

## Article

# Monitoring and evaluation of sandstone decay adopting Non-Destructive Techniques: on-site application on building stones

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**Abstract:** This paper focuses on the characterization approach to evaluate the decay state of *Pietra Serena* of historic buildings in Florence (Italy). *Pietra Serena* is a Florentine sandstone largely used in the city especially during the Renaissance; it is a symbol of cultural heritage of Florence and constitutes a large part of the city center, which was named a World Heritage Site by UNESCO in 1982. Unfortunately, many environmental factors negatively affect the stone, increasing damage and the danger of falling material. Any detachment of stone fragments, in addition to constitute a loss in cultural heritage, can be dangerous for citizens and the many tourists that visit the city. The use of Non-Destructive Techniques (NDTs) as ultrasonic and Schmidt hammer tests can quantitatively define some mechanical properties and help to monitor the decay degree of building stone. In this study, the NDTs were combined with mineralogical, petrographical, chemical and physical analyses to investigate the stone materials, in order to correlate their features with the characteristics of the different artefacts in *Pietra Serena*. Correlations between the NDTs results and the compositional characteristics of the on-site stone were carried out; such discussion allows to identify zones of weakness and dangerous unstable elements.

**Keywords:** NDT; decay; cultural heritage; *Pietra Serena*

## 1. Introduction

In Florence (Italy) and its surroundings, *Pietra Serena*, an easily workable sandstone outcropping nearby the city, has been mainly exploited for ornamental purposes. Its employment flourished during the Renaissance but its use continued until the nineteenth century. The recognition of the value of the architectural elements in *Pietra Serena* has drawn attention on the importance of preserving these artefacts since their life can be drastically curtailed when they are exposed to decay processes.

A stone placed in different environmental conditions (pressure, temperature, etc.) from those where it formed tends to reach new conditions of equilibrium through changes in its characteristics, which means that the stone begins to

degrade. Clearly, this depends on its lithological features invariably combined with physical, biological and chemical processes due to environmental factors. Moreover, in urban areas, building materials situated in the open air, in addition to the natural decay, are affected by the action of atmospheric pollutants [1,2].

In this paper, we focus on stone corbels placed below balconies and eaves, architectonic elements permanently exposed to weather, placed in urban areas. Indeed, in addition to performing a decorative function, these elements also have an important structural function. Over time, this exposure involves modifications of the intrinsic stone characteristics leading to a loss in terms of mechanical properties or to the impairment of use. Therefore, the corbels themselves can influence the mechanics, as they carry significant weights. Monitoring the state of damage and mechanical properties of these structural architecture elements means evaluating the performance of the support structure.

The aim of this paper is to improve the knowledge on *Pietra Serena* in architecture and cultural heritage conservation alike and to characterize the decay degree of stone architectonic elements using Non-Destructive Techniques (NDTs), namely the ultrasonic and Schmidt hammer tests. This assessment is also fundamental in the light of the Santa Croce Basilica tragedy happened on 19 October 2017, when a visitor died because of a stone corbel falling from the ceiling as well as in light of other similar events occurred in the Florentine area.

The ultrasonic and the Schmidt hammer tests are chosen to define the mechanical properties of materials and the weathering state of building stones [3-7]. In particular, these tests enable to calculate the uniaxial strength of the rock through a correlation with the velocity of P-waves ( $V_p$ ) travelling throughout the stone or with the rebound value (R) of a spring-loaded mass impacting against the surface, respectively. The portability of the instrumentation allows the operators to perform on-site diagnostic campaigns, making these techniques a popular solution for monitoring.

The corbels of five case studies have been investigated with NDTs. For each case, a corbel has been selected for sampling and described with the visual weathering evaluation method according to the ICOMOS International Scientific Committee for Stone (ISCS) illustrated glossary [8].

The selected corbels are used to understand how mineralogical, petrographical, chemical, physical features and the different state of decay influence the NDTs results. Then, a correlation between  $V_p$  and R was developed to obtain a new approach that can improve the diagnostic process on Florentine sandstone in cultural heritage applications.

## 2. Florentine *Pietra Serena* sandstone

Corbels used to adorn balconies or eaves are characterized by different sizes and may be simply or richly carved; typically, they are made of a Florentine blue-grey colored (when freshly cut) sandstone of medium strength and easy to work, called *Pietra Serena* ("the stone with the color of the sky"). For this reason, it

was widely employed mainly in the Renaissance as decorative and ornamental material in the monuments of Florence [9-11].

*Pietra Serena* is the commercial/artistic name of a sandstone that originally belongs to the Macigno/Monte Modino Formations (Upper Oligocene/Lower Miocene), cropping out in the northern Apennines [12,13]. *Pietra Serena* extracted from these formations can be defined as a medium-coarse-grained lithic arkose with a prevailing clay matrix [11,14].

