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Macigno sandstone from Monti d'Oltre Serchio: chemical, mineralogical, petrographic and physical characterization of a building material

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***Abstract* – The sandstones of the Macigno Formation have been widely used in Tuscany as a building material since Roman times and even earlier by the Etruscans. In this work, we focus on the Macigno sandstone of the Monti d'Oltre Serchio, on its physical properties and on its chemical, mineralogical and petrographic characteristics.**

I. INTRODUCTION

In the framework of the studies of stones historically used as building materials in western Tuscany, this work focuses on the sandstone belonging to the Macigno Formation, outcropping on the eastern side of the Monti d'Oltre Serchio.

The greatest local use of this stone occurred in the Middle Ages when some important fortifications were built in the Monti d'Oltre Serchio, near the Ripafratta Straits: The Castle of Cotone, the Castle of Castiglione and the Eagle Tower. The Macigno sandstone was also used to build the wall structures of the church of San Maurizio in Filettole, in which the use of sandstone dates back to the 9th century and, subsequently, it continued in the various restorations that took place over time [1]. This rock is also widely present in the load-bearing structures of numerous public and private buildings in the local urban area. In general, Macigno sandstone used as a building material has a medium grain size, a colour ranging from grey-blue to brownish yellow (when altered), with silver white mica slats oriented parallel to the stratification planes.

The purpose of this research is to characterize the Macigno sandstone outcropping in the Monti d'Oltre Serchio, from a chemical, mineralogical, petrographic and physical point of view, and to evaluate its local use as a building stone and investigate the main causes of degradation.

The samples studied in this work were taken in the only sandstone quarry located in the eastern portion of the Monti d'Oltre Serchio, about 1 km north of the Ripafratta (San Giuliano Terme, Pisa province).

II. GEOLOGICAL SETTING

In the Monti d'Oltre Serchio outcrop mainly formations of the Tuscan Nappe and, subordinately, formations of the allochthonous Subligure, consisting of argillites with alternations of limestones, marly limestones, sandstones and micro-breccias, Palaeocene-Eocene [2].

The Tuscan Nappe is made up of folded monoclinal layers, with immersion towards NW and inclinations around 45°, except for different and various values linked to particular minor structures.

The local Tuscan Nappe terrains have been studied extensively by Giannini and Nardi [3] and from top to bottom we have:

- Macigno: alternation of graded sandstones and argillites, with an overall thickness of a few hundred meters. Oligocene-lower Miocene.
- Scaglia: red and green clay and marl from pelagic sedimentation environments. The maximum thickness can reach 200 m. Upper Cretaceous - Eocene.
- Graded calcarenites: benches with a vertical classification of clastic elements, with intercalations of very fine-grained limestone (Maiolica type) of argillites and varicoloured marls (Scaglia type).
- Majolica: white and grey limestones, very fine grain, with flints, divided into layers and banks of total power around 300 m. They represent the sedimentation of a relatively deep-sea basin. Middle Jurassic - Lower Cretaceous [3].
- Diaspri (Jaspers): siliceous rocks of various colours (light pink, red, violet, green, grey) with clayey and marly interlayers. They represent a predominantly deep-sea silica sedimentation below the carbonate compensation level. The thickness varies between 50 and 300 m.
- Dark grey limestones with nodules and layers of black flint: these limestones are made up of layers from decimetric to metric, they have various

granulometry, from fine to calcarenitic. The thickness varies between 60 and 300 m.

- Radiolarites: siliceous rocks with rare intercalations of dark grey limestones, with black flint and with variable thickness that can exceed 120 m.
- Posidonomya marl and marly limestone: rocks of a pelagic environment, with a thickness of about 150 m, medium and upper Jurassic.
- Grey limestones with flint strips and nodules: They are fine-grained rocks, divided into layers from decimetric to metric, interspersed with thin layers of silty clay. These rocks represent a pelagic basin environment giving thickness varying from 150 300 m. lower Jurassic.
- Red ammonitic limestones: limestones in 10 cm thick layers, with an overall thickness of about 10 m. These limestones have a characteristic nodular structure, which is interpreted as an index of mobility of the seabed, connected to the beginning of the Mesozoic sin sedimentary tectonics. Lower Jurassic.
- Limestone: white and light grey limestones, finely crystalline, not stratified, laid in a carbonate platform environment, with a thickness of at least 700 m. Lower Jurassic.
- Dark grey limestone, like Portoro: they are limestones divided into very coarse banks, with a variable thickness that approaches the maximum 150 m. These rocks represent a strictly coastal and partly lagoon sedimentation environment, with bottom waters that are not perfectly oxygenated. Upper Triassic - Lower Jurassic.
- Black limestones and marls with Avicula contorta: succession of marly limestone layers, up to 2 m, and thin marly interlayers up to 120 m thick. These rocks represent a sedimentation environment of lagoon and coastal swamp. Upper Triassic.

