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Comprehensive Overview and New Research on Carbonate Rocks of the Sé Velha Cathedral in Coimbra, Portugal

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Abstract: In addition to the surrounding climatic environment, the intrinsic characteristics of the stones used in construction are a critical factor to understand a building's conservation state and define the necessary planning and conservation management activities. The use of environmentally susceptible stones, such as carbonate stones, in heritage buildings can be especially problematic. The present investigation presents an overview of past research and contributes to identifying the types of carbonate stones used over time in Coimbra's Old Cathedral in Portugal, which was classified as a National Monument and integrated into the Coimbra World Heritage site by UNESCO. Our mineralogical and chemical analyses revealed the use of carbonate stones from different quarries (Coimbra region), including Ançã limestone and dolostone (Porta Especiosa portal), Portunhos limestone and Outil limestone (in the perimeter of windows), and marlstones and Outil limestone (side facades). These stones, which were installed at various times during the construction and alteration of the monument, represent a great challenge for conservation planning due to their intrinsic vulnerability to adverse environmental conditions and pollution.

Keywords: built heritage; carbonate stone; limestone; dolostone; marlstone; Porta Especiosa; Coimbra UNESCO site

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1. Introduction

Carbonate rocks applied in heritage buildings present considerable challenges in urban contexts. To support the long-term preservation of cultural heritage, we must improve our understanding of the nature of the stones used in monuments and the different processes, factors, and characteristics that lead to their degradation [1].

Many external decay agents operate in combination with the inherent petrographical and petrophysical characteristics of stone to accelerate its deterioration. The principal catalysts for the deterioration of building stones are widely acknowledged to be water, salt, atmospheric pollutants, biological colonization, solar irradiation, wind stress, and fluctuations in temperature. Human activity also plays a major role in the deterioration of geological heritage [2–6].

However, the nature of the stone itself and its suitability as a construction material are not always considered as sources of problems. This is a critical factor to understand the real state of a monument's conservation and plan conservation management activities throughout the building or monument's lifetime. A heritage building's artistic characteristics are unlikely to be lost due to selecting inappropriate stone for its construction. Problems arise when carbonate stone with intrinsic problems is applied to a monument. This problem occurred at the iconic Old Cathedral of Coimbra (Sé Velha, Portugal, Figure 1a), a Romanesque structure that is part of the area classified by UNESCO as a World Heritage Site at the University of Coimbra Alta and Sofia [7–9]. This monument, which was classified as a National Monument in 1910 [7], features one of the most beautiful entrances in Coimbra, the renowned Renaissance Porta Especiosa portal (Figure 1b). The stone of this portal has continuously undergone an accelerated degradation process over time, currently impairing the readability of the sculptures. Some areas of the Cathedral walls also show damage. For two decades, researchers have questioned whether the problem stemmed from the origin of the stone itself. Moreover, the risk of completely losing the sculptural elements has motivated ongoing research [10–17] to support monument management decisions.

(a)

(b)

Figure 1. Different carbonate rocks in (**a**) Old Cathedral of Coimbra and (**b**) Porta Especiosa. Credits: Alice Tavares.

This paper analyses the carbonate rocks of Coimbra's Old Cathedral (primarily limestone and dolostone), which are characterized by their chemical homogeneity (one with a high percentage of carbonate and the other with dolomite), albeit with considerable variation in terms of texture, hardness, porosity, and fossil content. These differences have a significant impact on how these building stones behave and how easily they deteriorate [18–20]. Other researchers noted that the composition of limestone varies according to the sample's specific characteristics, geological conditions, and place of origin [7,11,12,14,21,22]. Nonetheless, limestone typically consists primarily of calcium carbonate minerals such as calcite and aragonite, as well as secondary minerals. Previous research also revealed the common presence of additional minerals, including quartz, dolomite, muscovite, organic compounds, and clay minerals, depending on the limestone's formation circumstances [23–25].