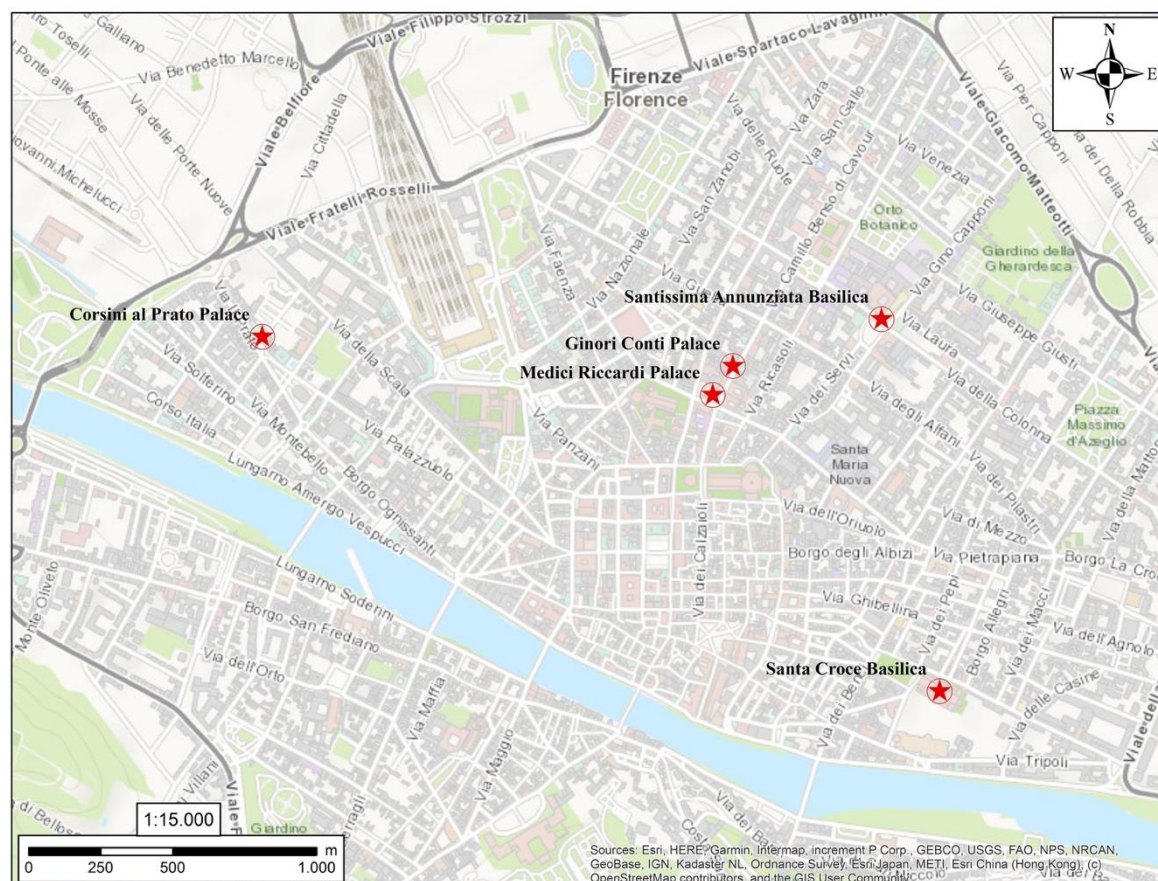
However, it is necessary to emphasize that, over the years, the request for *Pietra Serena* was so high that sometimes it was necessary to use other sandstones belonging to different geological formations and with slightly different characteristics from the original *Pietra Serena*: e.g. the sandstone coming from Monte Senario Formation, a feldspathic/lithic medium-coarse and sometimes medium-fine sandstone, with a binder mainly constituted by clay with a non-negligible quantity of calcite cement [15]. Another surrogate is Firenzuola sandstone, which is macroscopically similar to *Pietra Serena* but belongs to the Marnoso–Arenacea Formation and is characterized by a mineralogical and petrographical heterogeneity that strongly affects its physical and mechanical parameters [16].

As mentioned above, in general, the decay of stones depends on intrinsic parameters, like composition and textural/structural characteristics, and on extrinsic agents, like climate and anthropic work. Changes in temperature are a very important factor to be considered, since they can cause microfractures that can increase sandstone's porosity and enable penetration of rainwater, water vapor etc., which further contributes to the degradation, thus triggering a self-feeding loop [17-19]. In fact, in *Pietra Serena*, the rainwater and the air humidity play a fundamental role in the decay, accelerating the process: water can induce volumetric expansion of the crystal lattices (clay minerals of the matrix) and lead to consequent exfoliation and granular disintegration of the stone followed by contour scaling, until the loss of material. Water can also act mechanically by removing the clay matrix and leaving the stone completely disaggregated and with a dusty appearance. Water can also dissolve the calcite cement, increasing the porosity inside the stone. Consecutively, in the evaporation phase, the dissolved calcite can precipitate on the external surface forming up to one-centimeter-thick crusts, with low permeability; these crusts may be weakly bonded to the substrate and can often detach completely. Finally, on icy days, the water absorbed at a certain depth freezes and further widens the cracks, while the rise of temperature causes the thawing of the outer parts of block (cyclic freezing-thawing). Repeated cycles cause changes in the characteristics of the original rock, leading to significant increase in initial porosity, resulting in weaker areas [20-22].

### 3. Study sites description

In this paper, analyses on five monuments in Florence city center where the *Pietra Serena* was used in corbels, were carried out. In addition to performing a decorative function, these elements also have an important structural utility.

The five case studies represent important historical buildings and churches (Figure 1): Corsini al Prato Palace, Ginori Conti Palace, Santa Croce Basilica, Medici Riccardi Palace and Santissima Annunziata Basilica. In Table 1 the description of the most degraded corbel for each case, then chosen for sampling, is reported.



**Figure 1.** Map of Florence with the location of the case studies.

Corsini al Prato Palace (CP) was designed in 1591 and, over time, many interventions have been carried out. During the 19th century the building was enlarged following the purchase of adjacent land. Among the changes, the two balconies of the palace's façade were inserted: one supported by four corbels and one by eighteen corbels. All elements (twenty-two) were investigated. They are exposed in open air, in north-west/south-east direction. These artefacts present a varying degree of damage. The lateral areas of the balconies (in particular the two corbels at the end of the first balcony, and two on the right hand side and four on the left hand side of the second), given their higher exposure to the rain and atmospheric pollutants, are the most vulnerable. The level of decay was so high that, in 2018, a lateral corbel of the second balcony fell off. All the other corbels are in good state of preservation.



