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Natural and artificial stone materials from the medieval Castle of Condojanni (Sant'Ilario dello Jonio, Calabria, Italy)

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Abstract – **This work deals with the study of sixteen samples of natural and artificial stone materials taken from the medieval Castle of Condojanni in Sant'Ilario dello Jonio (Reggio Calabria, Southern Italy). Samples were studied using different analytical methods (Polarized Light Microscopy, X-ray Powder Diffraction; X-Ray Fluorescence Spectrometry and Energy Dispersion Microanalysis by Scanning Electron Microscope) in order to characterize their chemical, mineralogical and petrographic nature.**

The collected data allowed us to highlight similarities and differences among the samples, confirming the archaeological data, and to hypothesize the provenance of the limestones used for the production of the lime. In addition, the characterization of the samples was helpful to propose compatible stone materials for the restoration phase of the Castle.

I. INTRODUCTION

The medieval Castle of Condojanni, recently subjected to an extensive restoration project, is located in Sant'Ilario dello Ionio, in the province of Reggio Calabria, in Southern Italy (Fig. 1a).

The most recent studies, based on the typological comparison with similar structures present in the Calabrian territory, have updated the previous chronological evaluations [1] and allowed us to hypothesize that the Tower (Fig. 1b) and the Cistern were built in the same period, between the end of the 11th and the 12th centuries [2,3]. Despite its importance, very few studies have been carried out on the Castle, and in no case chemical, mineralogical and petrographic characterization have been performed on its materials.

In order to compensate this gap, recently, before the restoration works, a diagnostic phase has been started and an accurate characterization of sixteen natural and artificial stone samples used in the Castle was performed.

In particular, the characterization of the artificial stone samples, such as mortars and plasters, allowed us to determine the raw materials used, to hypothesize the provenance of the limestones employed in the mixtures and to highlight textural and compositional differences, related to the function of the materials or to different construction phases.

Indeed, as demonstrated by several works [4–8] the archaeometric study of mortars and plasters collected from historical and archaeological buildings aims to obtain information on the raw materials used, their provenance and the technological processes involved in their production, revealing important details on the constructive history of the buildings.

At the same time, the characterization of the stone samples, together with the use of mixing techniques [9-11], is also helpful to propose compatible stone materials to use for restoration works [12].

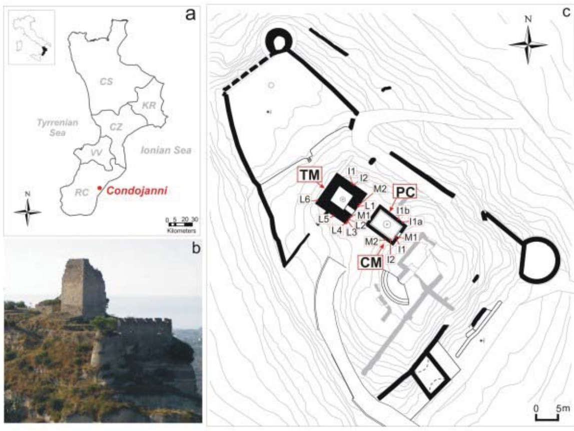

Fig. 1. a) Location of Condojanni in Calabria (Southern Italy). b) Detail of Condojanni Castle. c) Map of the Castle with location of the 16 samples.

II. MATERIALS AND METHODS

The sixteen stone samples studied in this work were collected from the Mastio Tower and from the Cistern of the Castle (Table 1 and Fig. 1c). In particular, two mortars, two plasters and six samples of natural stone were taken from the Mastio Tower (Fig. 2a). It is important to note that samples TML3, TML4 and TML6 are natural stone belonging to the Classical or Hellenistic period, reused for the construction of the Tower (their dating is based on the presence of *anathyrosis)*. In addition, two plasters and two mortar samples were collected from the outside of the Cistern (Fig. 2b, 2c) and two plasters from its inside (Fig. 2d).

Table 1. List of the samples with location, typology and probable dating.