The described lithological sequence is the typical one of the Tuscan series from the upper Triassic to the lower Miocene.

In the Oligocene - Lower Miocene, the Tuscany area was covered by the sub-Ligurian and Ligurian allochthonous formations which, overlapping the Tuscan Nappe, interrupted the sedimentation of the Macigno [4].

From the upper Miocene, were recent “Horst” and “Graben” stretching periods, mainly aligned with the Apennine [5, 6]. This type of activity led to the current geomorphology of the area, isolating the Monte Pisano and the Monti d’Oltre Serchio with depressions, subjected to marine and / or river sedimentation, and leading to the formation of the current plains of Pisa and Lucca.

III. USES OF MACIGNO SANDSTONE FROM MONTI D’OLTRE SERCHIO AS A BUILDING MATERIAL

Macigno sandstone has been used extensively in western Tuscany as a building material both in load-bearing structures and as a decorative element [7-9], thanks to its easy availability, extraction, processing, and pleasant aesthetic appearance. Furthermore, due to its good technical characteristics, it has also been used to build mill or crusher wheels.

The material used to build medieval buildings [1], could have come from both local outcrops and specialized quarries. Redi [1] distinguished the materials used in the area according to its building purposes: to build fortifications they were collected directly on the spot, while for the churches they could be taken within a maximum radius of 3 km. An exception is the church of Laiano, where limestone probably from Balbano is used for an obvious stylistic choice. About the exploitation of Macigno sandstone, it was preferred its extraction from large banks in specialized quarries, in particular the one located in Laiano, counted among the historical quarries of western Tuscany [1]. This quarry, used for sampling during this work, remained active until the mid-19th century, with a brief period in the 1950s when material was collected for the construction of the adjacent highway. It is believed that the abandonment of the quarry and the use of sandstone as a building material in the area is due to its low industrial value.

It is probable that most of the material used in the Eagle Tower, in the Castle of Cotone and Castiglione and in the church of San Maurizio in Filettole comes from the quarry in Laiano, both thanks to the macroscopic characteristics of the sandstone seen on site, and for the proximity of these to the extraction area. This last aspect is fundamental for military buildings that require short construction times and large quantities of material available.

It is also probable that material from the disintegration of the fortifications was then used for the construction of civilian dwellings located down in the valley, in the urban centre and in the countryside adjacent to the village of Filettole. In fact, the remains of the Castiglione and cotton castle are modest and only the plan of the buildings remain, with an average height of the walls of about half a meter.

IV. ANALYTICAL METHODS

The samples were collected in a quarry located on the north-eastern slopes of the Monti d'Oltre Serchio, about 1 km north of Ripafratta. On the basis of the macroscopic characteristics of the material observed during the inspections, about twenty samples of Macigno sandstone were taken from five different levels of the quarry; moreover, to better study the phyllosilicatic fraction, samples of clayey interstratification were collected.

Below are the analytical techniques used for this work:

- chemical analysis through X-ray fluorescence [10] 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 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% [11-12].

- CO_2 content was measured by calcimetry to estimate the amount of $CaCO_3$ in the tested sample [13]. The content of calcite was calculated with reference to a calibration curve constructed by linking the volume of CO_2 developed by acid attack of the powdered rock with the amount of pure $CaCO_3$.

- mineralogical analysis through X-ray diffractometry (XRD) $\lambda = 1.5406$ Å, angle range 4-66°2θ;

- petrographic analyses: 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 coefficient by capillarity, water absorption at atmospheric pressure, total and open porosity and saturation index have been determined following EN standards [14-16];

- real density (ρ_r) has been determined using a gas pycnometer (ultrapycnometer 1000 by Quantachrome Corporation) [14]. The measurements were performed on approximately 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;

- 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 [14]. The volume of the specimens was measured by means of a hydrostatic balance on water-saturated samples [17];

- water absorption coefficient by capillarity has been determined on the same samples used for apparent density determination following [15]. Measurements were taken after 1, 3, 5, 15, 30, 60, 120, 180, 240, 300, 360, 420, 480, 1440, 2880 minutes;

- the total porosity has been calculated according to (1)

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

- Dilatation by imbibition: The standard for the physical-mechanical characterization of stone materials does not consider yet the use of determining the volumetric variation of a stone material subjected to imbibition. However, the dilatation by imbibition of some rocks is certainly not to be underestimated and knowing its amplitude can allow to predict the behaviour of the material used.