The corbels are characterized by the granular disintegration of the stone and the presence of surface deposits. The loss of material depends on the high weathered state of the stone.

The sandstone elements on the façade show color changes (mainly red-brown) due to the development of an iron-rich patina, as a result of the oxidation of  $\text{Fe}^{2+}$  as a consequence of particular condition of decay, such as the presence of water,  $\text{CO}_2$ , the low pH [14]. In Table 1a the description of the most degraded corbel is reported.

Ginori Conti Palace (GC) was built in the mid-18th century on the ancient properties of the Medici family that once ruled Florence (from XV to XVIII centuries); the building has a balcony on the second level of the façade, supported by four stone corbels located in the open air and exposed in north-south direction. The four corbels were investigated. During a previous restoration campaign, mortar was added to improve the adhesion of the corbels to the balcony and avoid the detachment of material. Such finishing layer prevents from having a complete vision of the underlying stone, making a complete analysis of its degradation impossible. It is reported that in 2019 a corbel has fallen: a structural problem of the balcony, run-off water and significant variations in the environmental parameters caused a deep fracture, which over time led to its complete fall.

The other corbels do not show any evident fractures, with the mortar well linked to the base stone (Table 1b).




Santa Croce Basilica (SC) is the principal Franciscan church in Florence, located at the eastern side of Santa Croce square. The construction of the current church, to replace an older building, was begun in 1294, possibly by Arnolfo di Cambio, and it was consecrated in 1443. The interior of Santa Croce is characterized by a wide central nave and two lateral ones. The Basilica has a “*commissa*” cross plan characterized by a particularly large transept preceding the polygonal apse. The *Pietra Serena* element studied is one of the corbels (denominated “*peduccio*”) on which the trussed roof of the right transept was placed (Table 1c). Such corbel concerns the 19 October 2017 tragedy, when the element fell off on a visitor of the church and killed him. This is the only case, in our study, of a corbel not exposed to external weathering. Although it is kept indoors, the corbel is in a poor state of conservation and is characterized by intense decay, numerous cracks, exfoliation and advanced decohesion, as a probable consequence of a continuing exposure to masonry moisture caused by internal percolations of rainfall.

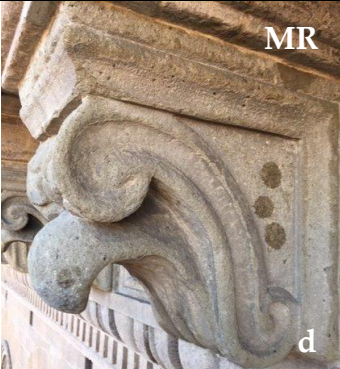

Medici Riccardi Palace (MR) is Renaissance palace, designed by Michelozzo di Bartolomeo for Cosimo de' Medici between 1444 and 1484. It was well known for its stone masonry, which includes architectural elements: rusticated blocks on the ground floor, the ashlar faces of the top story, and the cornice. The building overlooks de' Gori street (east-west direction) and C. Cavour street (north-south direction). Eighty-six elements below the eaves, on both sides of the Riccardi Medici building were investigated, of which fifty-five on the north-south façade and thirty-one on the east-west façade. The corbels are, in general, in a good state of conservation, superficial lesions are absent, and the detachment is very low. During

the recent restoration, some elements have shown slight contour scaling, (see example in Table 1d): such corbel is in good condition with a scarce pitting.

The Santissima Annunziata Basilica (SSA) was founded in 1250, located at the north-eastern side of the Santissima Annunziata square. In the mid-XV century the external portico composed of an arch was added by Antonio Manetti, to conform to the Renaissance characters of the square. In the XVII century Giovanni Battista Caccini extended the arcade of the Basilica. Below the eaves, there is a series of well carved stone corbels, of which fourteen elements were investigated. In general, these elements are in a good state of conservation, similarly to the MR case. In Table 1e the decay description of the corbel that has suffered the most degradation for each case study is indicated.

**Table 1.** Decay description of the corbels in studied sites.

CORBELS	Crack & deformation	Detachment	Material loss	Discoloration & deposit	Biological colonization
	Fracture	Delamination Disintegration Fragmentation Contour scaling	Erosion Missing part	Patina Encrustation Efflorescence	Lichen
	Crack	-	Erosion Missing part	Crust Deposit Efflorescence	-
	Crack Fracture	Exfoliation Disintegration Contour scaling	Erosion Pitting Missing part	-	-

 MR d	-	Disintegration	Pitting	-	-
 SSA e	Microfessure	Disintegration Contour scaling	Pitting	-	-

3. Analytical methods

In this study, the experimental research was carried out in two stages: on-site and in laboratory. About the on-site analyses, the NDTs measurements of  $V_p$  and  $R$  were performed on all corbels of the monuments by using two ultrasonic instruments (TICO equipment from Proceq and IMG 5200 CSD, with a resonance frequency of 54 kHz and 50 kHz, respectively), and two Schmidt hammers (N-type 58-C0181/N by Controls Group and L-type Geostone by Novatest), respectively. For the laboratory tests, the specimens were taken from stone pieces sampled from the corbels described in Table 1, that had fallen from the monuments and could not be used again as part of any restoration. They concerned mineralogical, petrographic, chemical and physical data.

3.1 NDT techniques application

The NDTs methods, such as the ultrasonic velocity and Schmidt hammer tests, are widely employed to investigate the mechanical properties of many materials [3, 23-25]. In particular, they can provide a valuable contribution in monitoring and evaluating the state of deterioration of building stones. NDTs are applied to clarify the level of damage, the presence of defects, cracks, weathering effects, without taking samples of material.