Sample	Location	Typology	Probable dating
TMM1	Mastio T.	Mortar	Norman period
TMM2	Mastio T.	Mortar	Norman period
TMI1	Mastio T.	Plaster	-
TMI2	Mastio T.	Plaster	-
TML1	Mastio T.	Natural stone	-
TML2	Mastio T.	Natural stone	-
TML3	Mastio T.	Natural stone	Classical-Hellenistic period
TML4	Mastio T.	Natural stone	Classical-Hellenistic period
TML5	Mastio T.	Natural stone	-
TML6	Mastio T.	Natural stone	Classical-Hellenistic period
PCI1a	Cistern	Plaster	Late 19th cent.
PCI1b	Cistern	Plaster	Late 19th cent.
CMM1	Cistern	Mortar	19th cent.
CMM2	Cistern	Mortar	Norman period
CMI1	Cistern	Plaster	Norman period
CMI2	Cistern	Plaster	Norman period

All samples were analyzed through different analytical methods. Petrographic analysis was performed by Polarized Light Microscopy (PLM), on thin sections, using a Zeiss petrographic microscope equipped with a Canon PowerShot A640 photo camera. X-ray Powder Diffraction (XRPD) was carried out through a Bruker D8 Advance, to study the mineralogical composition of the samples. X-Ray Fluorescence (XRF) was performed by a Bruker S8 Tiger WD X-ray fluorescence spectrometer, with a rhodium tube with 4 kW intensity and an XRF beam of 34 mm, to determine the chemical composition of major and trace elements of the natural stone samples. Instead the chemical composition of the binder used for the mortar and plaster samples was carried out by means Energy Dispersion Microanalysis by Scanning Electron Microscope (EDS-SEM) through a ZEISS CrossBeam 350, equipped with an EDS-EDAX OCTANE Elite Plus, Silicon drift type spectrometer.

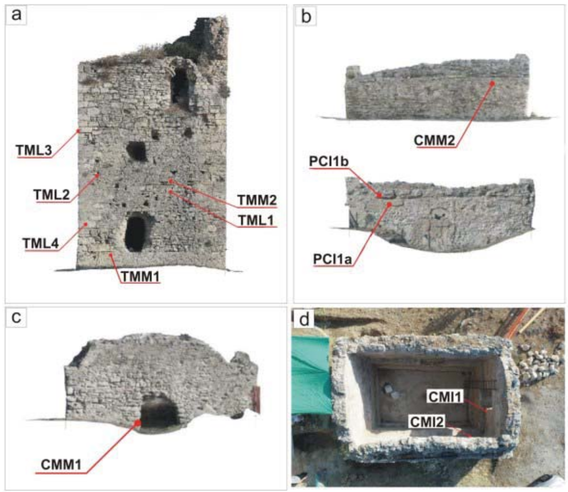

Fig. 2. Details of the sampling. a) Front of the Mastio Tower with location of some samples. b) c) Outside of the Cistern with location of the samples. d) Aerial photo with samples collected inside the Cistern.

III. RESULTS AND DISCUSSION

The analysis performed on the six natural stone samples, taken from the Mastio Tower, allowed us to identify the presence of granite (TML5) and carbonate rocks such as: biocalcarenites (TML1 and TML4) and limestones (TML3 and TML6). While the TML2 sample corresponds to a manganese nodule belonging, most likely, to the coarser aggregate of the masonry mortar.

The mortar and plaster samples analyzed generally show a very similar aggregate, with the presence of fragments of various geological origins. In particular slightly metamorphosed granite rock fragments (Fig. 3a); fragments of metamorphic rocks such as quartzites and phyllites (Fig. 3b) and fragments of sedimentary rocks, such as microsparite, crystalline limestone (Fig. 3c), biocalcarenite (Fig. 3d), sandstone (Fig. 3e) and argillites, some of which oxidized. Inside the aggregate, bioclasts are also visible in all samples, while traces of charcoal are present in TMI2 and CMI2. The mineralogical phases consist of: quartz, plagioclase (often very altered), orthoclase, microcline, calcite, muscovite, biotite, chlorite and opaque oxides. The presence of gypsum was highlighted in CMM2 and CMI2 samples, while the plaster samples collected inside the Cistern (CMI1 and CMI2) show a high content of cocciopesto fragments (Fig. 3f) used as pozzolanic material.