In addition, stones expand and contract in response to periodic temperature changes, which causes a constant redistribution of stress in the area where the heat front advances and retreats. This phenomenon has the potential to initiate and spread new discontinuities or reactivate pre-existing ones [26]. Stones placed outdoors are particularly susceptible to biodeterioration processes aided by the growth of different microorganisms in different types of stone (such as marble, sandstone, and limestone), impacted by the natural bioreceptivity of the stone [27].

1.1. The Old Cathedral of Coimbra Sé Velha and Porta Especiosa: A Case Study

The Old Cathedral (Sé Velha) of Coimbra (Figure 1a), one of Portugal's most outstanding examples of Romanesque architecture, was chosen for this case study. Built in the 12th century, this cathedral exhibits characteristics typical of the period, including robust stone construction, arched entryways, and ornate sculptures [28]. In the second half of the 12th century, the original Old Cathedral of Coimbra was rebuilt in place of another church. Construction of the current structure began in 1160, during the episcopate of Bishop Miguel Salomão [9,16]. This church was labelled a Romanesque building by Master Roberto, a French architect [9].

The Porta Especiosa portal (Figure 1b) was commissioned by the Bishop of the Cathedral of Coimbra, Jorge de Almeida, and is one of the most representative works of the Renaissance in Portugal [9].

However, no documentary evidence of its construction, the material conditions under which it was built, the precise chronology, the labour involved, or the relevant reference sources were found in the literature [9,16,28]. However, it is known that this structure was designed by João do Ruão and built in the 1530s [9,27]. Therefore, analyses of the sculptural language and materials themselves are used to enable an in-depth reading of the monument. Porta Especiosa is a medieval term given to the doors of cathedrals through which processions enter to recite the psalm Speciosa est Maria [9].

The Sé Velha Cathedral of Coimbra, including the Porta Especiosa, has been subject to restoration interventions since the 19th century along with successive attempts to maintain and reverse the severe degradation of the stone [9]. The detected pathologies are mainly related to the construction itself, the variety of carbonate rocks used, and the lithological characteristics leading to structural disintegration [10,12–14,16,27,28]. For this reason, a considerable portion of the Porta Especiosa was irretrievably lost; damage to the stone of the facade walls and internal vaults is also visible. This situation has led researchers to question the type of stone used and whether its characteristics make it suitable as a construction material.

1.2. Overview of Background Research

One common and significant obstacle to researching stone characterization in monuments is the different difficulty levels of direct physical contact, sample collection for lab testing, and in situ investigations. Consequently, less-destructive techniques, such as optical microscopy, X-ray diffraction (XRD), X-ray fluorescence (XRF), and Fourier-transform infrared spectroscopy (FTIR) are considered the most appropriate methods for assessing the quality of stones that possess historical or artistic value [29–31].

The origin of the stone used in this monument has been extensively debated within the scientific community due to the lack of clear documentation about the building's construction and stone provenance [10,12–14,16]. Consequently, in situ and laboratory analyses, along with comparisons to regional quarries, have been the primary sources of information in this area [12,15]. Other analyses have attempted to correlate the characteristics of the stones with their levels of decay susceptibility [13,14,16,29].

Throughout the 20th century, several analyses were conducted on the building's stone, primarily focusing on the Porta Especiosa due to its significant artistic value, with less attention given to the interior spaces of the Cathedral. The present study focuses on analysing these spaces to fill the aforementioned research gap. The following sections provide a summary of the research data collected prior to the current investigation.

1.2.1. Overview of Methods and Samples Collected

Most samples from Sé Velha Cathedral are loose fragments taken from damaged areas of the monument, mainly from the Porta Especiosa portal. In addition, some samples were collected in selected outcrops to compare their characteristics and composition with those of the carbonate rocks already identified in the monument [22]. Results from previous studies on these materials in both situations were also used. Thin sections were prepared and analysed using hand lenses, whenever necessary, and a petrographic microscope, combined with chemical analyses (for several samples) [16,22]. Special attention was given to the Renaissance Porta Especiosa portal located at the north façade, where the material distribution was mapped using a photogrammetric map provided by IPPC [16]. Analyses of limestone from regional quarries were used to study the altarpiece. These tests explored the macroscopic characteristics of the Ançã and Coimbra limestone based on thin sections, physical analyses, chemical analyses, the bulk density of limestone, diffractometric analyses, suction curves, porosimetry obtained via suction tests, porosimetry histograms, capillarity tests (for the mass of absorbed water), and the height of capillary saturation [16,22].