The ultrasonic testing is based on the acoustic properties of different materials. A piezoelectric probe generates ultrasonic waves. The velocity of the first wave able to travel through the rock material ( $V_p$ ) is calculated by measuring the travel time ( $t$ ) and the distance between transmitter and receiver ( $L$ ):

$$V_p=L/t$$

(1)

$V_p$  value is closely related to the physical properties of the material, such as density, elasticity, porosity, and water content. The propagation velocity also depends on the state of conservation of the stone and on the presence of concealed inhomogeneity and detachments, both surficial and internal [26-30].

The tests on the *Pietra Serena* corbels were performed with accuracy of  $\pm 1\%$  in direct transmission mode, meaning that the transmitter and receiver were placed on opposite and parallel faces. The effectiveness of the test increases with smooth and flat surfaces [31], therefore, to improve smoothness, a thin layer of aqueous coupling gel, reversible and harmless, is spread on the stone.

On each corbel, where possible, the measurements were carried out both in the central and in the outermost portion, to verify the uniformity of the entire element.

The Schmidt hammer test, originally designed for testing the hardness of concrete, has been widely used for estimating mechanical properties of many different rock types [32] and for the assessment of weathered stone hardness [33,34]. It is a minimally invasive test particularly effective in assessing the quality of the surfaces of stone elements.

This method involves the use of an instrument, the Schmidt hammer, which measures the rebound value (R), which refers to the resistance of the surface to successive  $n$  impacts of the hammer plunger. R values depend on the hardness of the surface and many other factors (type and orientation of the hammer, dimensions of the sample, smoothness of the surface, inclination of the hammer with respect to the surface) [35]. The working principles of the Schmidt hammer are shown in detail by [36] and the standard test method is described in [37].

For this work, at least 3 rebounds were performed on about 10 different points on each surface of the corbels corresponding to the same areas investigated with the ultrasonic test. The hammer was always kept perpendicular to the plane in order to minimize the error in the measurement due to the inclination of the instrument. The average values of R were obtained from these measurements. This method provides the better estimation of the surface hardness of the material [38].

### 3.2 Mineralogical Petrographic, chemical, and physical analysis.

The petrographic observations on thin sections of 30  $\mu\text{m}$  of thickness [39], were carried out by means of a ZEISS Axio Skope.A1 microscope, with videocamera, 5 Megapixel of resolution and image analysis software AxioVision [40]. The mineralogical analyses were made on the powder samples using X-ray Diffraction (Philips PW 1050/37 powder diffractometer with radiation  $\text{Cu K}\alpha_1$ ,  $\lambda=1.545 \text{ \AA}$  and graphite monochromator) operating at 40 kV, 20 mA, investigated range  $2\theta=5\text{--}70^\circ$  [41-43].

The amount of  $\text{CaCO}_3$  was determined with a gasometric method [44] using the Dietrich-Frühling calcimeter. The percentage of calcite was calculated with reference to a calibration curve constructed by linking the volume of  $\text{CO}_2$  developed by acid attack of the powdered rock with the amount of pure  $\text{CaCO}_3$ .



Laboratory testing, including apparent density, open porosity and imbibition coefficient, was carried out on the prismatic specimens of undamaged *Pietra Serena* [16,45].

Bulk density, open porosity and imbibition coefficient were calculated with Hydrostatic balance Mettler Toledo XS 204 with a maximum weight 220 g and a precision of 0.001g. Only distilled water was used. The specimens were dried in an oven at  $60 \pm 5^\circ\text{C}$  until a constant mass was reached ( $m_{\text{dry}}$ ). To maintain  $m_{\text{dry}}$ , the samples were kept in a desiccator when cooling down to room temperature.

In a typical procedure, the samples are placed in distilled water inside a crystallizer. To obtain wet weight ( $m_{\text{wet}}$ ), the specimens are measurement after a week and then at regular daily intervals to verify that they are completely saturated. With this technique the imbibition coefficient (CI) is evaluated through the weight, with the following equation:

$$\text{CI} = (m_{\text{wet}} - m_{\text{dry}} / m_{\text{dry}}) * 100 \quad (2)$$

A further in-depth analysis of imbibition is provided by measuring the hydrostatic weight ( $m_{\text{hyd}}$ ) and with it the apparent density and volume of the samples and therefore the open porosity, through the application of relationships between the different weights.

The apparent density is:

$$\bar{\rho} = m_{\text{wet}} / m_{\text{wet}} - m_{\text{hyd}} (\bar{\rho}_0 - \bar{\rho}_L) + \bar{\rho}_L \quad (3)$$

where  $\bar{\rho}_0$  is the air density and  $\bar{\rho}_L$  the density of the liquid, in this case distilled water.

