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The local black limestones used to make the typical black-and-white alternation of the Pisa's Romanesque Style

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***Abstract* – This paper documents the chemical, mineralogical and petrographic characteristics, and some physical properties of the black limestones that were exploited in the Middle Ages for building the Pisa's monumental architecture. The black limestones are worthy of particular importance in the medieval Pisa's constructions because they are used to build important buildings (S. Maria Assunta Cathedral, Leaning Tower, Baptistery and several other city churches) and, in particular, the typical black layers that characterize the Pisan architecture are almost always made with these stones. The main local black limestones used as building stones in Pisa belong to the Tuscan Nappe Unit: the Calcare a Rhaetavicula contorta formation, including the black limestone Portoro, outcropping in the Monte Pisano area, and the Calcare selcifero della Val di Lima formation, outcropping in the Monti d'Oltre Serchio area.**

I. INTRODUCTION

In the framework of the research on the stones historically used as building materials in Pisa (western Tuscany, Italy) [1-4], this work deals with the black limestones belonging to the Calcare a Rhaetavicula contorta Fm, outcropping in the Monte Pisano, and the Calcare selcifero della Val di Lima Fm., outcropping in the Monti d'Oltre Serchio.

The extensive use of these stones in Pisa occurred in the Middle Ages, when some important constructions were built [5-9]. For example, the black limestones together with the Monte Pisano marble were used to make the typical black-and-white alternation of the Pisan Romanesque style in S. Maria Assunta Cathedral [10, 11], Leaning Tower [12], Baptistery [7], San Nicola [13] and San Paolo a Ripa d'Arno [9], and together with the Monte Pisano quartzites [14] in San Piero in Vinculis.

These studied stones are black or dark grey on "fresh" surface, but they suffer from colour fading, and assume a light-grey colour when exposed also for a not too long time to weathering processes.

The aim of this research is to characterize the black limestones outcropping in the reliefs near Pisa, from a chemical, mineralogical, petrographic and physical point of view, and to evaluate its use as building stones in the Pisa's city.

II. GEOLOGICAL SETTING

The Monti Pisani, also including the Monti d'Oltre Serchio, are a mountainous system of modest size that is part of the Tuscan Sub-Appennine; they are located in the central-northern part of Tuscany, and separate Pisa from Lucca (Figure 1).

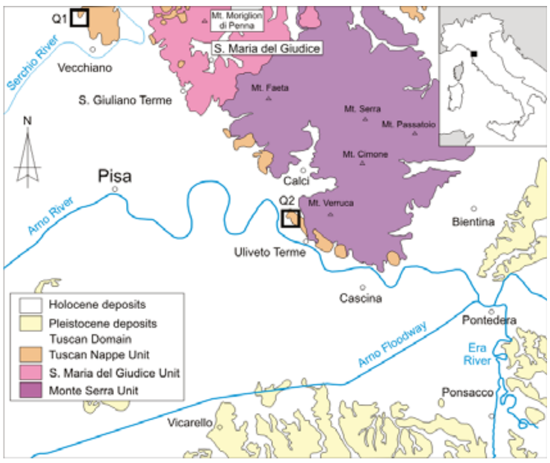

Fig. 1. Sketch map of the Monti Pisani area in 1:200000 scale (modified by [15]).

As reported by Giannini & Nardi [16] and Rau & Tongiorgi [17], the lithotypes outcropping in the Monte Pisano area belong to the stratigraphic sequence of the metamorphic units of Monte Serra and Santa Maria del Giudice (Tuscan Metamorphic Units). Conversely, the formations belonging to the Tuscan Nappe (Tuscan non-metamorphic Unit) outcrop extensively in the Monti d'Oltre Serchio and, locally, on the southern slopes of the Monte Pisano as outcrops of limited extension.

The Tuscan metamorphic succession is here represented by silicoclastic deposits from Paleozoic to Carnian age, and carbonate rocks of Trias-Cenozoic age, mainly developed in the Unit of Santa Maria del Giudice (northwest side of the Monte Pisano). In the Monte Serra Unit (southeast side of the Monte Pisano) the post-Carnic successions are limited to small outcrops of marble, meta-limestones with flint and meta-radiolarites [17].