1.2.2. Debate over Geological Origin

Since the beginning of its construction in the 12th century, the Sé Velha Cathedral used carbonate rocks as the construction material for its walls and vaults [16]. To determine their origins, previous researchers compared stones from the cathedral, mainly from the Porta Especiosa portal, with stones from other quarries.

Figure 2 shows the different geological layers presented by the LNEC, where the area of Sé Velha Cathedral belongs to the beds of Coimbra, which form the main body of the hill. The beds of Coimbra s.l. are of Lias age (inferior Sinemurian–Carixian) and composed of two units: the beds of Coimbra ss and the beds of S. Miguel [16].

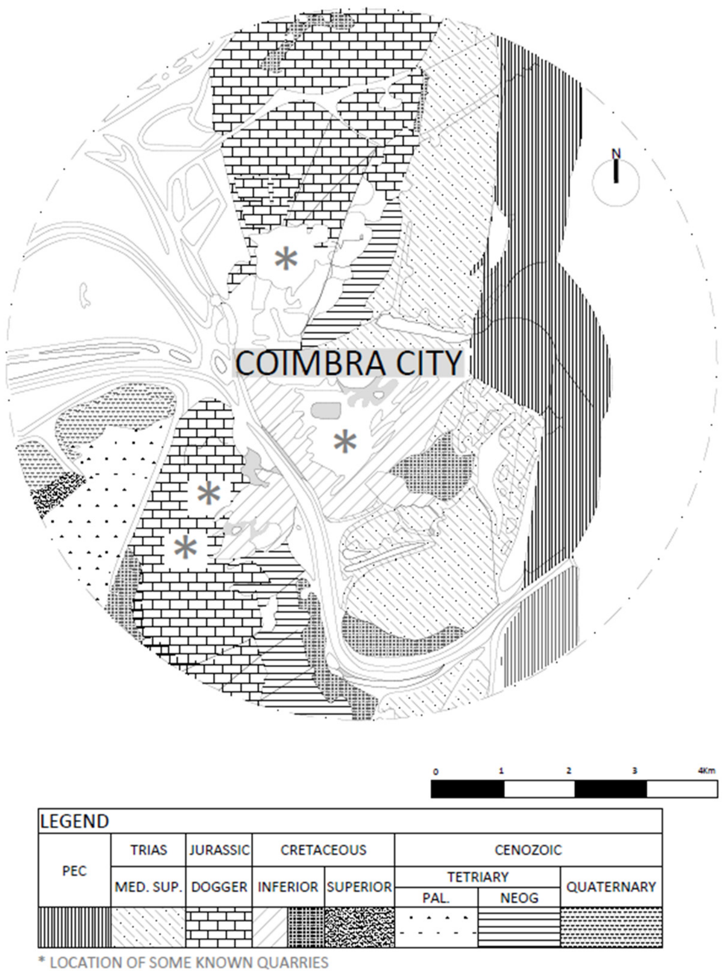


Figure 2. Geological map of the Coimbra region based on the LNEC map [16].

Coimbra is located over an area of transition between Precambrian phyllites in the east and the Meso–Cenozoic west border composed of sandstone and limestone units [16]. The correspondence between the geological time and the type of carbonate stones in Coimbra and its surroundings was also recorded [16], as follows:

- Bajocian age—Ançã limestone;
- Lias age (is Rhaetianto Toarcian in age)—dolostone and calcitic dolostone (beds of Coimbra) and limestone to dolostone (beds of S. Miguel);
- Toarcian domerian medium—marls and marly limestone of Pedrulha;
- Carixian domerian superior—marls and marly limestone of Eiras.

Table 1 presents the results from background research on the geological origin of the quarried stone.

Table 1. Results from background research on the geological origin and probable uses of the stone.