The porosity accessible to water is expressed by the percentage ratio between the volume of open pores and the apparent volume of the specimen, according to the following expression:

$$P_o = (m_{\text{wet}} - m_{\text{dry}}) / (m_{\text{wet}} - m_{\text{hyd}}) * 100 \quad (4)$$

#### 4. Results and discussion

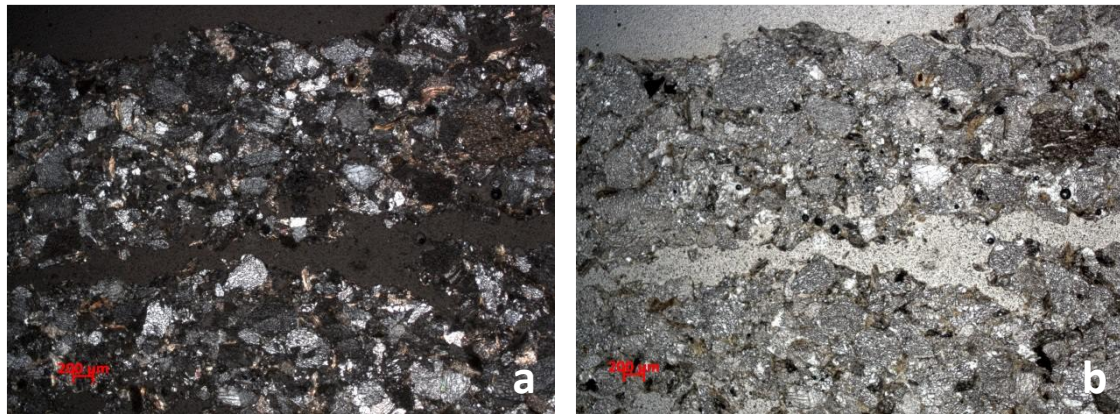
The X-ray diffraction analyses highlighted for all the samples of *Pietra Serena* (Table 2) a typical composition constituted mainly by quartz and feldspars; calcite, micas and clay minerals are in lower amount; only in SC gypsum, probably of secondary origin due to the state of decay, was detected, while in SSA traces of iron oxides were found.

**Table 2.** mineralogical analysis of the *Pietra Serena* sandstone.

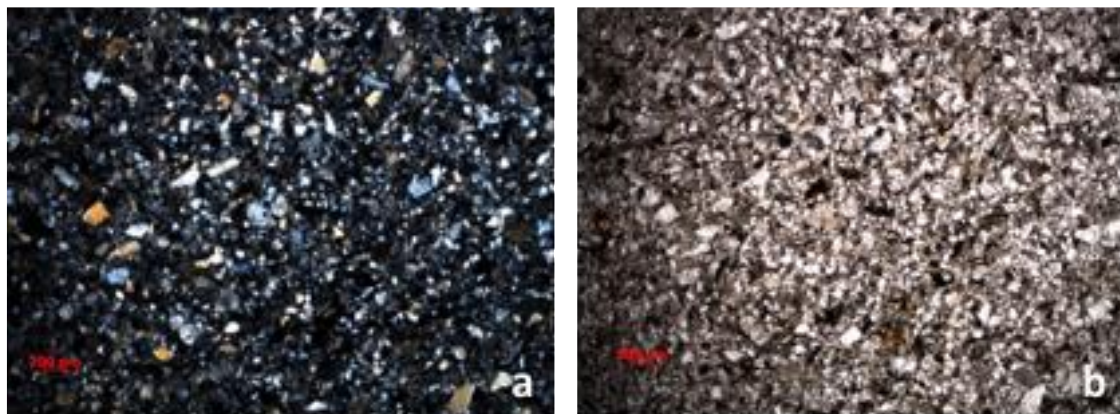
	Quartz	Calcite	Feldspars	Micas	Clay min.	Gypsum	Goethite
CP	xxx	tr	xx	tr	x	-	-
GC	xxx	x	xx	x	x	-	-
SC	xxx	x	xx	x	x	x	-
MR	xxx	x	x	x	x	-	-
SSA	xxx	x	x	x	x	-	tr

xxx= high content; xx= medium content; x=low content; tr= traces.

The petrographical analyses show in some samples (e.g. SC, and CP) a high state of decay with lack of the clay matrix, low amount of microsparitic calcite cement and presence of fractures; the sandstone shows clastic granules of medium coarse sizes constituted by quartz, feldspar fragments of metamorphic and magmatic rocks, muscovite and biotite often transformed into chlorite (Figure 2). Otherwise, in the cases of GC, SSA and MR, the sandstone shows a better condition of conservation, higher amount of microsparitic calcite cement and a higher compactness; the clastic granules are of medium-fine sizes always constituted by quartz, feldspars fragments of metamorphic and magmatic rocks, muscovite and biotite often transformed into chlorite (Figure 3). Mineralogical and petrographical results suggest that the examined samples belong to different Florentine quarries of Macigno/Monte Modino Formations [11].



**Figure 2.** (a) SC sample image of the thin section in cross polarized light (xpl), showing the presence of cracks and fractures parallel to the surface; (b) image in plane polarized light (ppl) of the same sample where cracking and decohesion between the granules is evident.



**Figure 3.** (a) GC sample image of the thin section in cross polarized light (xpl); (b) image in plane polarized light (ppl) of the same sample: in both images the medium-fine grain size of quartz and feldspars and the higher compactness of the rock are shown.

Table 3 gives an overview of the physical analysis results and shows the average values and variation coefficient measured for the five case studies. These values are probably related to the decay parameters determined in the monuments.

SC samples show a higher open porosity and thus a higher CI. The apparent density is inversely proportional to the other factors and so the GC, MR and SSA samples show a low CI and  $\phi$ . The % of  $\text{CaCO}_3$  obtained by the gasometric analyses shows different amounts among the samples, being lower for CP and SC (Table 2). The state of decay of some samples (CP and SC) is evidenced by the low amount of clay minerals, which probably were lost as a result of the water washout, and also by the low amount of calcite and consequently higher porosity; on the other hand, GC, MR and SSA case studies exhibit a better state of conservation.