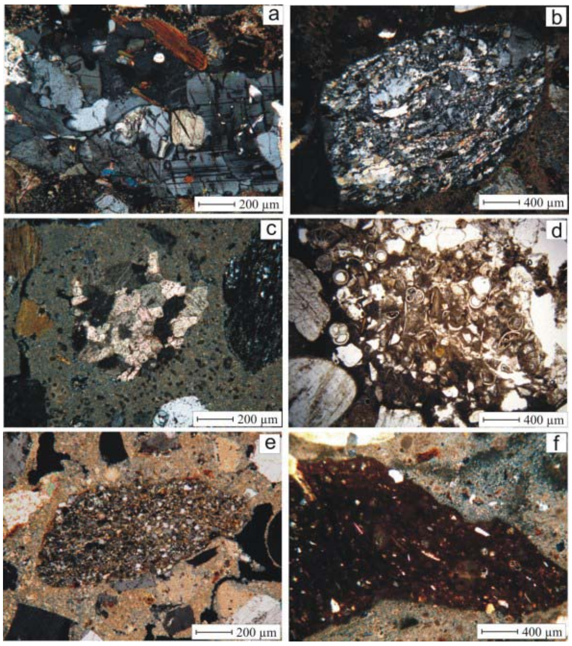

Fig. 3. Microphotos in thin section under crossed nicols (except "d" under parallel nicols). a) Slightly metamorphosed granite fragment in TMM1. b) Phyllite in TMM1 c) Crystalline limestone in TMM2. d) Biocalcarenite in TMM1. e) Sandstone in PCI1b. f) Cocciopesto in CMI1.

Despite the presence of a very similar aggregate, from a petrographic point of view, it is possible to highlight some differences among the samples, especially in relation to the average size of the aggregate, the sorting [13,14] and the percentage of aggregate used [15,16]. The mortar samples TMM2 and CMM2 are very similar, they show a moderately sorted aggregate with a coarse grain size and a percentage between 25% and 30% (Fig. 4).

Sample TMM1 shows very similar features, however, it has a coarser particle size, a slightly higher percentage of aggregate and a much higher porosity, probably linked to dissolution phenomena of the carbonatic binder. This last sample was taken from the base of the Tower, so it is possible that it belongs to the same constructive phase of TMM2 and CMM2 and the slight differences are related to the different function of the mortar.

On the other hand, as shown in Fig. 4, sample CMM1 shows percentages of aggregate, binder and macropores totally different from samples TMM2 and CMM2 (belonging to the Norman period) and, in addition, shows a very poorly sorted aggregate. These differences confirm that CMM1 belongs to a different constructive phase, in fact, the sample was taken from the opening of the Cistern (Fig. 2c) that was made in the 19th century (Table 1).

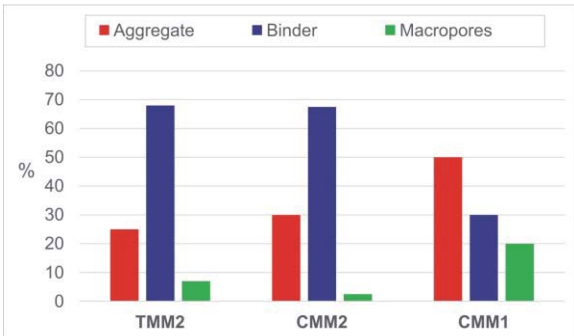

Fig. 4. Histograms with the comparison of the percentages of aggregate, binder and macropores present in samples TMM2, CMM2 and CMM1.

The plaster samples taken from the external part of the Cistern (PCI1a and PCI1b – Fig. 2b) and from the Mastio Tower (TMI1 and TMI2) show some differences linked to the particle size (smaller in the Cistern samples) and to the percentage of aggregate (much lower in the Mastio Tower samples), consequently, it is possible to hypothesize the presence of two different phases.

Instead, the plaster samples collected inside the Cistern (CMI1 and CMI2) differ from the others due to the presence of several cocciopesto fragments added in the mixture to create hydraulic plasters.

As regards the type of lime used, EDS-SEM analysis performed on the binder allowed to identify the presence of aerial lime [17] in the plaster samples taken from the external part of the Cistern (PCI1a and PCI1b) and in all the samples collected from the Mastio Tower (TMI1, TMI2, TMM1 and TMM2). The other samples coming from the Cistern (CMI1, CMI2, CMM1 and CMM2) show a hydraulic lime [17], to confirm its hydraulic function.

In addition, EDS-SEM analysis highlighted a high strontium and sulfur values in all mortar and plaster samples (Table 2). Strontium ranges from 1.75 wt% for sample CMI1 to 3.52 wt% for sample TMM1, while the sulfur content varies from 0.70 wt% for sample TMM1 to 12.49 wt% for sample CMM2.