Quarries/Region	Identified Stone	Possible Use in Sé Velha Cathedral	Reference
Beds of Coimbra and hill of Cathedral	Dolostone and calcitic dolostone (with 75–98% dolomite)	Cathedral and cloister	[16]
Ançã region (10 km northwest of Coimbra), Cantanhede	Ançã limestone, milky white rocks with a very pure appearance, oolitic limestone	Porta Especiosa portal Altarpiece of Baptistery Chapel	[11,21,22]
Santo António da Pedreira (250 m south of the cathedral	White-to-grey limestone, greyish limestone, slightly marly, yellowish to white	Porta Especiosa portal	[16]
Outcrop in the south of Coimbra	White créme and greyish limestone with a residual silicate fraction similar to Cantanhede but not Ançã limestone	Porta Especiosa portal	[12,14]
D'El Rei quarry in Portunhos (Ançã region)	Dolomitic limestone	Cathedral	[21]
Santa Clara quarry in Coimbra	Dolomitic limestone	Altarpiece of the Baptistery Chapel	[22]
Ançã, Portunhos, Pena, Outil	Marlstone (probable Lower Jurassic) and Ançã limestone (with 97% calcium carbonate)	Lower part of the Porta Especiosa portal	[17]

1.2.3. Material Mapping of the North Wall (Including the Porta Especiosa Portal)

From the early 18th century until 2023, restoration work was carried out at Sé Velha Cathedral, but to the best of our knowledge, no documentation is available on the interventions prior to 1930 [16,30]. For this reason, mapping the different types of carbonate rocks is helpful to better understand the different moments of construction and repairs as well as the monument's state of conservation and to prepare future conservation and maintenance plans.

Previously, detailed mapping was conducted exclusively on the North façade, as this wall was presumed to exhibit the most severe deterioration issues. A collection of carbonate rock types was also gathered for identification purposes [16], as shown in Figures 3 and 4, corresponding to different construction phases and alterations over time. Dolostone and calcitic dolostone from the Coimbra beds were used in the main body of the cathedral (1162–1181), while limestone from Ançã was employed in the construction of the Porta Especiosa (1530). The limestone exhibits a white to grey, marly colouration, whereas the dolostone, when exposed to outdoor conditions, presents a dark patina that obscures its natural yellowish hue [16]. Although the dolostone components are generally in fair condition, certain areas show significant weathering. In contrast, the limestones are extensively deteriorated and require urgent restoration (Figure 3). However, the differences in colour and level of decay combined with the need to identify the stone types of the portal led to an ongoing debate without a consensus position. Near the windows, replacement materials were used to restore the original architectural design of the cathedral, close the aperture of the windows to their original size, and replace deteriorated blocks. These materials were also used to increase the sizes of windows in different epochs, to increase the light inside the Cathedral, and for repair interventions [16]. As shown in Figure 4, white-to-yellowish Ançã limestone and marly and grey Ançã limestone were identified in the Porta Especiosa portal, light yellow dolostone was used in several arrangements of windows, a brownish dolostone was used in the secondary lateral entrance, and dolostone was used in the rest of the cathedral walls [16].

(**a**) (**b**)

Figure 3. Details of different carbonate rock types and decay in the Porta Especiosa portal (**a**) credits: [15]; (**b**) credits: Alice Tavares.