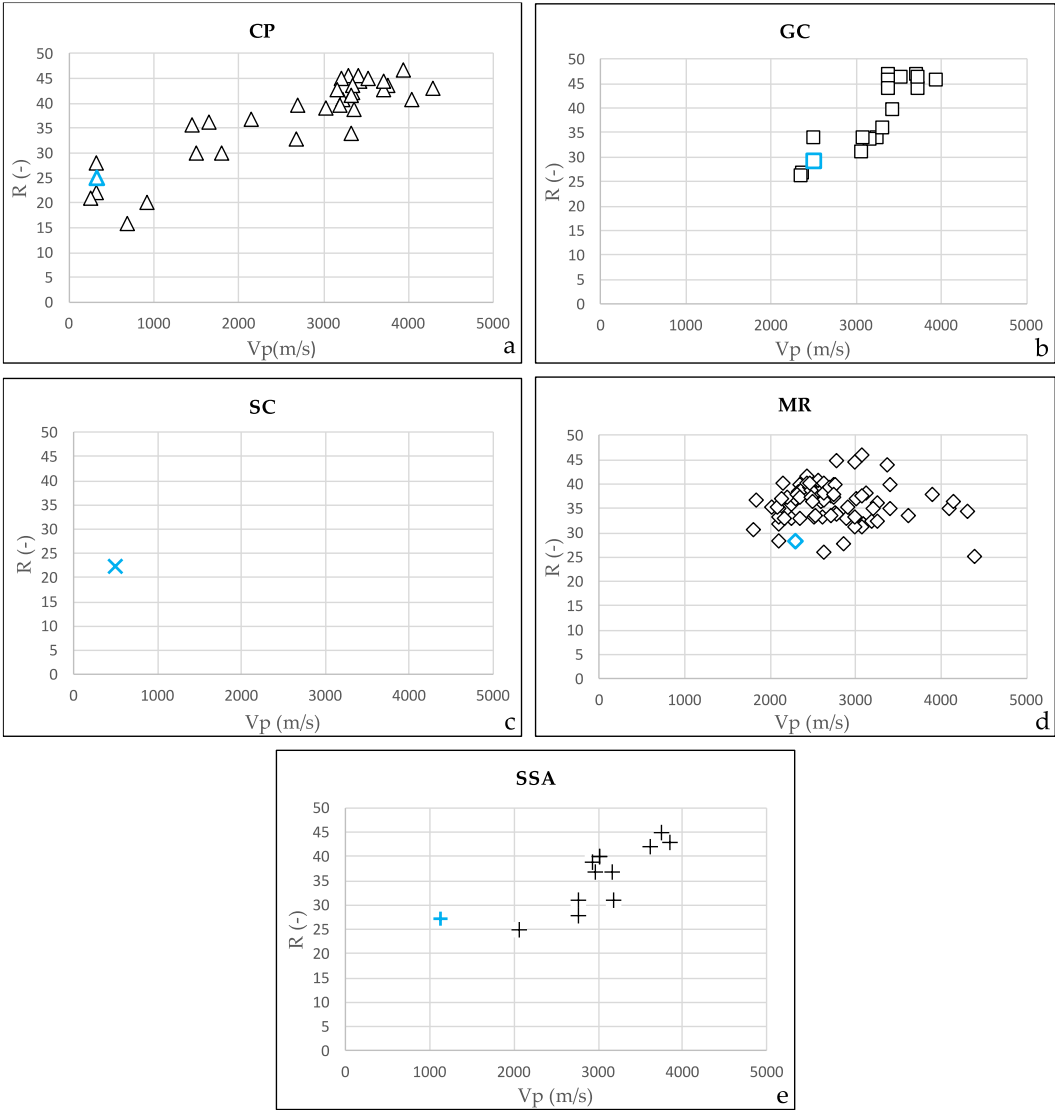
**Table 3.** Results of physical and gasometric analyses.

	$\delta$ (g/cm <sup>3</sup> )	CI (%)	$\phi$ (%)	$\text{CaCO}_3$ (%)
CP	$2.616 \pm 0.001$	$1.720 \pm 0.042$	$4.436 \pm 0.107$	2.7
GC	$2.651 \pm 0.001$	$1.273 \pm 0.017$	$3.341 \pm 0.046$	6.4
SC	$2.528 \pm 0.021$	$2.043 \pm 0.192$	$5.097 \pm 0.426$	2.7
MR	$2.638 \pm 0.008$	$1.268 \pm 0.037$	$3.317 \pm 0.115$	15.0
SSA	$2.642 \pm 0.003$	$1.137 \pm 0.049$	$2.978 \pm 0.130$	10.7

The analyses results of the ultrasonic and Schmidt hammer tests are reported in Figure 4. By comparing the results of NDTs performed on corbels selected for sampling (in blue in Figure 4), a good correlation between the distribution of  $V_p$  and R values and laboratory tests results was observed. This influence distinguishes the five case studies from a dynamic point of view.

It can be seen that the stone of SC is the lithotype characterized by the lowest  $V_p$  and R values, in fact it shows medium-coarse grain sizes of the clastic granules, higher porosity and a lower content of  $\text{CaCO}_3$  than the others. These characteristics are related both to the presence of fractures parallel to the surface and to the decohesion between the granules, probably also due to dissolution phenomena (see low content of calcite). Similarly, the CP corbel display low values of  $V_p$  and R and in fact has a high porosity and a low content of  $\text{CaCO}_3$ .

The corbels of GC, MR and SSA, instead, show high values of  $V_p$  and R, and present medium-fine grain size of the clastic granules, which makes the rock more compact with respect to the other cases. It should also be noted that the *Pietra Serena* of these case studies is characterized by a higher  $\text{CaCO}_3$  content.