The Tuscan Nappe, originally placed in a paleogeographic area between the Apuan Alps zone towards the west and the Umbria-Romagna basin towards the east [18-20], is related to part of the late Triassic-early Miocene sedimentary cover and stratigraphically is made up of, from the bottom: evaporitic (late Triassic), carbonate (late Triassic-early Cretaceous) and pelagic-turbiditic (Cretaceous-early Miocene) successions [17].

For the sake of clarity, the black limestones analysed in the present work belong to the Tuscan Domain and, in particular, the Calcare a Rhaetavicula contorta and the Calcare selcifero della Val di Lima are deposits related to the Tuscan Nappe of Upper Trias and Middle/Upper Jurassic age [21-27], respectively.

III. ANALYTICAL METHODS

A total of 47 samples from two abandoned quarries have been collected and analysed: twenty-eight samples of Calcare selcifero della Val di Lima (SVL) were taken from the quarry Q1, about 1 km north of Vecchiano and eighteen samples of Calcare a Rhaetavicula contorta (RET) from the quarry Q2, opened in the south slopes of the Monte Pisano near Caprona (Figure 1).

The analytical procedures used for this work are as follows:

- chemical analysis by X-ray fluorescence [28-29] 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); total volatile components were measured as loss of ignition at 950 °C on samples dried at 105 ± 5 °C;
- mineralogical analysis by X-ray powder diffraction (XRPD) $\lambda = 1.5406$ Å, angle range 4-66 °2θ;
- petrographic analyses by transmitted light microscopic observation of thin sections (Zeiss Axioplan microscope);
- physical properties of the stones like real (ρ_r) and apparent (ρ_a) density, water absorption at atmospheric pressure, total and open porosity have been determined following the EN standards [30-31]. The real density (ρ_r) has been determined using a gas pycnometer (Ultrapycnometer 1000 by Quantachrome Corporation) [30]. The measurements were performed on about 10 g of very-fine-grained powders dried at 105 ± 5 °C for 24 h under the following experimental conditions: ultrahigh purity compressed Helium with outlet pressure of 140 kPa; target pressure, 100 kPa; equilibrium time, automatic; purge mode, 3 minutes of continuous flow; maximum number of runs, 6; number of averaged runs, the last three. The apparent density (ρ_a) has been determined by ratio between dry mass 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). Then the specimens were immersed in distilled water following [30]. The volume of the specimens was measured by means of a hydrostatic balance on water-saturated samples [32]; water absorption at atmospheric pressure was determined according to [31] on cylinder specimens with an approximative volume of 30 cm^3. Total porosity has been calculated according to (1)

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

IV. RESULTS AND DISCUSSION

From a field check of several important historical buildings in Pisa, we found the representative presence of RET in the church of San Paolo a Ripa d'Arno (Figure 2) and of SVL in the Cathedral of Pisa (Figure 3). Even if these materials are altered, it is quite easy to recognize them thanks to their characteristic features (Figure 4): the RET limestone present an alteration colour from light to dark gray with white calcite veins and rarely yellowish marly veins; the SVL limestone present an alteration patina from light to dark gray, but unlike RET, it has black flint nodules and strips.

Fig. 2. Wall facing of the N side of the church of San

Paolo a Ripa d'Arno at Pisa, showing the presence of RET limestones (black stones) and Breccia di Caprona (white stones).

Fig. 3. Wall facing of the transept S of the Santa Maria Assunta Cathedral at Pisa, showing the presence of SVL limestones with a typical black flint.

Fig. 4. Photographs of selected samples (the thickness of the samples is about 10 cm): on the left, a RET sample with white thin intersecting veins of calcite; on the right, a SVL sample characterized by typical chromatic alteration (from black to gray) and by the presence of a centimetric black flint.

The samples analysed through XRF show the average chemical composition reported in Table 1. The average content of CaO for the analysed limestones is between 51.56 wt.% to 54.36 wt.%, while the values of SiO_2 range from 0.38 to 5.96 wt% and those of MgO from 1.05 to 0.61 wt% for RET and SVL black limestones, respectively. The sum of other chemical components is less than 1 wt%.

Table 1. Chemical compositions (wt. %) of the black limestones used as ancient building materials in Pisa constructions.