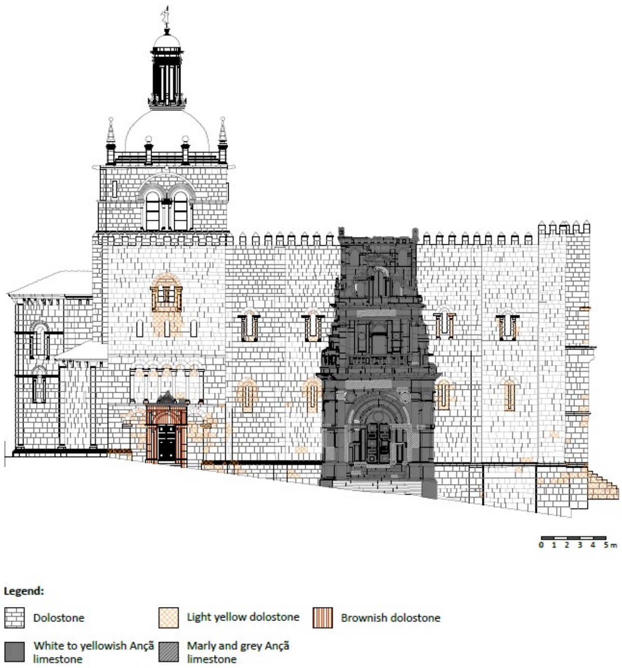


Figure 4. Mapping of stones from North facade of Coimbra's Old cathedral (based on the LNEC drawing) [16].

Table 2 shows some of the physical properties of those stones in the literature.

Table 2. Range of some physical properties of the Sé Velha materials [16].

	Dolostone to Calcitic Dolostone	White Yellow Ançã Limestone	Marly Ançã Limestone
Porosity %	8.5–24.2	23.2–29.0	11.3–11.4
Dry Unit weight (KN/m^3)	21.13–23.97	18.87–19.52	23.51–23.53
Grain Unit Weight (KN/m^3)	26.61–28.03	25.88–26.62	26.52–26.54

1.3. Chemical and Mineralogical Analysis Background

The characteristics and properties of stone materials from the first-floor construction elements, bases of the facades, and Porta Especiosa were assessed. The provenance of the stone was assumed based on similarities between rocks and outcrop rocks known around Coimbra. Based on these studies, the researchers concluded that more than 90% of the materials used in the Cathedral are from beds in Coimbra of the Lias age [16]. The remaining stones are generally Ançã limestone of the Dogger age.

Table 3 presents the range of variation among the main chemical components of the samples analysed from the cathedral and regional quarries (Portunhos—Limestone Ançã: CA1, CA2, CA3; CC4 Coimbra limestone—calcitic dolostone).

Table 3. Range of values in the literature for the chemical analysis of carbonate materials from Sé Velha [16] and regional quarry stones [21].

Classification	% Dolomite	CaO	MgO	Fe_2O_3	Na_2O	K_2O	Al_2O_3
Dolostone	>90	29.11–30.70	19.87–21.50	0.99–2.11	0.01	0.06	0.89
Calcitic dolostone	50–90	23.42–31.43	16.42–19.55	0.83–3.77	0.01–0.94	0.06–1.42	0.89–3.35
Dolomitic limestone	10–50	39.06–43.32	8.02–8.90	0.94–1.47	-	-	-
Limestone:							
White and yellowish	<10	53.09–55.48	0.32–0.60	0.05–0.20	0.00–0.02	0.00–0.05	0.50–0.70
Grey		54.71–54.98	0.47–0.60	0.28–0.49	0.01–0.03	0.07–0.09	0.66–0.93
Marly		49.79	0.91	0.83	0.01	0.11	1.33
Regional quarries:	SiO_2	CaO	MgO	FeO_3	SO_3	CO_2 (read heat loss)	Al_2O_3
CA1—limestone	2.29	53.90	0.60	0.07	0.0	42.55	0.70
CA2—limestone	1.80	54.33	0.60	0.05	0.0	42.77	0.50
CA3—limestone	1.76	54.33	0.40	0.08	0.0	42.81	0.55
CC4—calcitic dolostone	2.06	29.35	19.30	0.85	remains	45.46	3.35

Ançã limestone is heterogeneous in its colour and composition, with the white-to-yellowish limestone commonly used for cornerstones and sculptures. Macroscopically, two groups can be distinguished: white-to-yellow limestone and marly and grey limestone [16]. The white-to-yellow limestone has a compact appearance, sometimes with a chalky quality. Researchers identified some marly limestone in the Porta Especiosa [16]. However, this discovery was surprising since this limestone is a poor construction material due to its fine grains and light-to-dark grey colouration. The authors emphasized that when compared to the white limestone, the marly limestone presented a larger amount of Al_2O_3 and Fe_2O_3 and a smaller amount of CaO due to the presence of clay minerals [16]. The high Fe_2O_3 content is due to the impregnation of clay minerals with colloidal iron such as $Fe(OH)_3$ [16]. On the other hand, there is a significant amount of Fe_2O_3 in the dolostone. Consequently, weathering of these rocks typically results in colour changes due to iron oxidation [16].