**Figure 4.** Ultrasonic velocity ( $V_p$ ) versus rebound values ( $R$ ). In blue the corbels selected for sampling.

Considering the average values of  $V_p$  and  $R$  (Table 4), it is possible to note that the values obtained with the ultrasonic test are between 2200 and 3200 m/s in all the case studies, with the only exception of those measured on the corbel of SC (where only the fallen down corbel was analyzed), which is largely below the average. Also, the Schmidt hammer test recorded average results, with  $R$  values comprised between 33 and 39, except for SC.

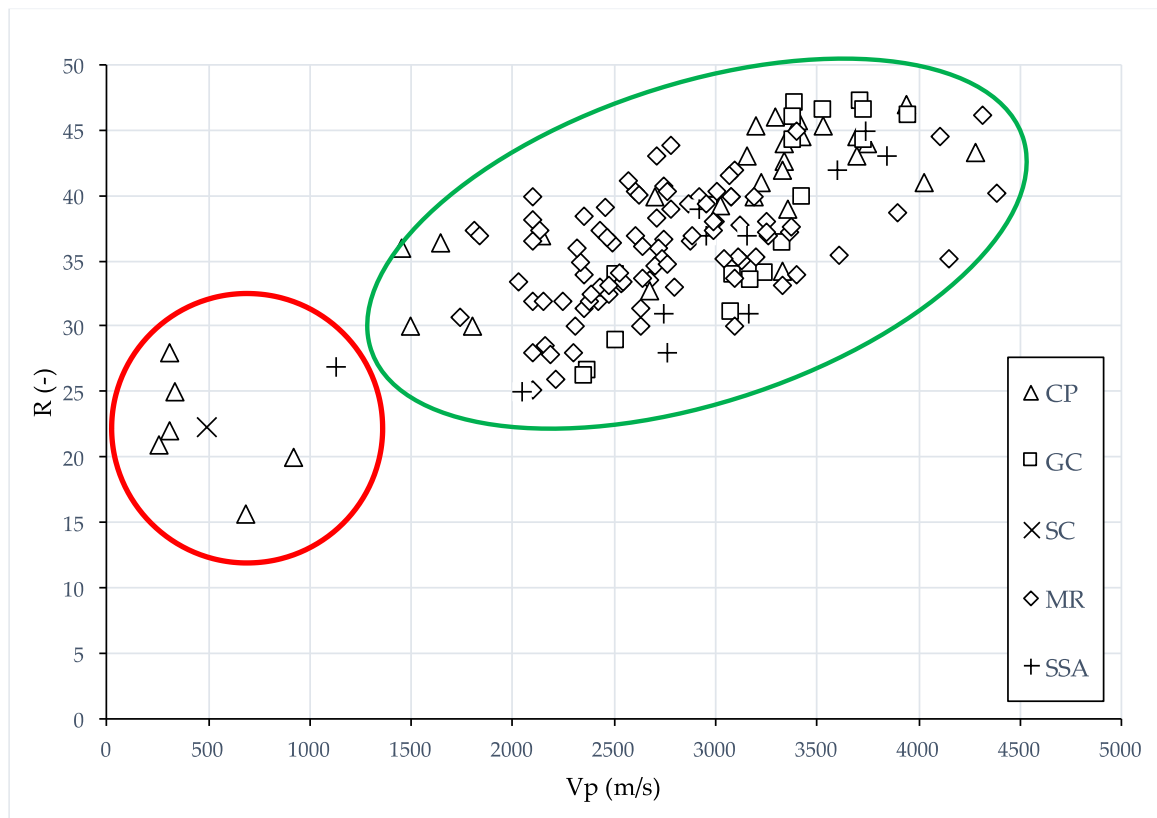
**Table 4.** Ultrasonic and Schmidt hammer tests average values for each case study.

	$V_p$ (m/s)	$R$ (-)
CP	$2616 \pm 1241$	$35 \pm 9$
GC	$3217 \pm 489$	$39 \pm 8$
SC	$497 \pm 143$	$22 \pm 2$
MC	$2746 \pm 533$	$36 \pm 4$
SSA	$2932 \pm 716$	$36 \pm 7$



All corbels investigated are summarized in Figure 5, where the correlation between  $V_p$  and  $R$  is shown. The values distribution is linear and  $V_p$  is directly proportional to  $R$ . The red cluster represents low  $V_p$  and  $R$  values, correlated to decay and weakness zones of the corbels (in this area the corbels of CP, SC and only one corbel of SSA are represented). A comparison between the description of degradation forms (Table 1) and the results of  $V_p$  and  $R$  values shows that the *Pietra Serena* characterized by very low  $V_p$  and low  $R$  generally corresponds to degraded areas suffering from exfoliation with the relative loss of shallow material, and in some cases represents the fallen corbels or those at risk of falling.

The green cluster represents the high  $V_p$  and  $R$  values, which indicate a good state of preservation of *Pietra Serena* (in this area are mainly represented the corbels of GC and MR described above and also most of the corbels of SSA). The only case studies that are represented in both cluster are CP and, to a lesser extent, SSA. Such results are often due to the considerable variability of the measurements for the bad state of conservation of on-site corbels.