The behaviour of the sandstone specimens completely immersed in water during the was studied by means of a specially constructed dilatometer [18].

V. RESULTS AND DISCUSSION

The sandstones of the Monti d'Oltre Serchio are characterized by a grain size from medium (1 / 2-1 / 4 mm) to fine (1 / 4-1 / 8mm).

The quartz-feldspathic clastic component has medium-high sphericity with a sub-rounded to sub-angular shape. Generally, phyllosilicates, in some cases also some feldspathic grains, give the rock a marked orientation. The grains are thickened, and the interstices are filled with phyllosilicate matrix and binder, consisting of autigenous calcite.

The silicate clasts are mainly represented by quartz and feldspars, with more plagioclase than K-feldspar. The phyllosilicate component is made up of white mica (muscovite), chlorite s.l. and more or less altered biotite. The rock fragments are mainly phyllites, schists and to a lesser extent siltstones and flints. The accessory minerals are garnets, zircons, epidotes, opaque phases (iron oxides and hydroxides).

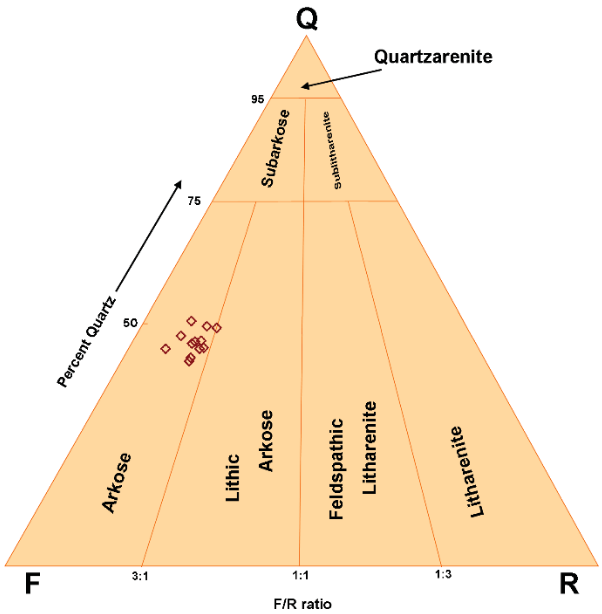

Fig. 1: QFR diagram for Folk's sandstone classification. The analysed samples can be classified as arkose/lithic arkose.

The modal analysis of thin sections, following Gazzi [19] and Dickinson [20] instructions, have shown an homogeneous composition of all the studies samples, excepting those with a higher carbonate binder content. According to Folk [21] sandstone classification diagram the analysed samples can be classified as arkose or lithic arkose (Fig. 1).

The average chemical analysis data by means of XRF is reported in Table 1. The most abundant components are SiO_2 (60,66%), Al_2O_3 (12,49%), CaO (6,20%) and MgO (5,08); while the sum of the other chemical components is less than 5 wt.% of the whole rock.

Table 1: Average chemical composition of Macigno sandstone samples from Monti d'Oltre Serchio determined by XRF analysis: the major elements are expressed in oxides wt.%. M., mean; st. D., standard deviation.

	H_2O	CO_2	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
M.	2,57	3,79	2,12	5,08	12.49	60,66	0,10	2,45	6,20	0,48	0,07	3,98
st. D.	0,48	5,21	0,27	0,84	2,07	8,98	0,03	0,34	7,90	0,07	0,02	0,56

The components with the largest variation are CaO and CO_2. This variability is essentially due to the presence of a greater or lesser quantity of calcite fraction. The H_2O content, ranging from 1.02% to 3.12%, indicates that there is also a significant amount of hydrated minerals (phyllosilicates) in the rock. The total iron content, without distinction between ferrous and ferric iron, is on average equal to 3.98% and it is constant in all the examined samples.

A deep XRD study focusing on the phyllosilicates (fraction<4μm) has allowed to distinguish between two different chlorite phases: chlorite s.s. and interlayered chlorite / smectite. The average composition of chlorites for both sandstone and clayey interlayers is reported in Tables 2 and 3.

Table 2: Mineralogical characteristic of chlorite fraction inside Macigno sandstone from Monti d'Oltre Serchio. Chl: Chlorite; S: smectite.

