyses have been carried out according to the procedures described in several works about soft carbonate rock characterization [11, 23]. Samples have been taken from the old quarries in La Vaglia and La Palomba, specifically in Paradiso Quarry (A1, A2, A3), La Palomba quarry (B1, B2, B3), the monumental quarry (C1) and from Petragallo active quarry (P1, P2, P3) as representative of the whole calcarenite in the Matera area [23]. XRF analyses have been performed on total bulk samples to obtain the major and minor chemical components (Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3). 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% [24-25]; the volatile components (mainly H_2O^+ and CO_2) were determined as loss on ignition (L.O.I.) at 950°C. XRD has been performed, as the XRF measures, on total bulk samples (random powder diffractogram) to obtain a qualitative mineralogical characterization. X-ray powder diffraction spectra were collected by an automatic diffractometer with Bragg-Brentano geometry, Bruker model D2 PHASER 2nd Generation equipped with a Lynxeye 1D detector and Ni-filtered Cu Kα radiation (λ =
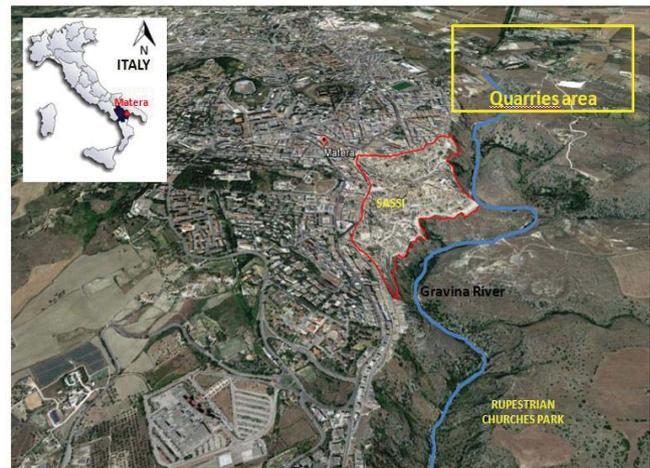

Fig. 2 – Geographical localization of Sassi di Matera and quarries area where samples have been taken. Images from Google Earth.

1.5406 Å), from 5 to 65°2Θ, step size 0.02° and counting time 0.3 s/step. For identifying the mineralogical phases the Brucker AXS DIFFRAC.EVA software was used.

Determination of the main petrophysical properties of the samples has been performed in the Cultural Heritage and Environment Laboratory of the Pisa University. Specifically, determination of real density, apparent density and of total and open porosity was performed according to EN 1936. The volume of the specimens was measured by means of a hydrostatic balance on water-saturated samples [26]. Water absorption coefficient by capillarity, water absorption by total immersion at atmospheric pressure were measured according to EN 1925 and EN 13755, respectively.

IV. RESULTS AND DISCUSSION

Petrographical characterization highlighted the presence of poorly cemented grainstone to packstone. Often rustone have been described. Lithoclasts are well rounded and comes from the erosion of the Altamura limestone. The siliciclastic components (well rounded quartz and plagioclase and feldspar), are from the Apennine domains. Bioclasts are very abundant, in particular echinoderms, bivalves (e.g. pecten and oyster), bentic and planctic foraminifera, red algae, brachiopods, bryozoan, ditrupa and not identified calcitic shell fragments. Chemical analyses performed on ten selected samples show that 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 less than 5 wt%; the CO_2 contents are stoichiometrically related to the contents of CaO to

Tab. 1 – XRF analyses of selected samples expressed in wt%.