The enrichment of these two elements derives, most likely, from the use of a lime coming from the firing of evaporitic limestones [13,18]. By observing the geological map in Fig. 5, near the city of Sant'Ilario dello Ionio there is the clastic and evaporitic succession of the upper Miocene with the presence of Messinian carbonates and in particular of limestone ("Calcare di Base") which occurs in massive banks of plurimetric thickness with intercalations of clayey marl and a texture variable from massive to laminar [19]. Consequently, it is probable that the limestone coming from this outcrop was used for the production of the lime.

Table 2. Chemical composition of the mortar and plaster samples in weight percentage (wt%) obtained by SEM-EDS analysis [udl: under detection limit].

	TM M1	TM M2	TM I1	TM I2	PC I1a	PC I1b	CM M1	CM M2	CM I1	CM I2
SiO_2	8.15	4.79	4.92	5.96	3.78	4.64	25.45	15.02	20.7	8.58
TiO_2	udl	0.96	0.76	0.57	0.15	0.17	0.71	0.10	0.10	0.15
Al_2O_3	2.52	2.49	1.92	2.31	2.01	1.98	8.33	4.55	6.46	2.66
Fe_2O_3	0.40	0.56	0.38	0.45	0.91	0.81	2.07	1.47	0.61	0.65
MnO	udl	0.13	0.18	0.10	udl	0.07	0.20	0.00	0.10	0.05
MgO	1.71	2.18	1.59	1.83	1.06	1.41	2.98	1.37	1.75	1.00
CaO	81.1	80.57	84.2	82.0	87.5	84.6	49.09	59.23	65.6	82.4
Na_2O	0.70	2.08	1.24	1.34	0.81	1.11	2.22	2.73	0.57	1.00
K_2O	1.01	0.86	0.76	0.88	0.25	0.47	2.32	0.66	0.61	0.20
P_2O_5	0.20	1.09	0.76	0.68	0.55	0.57	0.61	0.46	0.34	0.35
SO_3	0.70	1.70	1.08	1.16	1.16	1.31	2.83	12.49	1.45	0.80
SrO	3.52	2.59	2.22	2.78	1.81	2.86	3.18	1.92	1.75	2.06

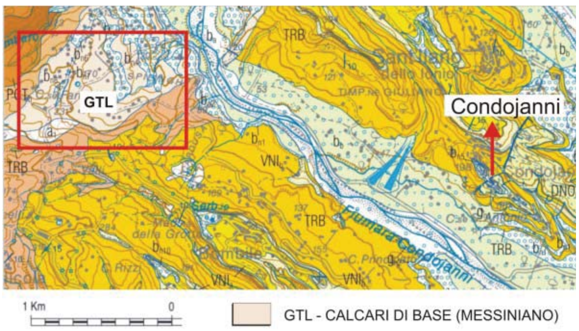

Fig. 5. Detail of the geological map of Taurianova with the area of Sant'Italio [19].

IV. CONCLUSION

The study performed on the samples coming from the Castle of Condojanni (Sant'Ilario dello Jonio, Calabria, Italy) allowed us to characterize the materials used to its building. In particular, for the construction of the Mastio Tower, the use of granite, biocalcarenites and limestones was identified. The natural stone samples reused in the construction of the Tower and belonging to the Classical or Hellenistic period are limestones (TML3 and TML6) and biocalcarenites (TML4).

For the mortars, the similar minero-petrographic features among the samples allowed to confirm the hypotheses made on their dating. Consequently, samples TMM1, TMM2 and CMM2 belong to the same constructive phase (Norman period - late 11th - early 12th centuries) and the slight differences visible in sample TMM1 (collected from the base of the Tower) probably are related to the different function of the mortar. On the other hand, the mortar collected from the opening of the Cistern (CMM1) belongs, most likely, to a different constructive phase, in fact it was taken from the opening of the Cistern made in the 19th century.

The plasters show a high variability: samples taken from the external part of the Cistern (PCI1a and PCI1b) and from the Mastio Tower (TMI1 and TMI2) show differences linked to the particle size and to the percentage of aggregate, consequently it is probability that they belong to a different constructive phase. On the contrary, the samples collected inside the Cistern (CMI1 e CMI2) show a high amount of cocciopesto, used as pozzolanic material, due to the hydraulic function of the Cistern.

The study of the binder revealed the use of hydraulic lime for some samples coming from the Cistern (CMI1, CMI2, CMM1 and CMM2) and the use of aerial lime for the other samples.