Comparative analyses of quarry stones were also performed. The researchers concluded that Coimbra limestone is macroscopically a very fine-grained rock composed primarily of calcite and dolomite [22]. These stones present a higher proportion of very fine pores, much less than that in Ançã limestone, with half the porosity (14%) and a significantly higher apparent density [22].

Analyses were carried out on four quarry samples—CA1, CA2, and CA3 from the Portunhos quarry (Ançã) and CC4 from the Santa Clara quarry (Coimbra limestone)—with the results shown in Table 4. The following conclusions can be drawn from the chemical analysis. The CA samples were mainly composed of calcite with traces of quartz, while the CC sample was mainly composed of dolomite with slight traces of quartz and calcite [22]. At that time, Ançã limestone was classified as semi-compact limestone, deemed unsuitable for construction and exposure to atmospheric agents if no preliminary tests for its approval were performed [10,22], whereas Coimbra limestone was designated as hard limestone, with some application in construction, as outlined by M. Mamillan [29].

Table 4. Analysis of stone samples from the Porta Especiosa, LNEC 1985 [11].

Sample Location	Infrared Spectroscopy	X.R.D	Thermo-Differential Analysis AID	Microscopy
Sample 1 Grey limestone slabs from the right threshold 2 metres from the staircase landing	Calcite, clay product. In addition to the above, there is an area with dark spots showing traces of sulphates. Phosphates confirmed via chemical tests.	Calcite Quartz (low content)	Calcite	Fine-grained limestone with quartz clasts scattered throughout the matrix.
Sample 2 Gray crusts collected from the recess at the base of a bas relief on the right side of the portico	Calcite and a great deal of gypsum-type sulphate. Traces of nitrates. Phosphates confirmed via chemical tests.	Calcite Gypsum	Calcite Gypsum	--
Sample 3 Yellowish crusts on the right doorframe	Calcite and a great deal of gypsum-type sulphate. It contains nitrates and clay products and phosphates confirmed by chemical tests.	Calcite Gypsum	Calcite Gypsum	Fine-grained limestone with a profusion of quartz granules and a rich matrix of isotropic clay-type products.

The authors also noted that the apparent density of Ançã limestone ranged from 1924 to 1990 kg/m^3 with a porosity of approximately 28% and an absorption coefficient of about 0.91. In contrast, Coimbra limestone had an apparent density of 2444 kg/m^3, a porosity of 14%, and an absorption coefficient of 0.77 [22].

The comparison between sound stones (from the quarries) and stones from the altarpiece showed that dolomitic limestone (Coimbra limestone) was unlikely to be used in the altarpiece due to its magnesium oxide content. However, the use of Ançã limestone, which has a very similar composition, was considered a possibility [22].

In 1985, new analyses were conducted on three damaged stone samples from the Porta Especiosa [11], and the conclusions are summarized in Table 4.

Between 1998 and 2000, several studies were conducted on the various qualities of stone used in the Porta Especiosa [10,12–14,17,28]. These studies resulted in several reports, journal articles, and scientific papers; these publications formed the basis for the specifications outlined in the intervention dossier of 2002. In the preliminary phase before the 2002 restoration [12–14,17,28], the limestone known as "brando de Ançã" was noted to vary in its composition and exhibit different colorations such as white, dirty white, yellowish, and grey [17]. One of the factors influencing this limestone's weathering behaviour is the percentage of clay content [17]. Grey Ançã limestone is predominant in the Porta Especiosa, where the highest levels of degradation are observed.

2. New Research Results—Materials and Methods

Samples from different locations within the monument (Figure 5) were analysed to provide an updated contribution to characterizing the stone, particularly in areas where the decay is most significant. To this end, only small samples were collected from the collapsed sections of the wall surface, both inside and outside the monument, without employing intrusive sampling methods (Figure 6). The collection of larger samples was not authorized due to the high loss of material in some areas. However, samples were sought from different locations to facilitate a more general approach and not merely concentrate on the Porta Especiosa portal. These small samples were analysed to determine their chemical and mineralogical composition, and the corresponding results are presented in the following sections.