Sample	LOI	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
RET	43.85	0.01	1.05	0.18	0.38	0.00	0.06	54.36	0.01	<0.01	0.10
(n = 19)	*0.15*	*0.01*	*0.62*	*0.16*	*0.31*	*<0.01*	*0.04*	*1.02*	*<0.01*	*0.01*	*0.04*
SVL	41.19	0.04	0.61	0.24	5.96	0.04	0.06	51.56	0.01	0.09	0.20
(n = 28)	*0.55*	*0.01*	*0.02*	*0.06*	*1.18*	*0.01*	*0.02*	*0.68*	*<0,01*	*0.01*	*0.04*

RET: Calcare a Rhaetavicula contorta Fm.; SVL: Calcare selcifero della Val di Lima Fm.; LOI = Loss On Ignition at 950 °C; Fe_2O_3 = total iron expressed as Fe_2O_3.

From the mineralogical point of view, the analysed samples are essentially made up of calcite and subordinate quartz (Figure 5).

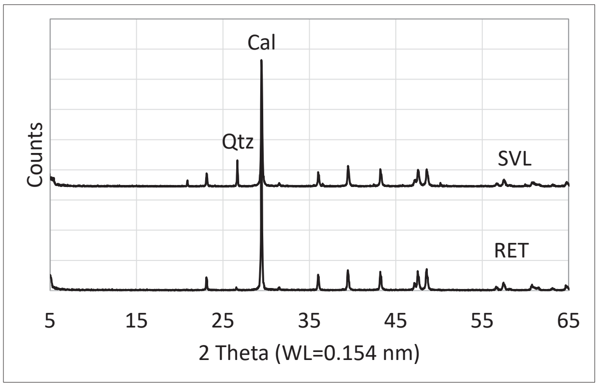

Fig. 5. Diffractograms of representative analysed samples (RET = Calcare a Rhaetavicula contorta Fm.; SVL = Calcare selcifero della Val di Lima Fm.).

The thin section observations allowed us to distinguish some petrographically distinctive features of the two rocks under examination:

- RET limestone: presence of mudstone and wackestone with bioclasts, pellets and very rare ooids;
- SVL limestone: presence of mudstone and wackestone, with pellets intraclasts, packstone, black flint and quartz.

In table 2 the main physical properties of the analysed samples are reported. Both of analysed stones are characterized by real density like calcite (2.71 g/cm^3), low values of water absorption at atmosferic pressure, less than 0.5 wt% on average, and consequentely low porosity, respectively, 1.1 ± 0.5 by vol. for RET samples and 0.6 ± 0.2 by vol. for SVL samples.

Table 2. Main physical properties of the black limestones used as ancient building materials in Pisa constructions.

Sample	ρ_r	ρ_a	IC_{Wt}	$IC_{Vol.}$	P	S.I.
RET	2.71	2.68	0.3	0.9	1.1	87
(n = 19)	*<0.01*	*0.01*	*0.2*	*0.5*	*0.5*	*19*
SVL	2.71	2.69	0.2	0.5	0.6	85
(n = 28)	*<0.01*	*0.01*	*0.1*	*0.3*	*0.2*	*26*

RET: Calcare a Rhaetavicula contorta; SVL: Calcare selcifero della Val di Lima; ρ_r (g/cm^3) = real density; ρ_a (g/cm^3) = apparent density; Ab_{wt} and Ab_{vol} = water absorption at atmospheric pressure referred to weight and to volume, respectively; P (% by vol.) = total porosity; S.I. = saturation index.

V. CONCLUSIONS

The RET limestones (Calcare a Rhaetavicula contorta Fm.) are the stratigraphic passage term between the evaporitic sedimentation of the *Calcare Cavernoso* and the carbonate sedimentation of the *Calcare Massiccio*. These rocks are made up of micrites and biomicrites with variable proportions of bioclasts (bivalves and gastropods: Aviculites and Ceritidia with rare Ostreids). From a chemical and mineralogical point of view, they are carbonate-rich limestones, consisting essentially of calcite and traces of quartz.

The SVL limestone is an alternation of calcarenitic and calcilutitic layers and, sporadically, of levels of micro-breccias. Centimetric black flint lists and nodules are frequent and characterize the rock; the presence of black flint greatly facilitates recognition and identification of the stones in situ. The microscopic study confirmed the presence of three microfacies: mudstone, packstone and wackstone.

The wide availability of the outcrops and the good macroscopic and microscopic features together with good physical properties allowed their use as building materials in the area of the city of Pisa. By observing the relative abundance on site, it is possible to affirm that the Jurassic limestones were used more widely than the Rhaetian ones. In general, the RET limestones were carved in ashlars with greater thickness in respect to the SVL limestones.

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