| 10 samples	ID sample	L.O.I.	Na2O	MgO	Al2O3	SiO2	P2O5	K2O	CaO	TiO2	MnO	Fe2O3
A12	**A1**	42.32	<0.01	0.34	0.4	2.38	0.26	0.01	53.47	0.03	0.03	0.76
A4	**A2**	43.33	<0.01	0.11	<0.01	0.52	0.17	<0.01	55.05	0.02	0.03	0.77
C3A	**A3**	43.53	<0.01	0.1	<0.01	0.15	0.14	<0.01	55.34	0.01	0.03	0.7
B1	**B1**	43.43	<0.01	0.1	<0.01	0.4	0.14	<0.01	55.2	0.02	0.03	0.68
B12	**B2**	43.39	<0.01	0.1	<0.01	0.43	0.13	<0.01	55.15	0.01	0.03	0.76
B2bis	**B3**	43.45	<0.01	0.11	<0.01	0.37	0.14	<0.01	55.22	0.01	0.03	0.67
B35A	**C1**	43.19	<0.01	0.2	0.02	0.92	0.19	<0.01	54.75	0.02	0.03	0.68
P18	**P1**	42.89	<0.01	0.21	0.09	1.2	0.23	<0.01	54.37	0.03	0.03	0.95
P20	**P2**	43.31	<0.01	0.19	<0.01	0.63	0.24	<0.01	54.92	0.02	0.03	0.66
P2bis	**P3**	43.39	<0.01	0.12	<0.01	0.44	0.22	<0.01	55.12	0.01	0.03	0.67
mean	**mean**	43.22	<0.01	0.158	0.17	0.74	0.19	0.01	54.86	0.02	0.03	0.73
max	**max**	43.53	0,00	0.34	0.4	2.38	0.26	0.01	55.34	0.03	0.03	0.95
min	**min**	42.32	0,00	0.1	0.02	0.15	0.13	0.01	53.47	0.01	0.03	0.66
st.dev.	**st.dev.**	0.36	0,00	0.08	0.20	0.65	0.05	0,00	0.56	0.01	0,00	0.09
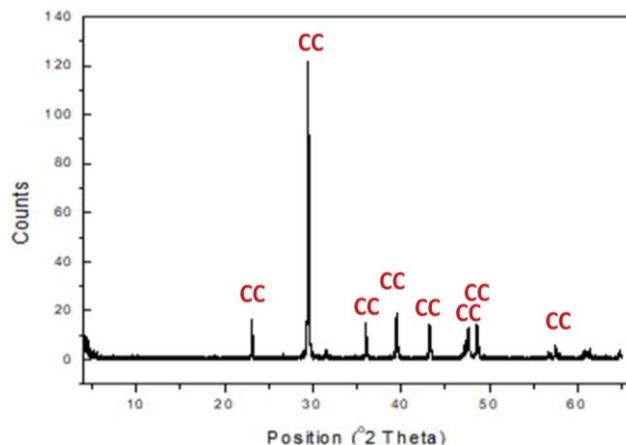
Fig. 3 –XRD spectra of the analyzed samples showing the same mineralogical composition for all lithofacies (CC means calcium carbonate).

form $CaCO_3$. Chemical analysis highlights small differences in relation with the content of silicates (0.15 - 2.38 %) followed by aluminium content (0.02 - 0.40%) and magnesium content (0.10 – 0.34%) (Tab. 1). The provenance of silicates in the calcarenites is likely related to erosion of tectonic units of the Apennine chain. While content of MgO and Al_2O_3 that are often correlated to the presence of clay minerals.

XRD analyses show roughly the same mineralogical composition for whole facies. Calcite ($CaCO_3$) is the main mineralogical phase (> 95 wt%) (Fig. 3).

The insoluble residue (from 3 to 5%) is composed, as confirmed by chemical analyses and literature data [11], of clay minerals (kaolinite, illite, chlorite, smectite and halloysite), quartz and feldspar grains and gibbsite and goethite as later formations under surface conditions.

In some studies [8,13,14,27], petrophysical data (porosity, permeability) of calcarenites were presented, and the wide range of values reflects the different composition and the varying degrees of lithification.

In table 2 are presented the main petrophysical parameter value obtained on the Calcarenite di Gravina representative samples. They confirm the high variability between the bioclastic and lithoclastic calcarenite as previous demonstrate by Bonomo et al. [3]. The lithoclastic calcarenite has a high range of water absorption, responsible for its attitude to include water quickly. The more used calcarenite for its characteristic of workability is the fine bioclastic calcarenite, that despite its apparent homogeneity after a fresh cut in a quarry, shows the most different behaviours with respect the water absorption and water retention. Indeed the differences in capillarity absorption are probably due to more relics of micrite in the bioclastic calcarenite and/or by a higher amount of micritic lithoclasts in the lithoclastic calcarenite.

IV. CONCLUSIONS

The analysed rocks show different petrographic and compositional characteristics with respect to the amount of lithoclasts and bioclasts, as confirmed by the description of the six lithofacies. They are bioclastic and lithoclastic grainstone to packstone and rarely rudstone, poorly cemented with high connected porosity.

Tab. 2 – Summary of petrophysical data performed on representative samples of the Calcarenite di Gravina.

Commercial name	Tuff				
Geological formation	Calcarenite di Gravina				
Microfacies name	grainstone-packstone, rarely rudstone				
City/sampling localities	Old quarries area in La Palomba and La Vaglia (Matera)				
Country	Italy				
Physical and mechanical properties	n.	min	max	mean	s
Real density [g/cm^3]	3	2.71	2.71	2.71	0.01
Apparent density [g/cm3]	10	1.45	1.98	1.72	0.08
Open Porosity [vol. %]	10	40.65	21.4	29.6	2.8
Total Porosity [vol. %]	10	26.67	47.1	36.88	2.8
Water absorption at atmospheric pressure w[t%]	10	11.02	27.3	23.4	3.0
Water absorption coefficient by capillarity [g/m^{2}s$^{0.5}$]	10	442.72	945.5	677	128
n. = number of specimens; min = minimum value; max: maximum value; mean = average value; s = standard deviation.					

Chemical composition and mineralogical analyses performed on total bulk samples confirm that the analysed rocks are pure limestones, with small amount of non-carbonate minerals. In this regards, the calcite content results in all the analysed samples to be higher than 95 wt% and this confirms the good quality of Calcarenite di Gravina for the production of aerial lime. Therefore, the Calcarenite di Gravina was not only a good building material, but it is also an excellent material for the production of binder to be used in restoration mortars that are perfectly compatible with the stones to be restored.

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