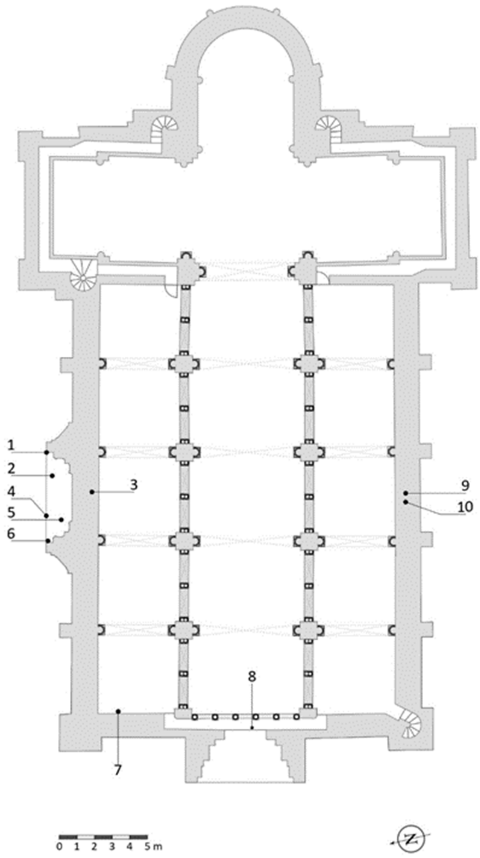
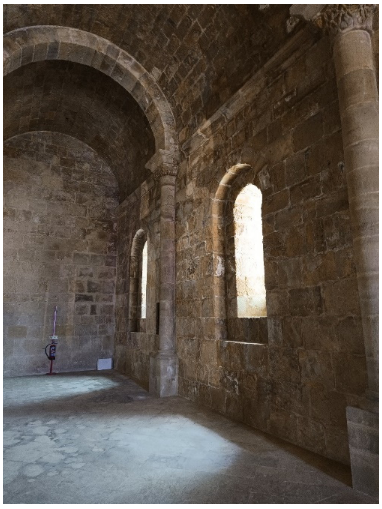


Figure 5. 1—PEE; 2—PEch; 3—PES; 4—PEC; 5—PE1; 6—PER; 7—PLE; 8—PPch; 9—PEt; 10—P3P.


(**a**)

(**b**)

(**c**)

(**d**)

(**e**)

(**f**)

(**g**)

(**h**)

Figure 6. (**a**) Samples collected from windowsills (PEt; P3P); (**b**) sample collected from the windowsill of the front façade (PPch); (**c**) sample collected from the balcony guard (PEC); (**d**) sample collected the wall at the entrance (PES); (**e**) sample collected from the wall near the floor and colonnade (PE1, PER); (**f**) sample collected from the base guardrail (PEch); (**g**) sample collected from the sill guard (PEE); (**h**) sample collected from the base of the wall (PPch). Credit: Alice Tavares.

2.1. Stone Materials

The new investigation focused on the stone of the interior faces on the side facades and the main facade, as well as that on the Porta Especiosa portal. As it was not possible to collect samples of "healthy" stone, which is considered an intrusive operation, we instead used very small splinters of stone that collapsed from the construction elements and were retained on the interior windowsills, at the top of the balcony, or on the floor of the Porta Especiosa. All samples were collected at the level of the first floor, which is not accessible for public visitation. Only very small samples that could not be used again for replacement as part of conservation or restoration activities were used. This factor informed the type and number of analyses carried out.

The following plan for the first floor of the cathedral identifies the sample collection locations. Table 5 presents the identification of the samples.

Table 5. Basic description of the samples studied.