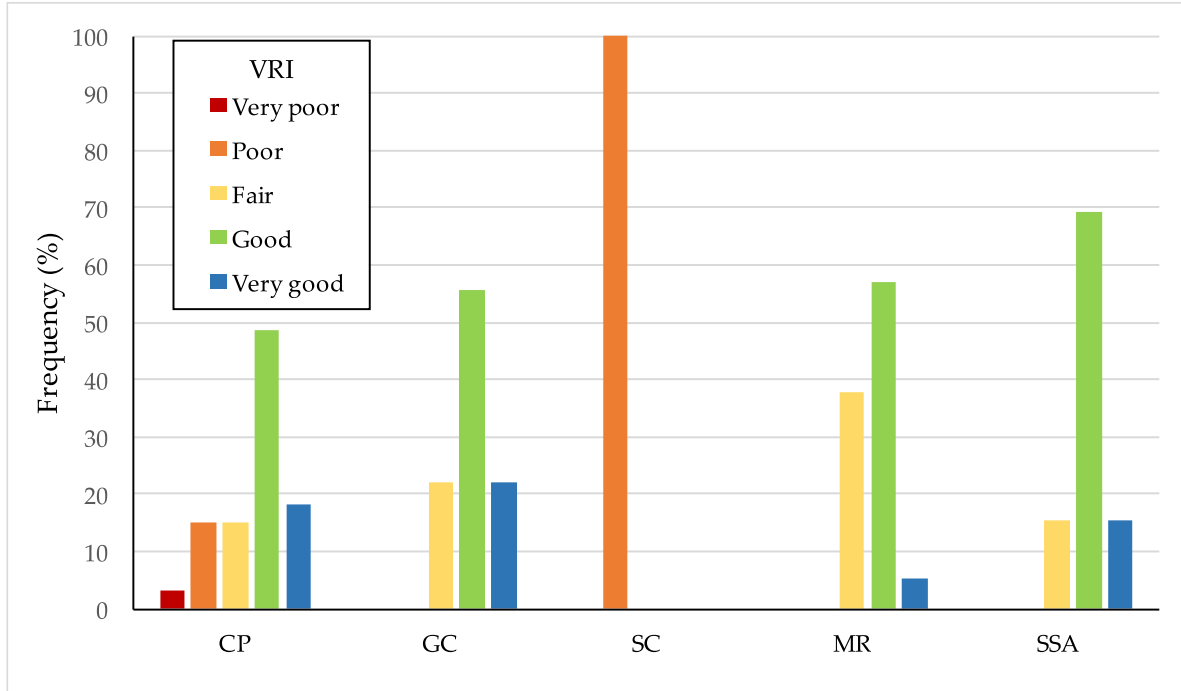
**Figure 5.** Ultrasonic velocity ( $V_p$ ) versus rebound values ( $R$ ) correlation; red cluster represents low  $V_p$  and  $R$  values corresponding to the most degraded corbels, while the green cluster represents high  $V_p$  and  $R$  values, which indicate a good state of preservation of *Pietra Serena*.

Further information about the quality of *Pietra Serena* corbels was provided by calculating the velocity ratio index (VRI) [46]. The index was computed from ultrasonic measurements for the corbels and highlights the strong influence of degradation or fracturing. This methodology has been successfully used on carbonate rocks [47]. The VRI formulation is given below:

$$VRI = \sqrt{\frac{V_p}{V_L}} \quad (5)$$

where  $V_p$  is the wave velocity measured on-site on the corbels and  $V_L$  is the velocity of the intact block of *Pietra Serena* (about 4500 m/s, measured in laboratory tests on different quarry blocks). VRI values range from 0 to 1. The block quality was divided into five categories according to VRI as suggested by [46].

Figure 4 shows that the stone of SC and several corbels of CP are classified as very poor based on VRI, while all the corbels of GC, MR and SSA are mostly classified as good and very good stones.



**Figure 4.** Percentage of *Pietra Serena* corbels of different qualities according to velocity ratio index (VRI).

## 5. Conclusions

The monitoring of the decay state of *Pietra Serena* used in Florentine historical buildings with NDTs constitutes an important starting point for a database, since it allows for the collection of practical and quick data for restoration and preservation purposes. In this study, several stone corbels placed below balconies and eaves were examined. The proposed methodology is based on the integrated application of mineralogical petrographic, chemical, and physical analysis with ultrasonic and Schmidt hammer tests.

The analyzed samples have mineralogical and petrographic features that suggest their belonging to different Florentine quarries of the Macigno/Monte Modino Formations. Comparing the physical and chemical analyses with NDTs results, it is possible to identify the five case studies from a dynamic point of view.

The corbels selected for sampling of CP and SC are characterized by both low  $V_p$  and R values, in fact it shows a higher porosity and a lower content of  $\text{CaCO}_3$ .

than the other cases. Indeed, this confirms the high level of decay shown by the macroscopic description.

On the other hand, GC, MR and SSA corbels show high  $V_p$  and R values and are characterized by a higher  $\text{CaCO}_3$  content, and low porosity and CI. This demonstrates a good state of conservation of the sandstone elements. This also means that the NDTs results are influenced by the content of  $\text{CaCO}_3$ , porosity, and density, all of which change due to the normal environmental decay of the *Pietra Serena*.

All the corbels were investigated with NDTs, in order to obtain a correlation that makes it possible to evaluate the on-site state of conservation of the ornamental stone elements. The results show a good correlation between  $V_p$  and R values, that clearly identifies two classes separating the well-preserved corbels from the fallen and the degraded ones.

A concluding observation is that the quality classification and estimation of decay can be made combining the selected NDTs methods. The results can be used for further investigation as a reference database, to quickly understand the decay state of other *Pietra Serena* ornamental elements. Moreover, the collected data, repeated in time, will allow us to perform a simple and scheduled monitoring of the conditions of the stones.

## 6. Patents

**Author Contributions:** Conceptualization, T.S.; Data curation, T.S., S.C, I.C., and E.P.; Investigation, T.S., S.C. and I.C.; Methodology, T.S., S.C., I.C. and E.P.; Supervision, E.I and C.A.G; Writing—original draft, T.S., S.C., I.C. and E.P.; Writing—review & editing, E.I. and C.A.G.. All authors have read and agreed to the published version of the manuscript.

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