<table>
<tr><th rowspan="3">Sample</th><th colspan="6">Chl. s.l.</th></tr>
<tr><th rowspan="2">Chl</th><th colspan="4">Chl/S</th><th>Tot.</th></tr>
<tr><th>Chl</th><th>% S in Chl/S</th><th>S</th><th>Tot.</th><th></th></tr>
<tr><td>Mean</td><td>8</td><td>10</td><td>19</td><td>2</td><td>12</td><td>20</td></tr>
<tr><td>St. D.</td><td>3,06</td><td>2,67</td><td>7,79</td><td>1,25</td><td>3,13</td><td>3,14</td></tr>
</table>

Table 3: Mineralogical characteristic of chlorite fraction inside clayey interlayers of Macigno sandstone from Monti d'Oltre Serchio. Chl: Chlorite; S: smectite.

<table>
<tr><th rowspan="3">Sample</th><th colspan="6">Chl. S.l.</th></tr>
<tr><th rowspan="2">Chl</th><th colspan="4">Chl/S</th><th>Tot.</th></tr>
<tr><th>Chl</th><th>% S in Chl/S</th><th>S</th><th>Tot.</th><th></th></tr>
<tr><td>Mean</td><td>8</td><td>11</td><td>25</td><td>4</td><td>15</td><td>24</td></tr>
<tr><td>St. D.</td><td>2,92</td><td>3,36</td><td>10,43</td><td>2,61</td><td>5,09</td><td>5,07</td></tr>
</table>

The average physical properties of Macigno sandstone samples from Monti d'Oltre Serchio are reported in Table 4. The real density, ρ_r, ranges from 2,685 g/cm^3 to 2,723 g/cm^3, while the apparent density, ρ_a, varies between 2,463 g/cm^3 to 2,673 g/cm^3. According to the real density values it is possible to classify the sandstone from Monti d'Oltre Serchio as heavy rocks. The imbibition capacity values are quite variable (from 0.49% to 2.26%) with an average of 1.06 wt.%. The most altered samples (yellowish brown) show values of imbibition capacity higher than 1.51%, while the less degraded ones have values lower than 0.73%.

Table 4: Average physical properties of Macigno sandstone samples from Monti d'Oltre Serchio: ρ_r real density; ρ_a apparent density; P, porosity; W.A.C., water absorption coefficient; Ci_p weight related imbibition; Ci_v volume related imbibition; S.I. saturation index.

Sample	Mean	St. Dev.
ρ_r (g/cm^3)	2,704	0,012
ρ_a (g/cm^3)	2,615	0,056
P (%)	3,29	1,87
W.A.C. g/cm^2*s^{½}	3,78E-04	2,58E-04
Ci_p (%)	1,06	0,51
Ci_v (%)	2,76	1,26
S.I. (%)	88	15

VI. CONCLUSIONS

The sandstone of the Macigno Formation was a stone material used in the past, especially in the Middle Ages, for the construction of military, civil and religious buildings in the Filettole area. The use of this material was intended for elements of masonry structures.

From a petrographic point of view, it is a feldspathic sandstone with a generally arenitic medium grain size, with clasts mainly consisting of quartz, feldspars, phyllosilicates, and lithic fragments.

The substantial mineralogical uniformity was also confirmed by the diffractometric analyses.

The analyses carried out on the clay fraction revealed the presence of mica, chlorite and chlorite / smectite interlayers.

The data relating to the measured physical properties show the existence of positive correlations between the absorption coefficient and the imbibition capacity and negative correlations between the imbibition capacity and the apparent density.

These relationships suggest that in fields where capillary absorption is faster, the total amount of water absorbed is also greater and that the decrease in apparent density is accompanied by an increase in open porosity.

Capillary water absorption curves show a difference in the way water is absorbed. In fact, in some cases, especially for the altered samples, they have a strong slope of the initial section followed by a section with a lower inclination.

One of the most interesting aspects that emerged from the examination of the collected data concerns the relationships existing between the quantity of smectite present in the rock, the quantity of total water absorbed by imbibition and the value of the linear expansion coefficient by imbibition. The greater or lesser quantity of smectite layers present in Macigno sandstone not only affects the quantity of water that the rock is able to absorb, but also its greater or lesser expansion. Since the smectite absorption and transfer of water start through dilations and contractions of its lattice and these processes are strongly linked to atmospheric conditions (temperature and amount of precipitation) it is plausible to believe that the presence of smectite may represent one of the factors that contribute to the degradation of Macigno sandstone, in particular the degradation that occurs as surficial exfoliation of the stone. The repeated dilations and contractions caused by the hydration and dehydration of expandable mineralogical phases could in fact be the primary cause of the decohesion of the rock granules and, therefore, to lead to the detachment of larger or smaller portions of this stone.

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