Finally, in the binder of all mortar and plaster samples a high amount of strontium and sulfur was revealed, consequently it is possible to hypothesize the use of lime coming from the firing of evaporitic limestones which, most likely, correspond to the evaporitic Messinian carbonates identified as "Calcare di Base", located near the Sant'Ilario area.

REFERENCES

[1] F.Martorano, "Chiese e Castelli Medioevali in Calabria", Rubbettino Ed., Soveria Mannelli, 1996.

[2] V.de Nittis, "Il Castello di Condojanni. Storia e Restauro", Rubbettino Ed., Soveria Mannelli, 2022.

[3] F.Martorano, V.de Nittis, "Condojanni e i castelli normanni in Calabria", Rubbettino Ed., Soveria Mannelli, 2022.

[4] R.De Luca, M.A.Cau Ontiveros, D.Miriello, A.Pecci, E. Le Pera, A. Bloise, G.M.Crisci, "Archaeometric study of mortars and plasters from the Roman city of Pollentia (Mallorca - Balearic Islands)", Periodico di Mineralogia. 82, 2013, 353–379.

[5] R.De Luca, D.Miriello, A.Pecci, S.Domínguez-Bella, D.Bernal-Casasola, D.Cottica, A.Bloise, G.M.Crisci, "Archaeometric study of mortars from the Garum shop at Pompeii, Campania, Italy", Geoarchaeology. 30, 2015, 330–351

[6] D.Miriello, D.Barca, A.Pecci, A., R.De Luca, G.M.Crisci, L.L.L´opez, L.Barba, "Plasters from different buildings of the sacred precinct of Tenochtitlan (Mexico city): characterization and provenance", Archaeometry. 57, 2015,100–127.

[7] D.Miriello, A.Bloise, G.M.Crisci, R.De Luca, B.De

Nigris, A.Martellone, M.Osanna, R.Pace, A.Pecci, N.Ruggieri, “New compositional data on ancient mortars and plasters from Pompeii (Campania – Southern Italy): archaeometric results and considerations about their time evolution”, Materials Characterization. 146, 2018, 189–203.

[8] M.Lezzerini, S.Raneri, S.Pagnotta, S.Columbu, G.Gallello, "Archaeometric study of mortars from the Pisa’s Cathedral Square (Italy)", Measurement. 126, 2018, 322-331.

[9] D.Miriello, G.M.Crisci, “The mixing and provenance of raw materials in the bricks from the Svevian castle of Rocca Imperiale (North Calabria-Italy)”, European Journal of Mineralogy. 19, 2007, 137–144.

[10] D.Miriello, M.Lezzerini, F.Chiaravalloti, A.Bloise, C.Apollaro, G.M.Crisci, “Replicating the chemical composition of the binder for restoration of historic mortars as an optimization problem”, Computer and Concrete. 12, 2013, 553–563.

[11] D.Miriello, A.Bloise, R.De Luca, C.Apollaro, G.M.Crisci, S.Medaglia, A.Taliano Grasso, “First compositional evidences on the local production of Dressel 2-4 amphorae in Calabria (Southern Italy): characterization and mixing simulation”, Applied Physics A: Materials Science & Processing. 119, 2015, 1595–1608.

[12] L.Schueremans, O.Cizero, E.Janssens, G.Serre´, K.Van Balen, “Characterization of repair mortars for the assessment of their compatibility in restoration projects: Research and practice”, Construction and Building Materials. 25, 2011, 4338–4350.

[13] S. Jr. Boggs, “Petrology of sedimentary rocks”, Cambridge University Press. Cambridge UK.F, 2010.

[14] D.A.Jerram, “Visual comparators for degree of grain-size sorting in two and three-dimensions”, Computers & Geoscience. 27, 2001, 485-492.

[15] F.Ricci Lucchi, “Sedimentologia parte I: Materiali e tessiture dei sedimenti”, Clueb, Bologna, 1980.

[16] G.Myron Best, “Igneous and Metamorphic Petrology”, 2nd edn. Blackwell Publishing, Oxford, 2003.

[17] R.S.Boynton, “Chemistry and Technology of Lime and Limestone”, John Wiley & Sons, New York, 1966.

[18] J. K. Warren, “Evaporites: sediments, resources and hydrocarbons”, Springer Science & Business Media, , Berlin, 2006.

[19] ISPRA, ENI, OGS, “Cartografia Gravimetrica Digitale d'Italia alla scala 1:250.000”, Foglio 590, 2009.