Specimen Descriptions	Abbreviation
Collapsed stone close to the entrance of the Porta Especiosa	PES
Collapsed stone on the floor of the Porta Especiosa	PEch
Collapsed stone on the floor of the Porta Especiosa (another one)	PE1
Stone on the inside of the façade wall on the right-hand side	PEt
Colonnaded stone from the Porta Especiosa (on the guardrail)	PER
Collapsed stone on the sill of the Porta Especiosa guard (left side)	PEE
Stone from the colonnade base of the Porta Especiosa (on the balcony guard)	PEC
Stone section of the inner face of the main façade, left side	PLE
Stone in the passageway adjacent to the main façade (close to the floor)	PPch
Collapsed stone next to the third section on the right-hand side	P3P

The following figures show the sample collection locations (Figure 6).

2.2. Methods

Observations were conducted using a Zeiss Jenapshot 2000 Optical Microscope (Jena, Germany) to investigate the surfaces of the samples. Additionally, a Konica Minolta Sensing Chroma Meter CR-400 (Ramsey, NJ, USA) colorimeter was used to analyse the colour properties of the stones. The colour analysis was based on the CIELAB colour space, utilizing the parameters a*, b*, and L*. For each sample, three measurements were performed using both sides of the samples.

The mineralogical composition of the samples was determined via X-ray diffraction (XRD) with a Philips Panalytical X'Pert-Pro MPD diffractometer (Malvern, UK), Cu Kα (λ = 1.5405 Å) radiation, and a goniometer speed of 0.02° 2θ s^{-1}. The parameters for this analysis were set to 50 kV and 30 mA, with a 2θ range from 4.01° to 64.99° and a scan step time of 1 s. Analysed sample was random (unoriented) powder, about 0.500 g. For qualitative and semi-quantitative identification of the minerals, we followed the criteria provided by [30,31].

The chemical composition of the major, minor, and trace elements in the samples was determined via X-ray fluorescence (XRF) using a Panalytical Axios spectrometer PW4400/40 X-ray (Marvel Panalytical, Almelo, The Netherlands) equipped with an Rh tube under argon/methane. Reference samples were analysed using Omnian37 and Pro-Trace2021 softwares for major and minor elements analyses, respectively; Lost on Ignition was assessed on furnace at 1000 °C, for 4 h. Monument analysed samples were powders, about 0.400 g since there was very limited quantity; therefore, the used program was Malvern Panalytical OmnioanHelium (Powder Compounds Marvel Panalytical, Almelo, The Netherlands), which is semi-quantifying.

SEM/EDS analyses were also conducted using an Analytical UHR Schotty emission scanning electron microscope SU-70 (Hitachi, Bruker, Tokyo, Japan) with a voltage of 15 kV.

3. Results

3.1. Morphological and Colourimetric Analysis

Past researchers considered stone colour as a guiding parameter for stone characterization and a method for distinguishing between different types of stone. However, this information was mainly based on visual observations, with no quantitative data. In the present investigation, the colour and texture of the stones (on both sides) were recorded using a colourimeter to enable a possible comparison with future studies. A colourimetric analysis of the samples was then conducted, with the results corresponding to the obtained colour coordinates presented in Table 6. This type of analysis allows the specific properties of the samples to be determined, e.g., the presence of certain elements. Figure 7 shows the characteristics of the samples from this perspective.

Table 6. CIELAB colour coordinates for the samples under investigation.

Sample	L*	a*	b*
PEE	62.6 ± 1.6	1.0 ± 0.3	13.7 ± 0.8
PEt	60.8 ± 5.0	0.2 ± 0.2	8.0 ± 1.8
PPch	70.7 ± 3.2	2.5 ± 0.9	24.7 ± 2.2
PEch	84.5± 1.0	0.1 ± 0.09	7.8 ± 0.4
PEC	67.7 ± 0.8	1.0 ± 0.2	12.6 ± 2.6
PER	64.8 ± 8.0	1.0 ± 0.6	11.6 ± 2.2
PE1	65.9 ± 1.5	2.9 ± 0.2	19.4 ± 0.5
PLE	73.6 ± 6.4	2.6 ± 1.5	19.8 ± 5.2
P3P	60.6 ± 3.2	0.4± 0.3	6.6 ± 3.5
PES	76.8 ± 0.3	0.4 ± 0.2	8.4 ± 0.6

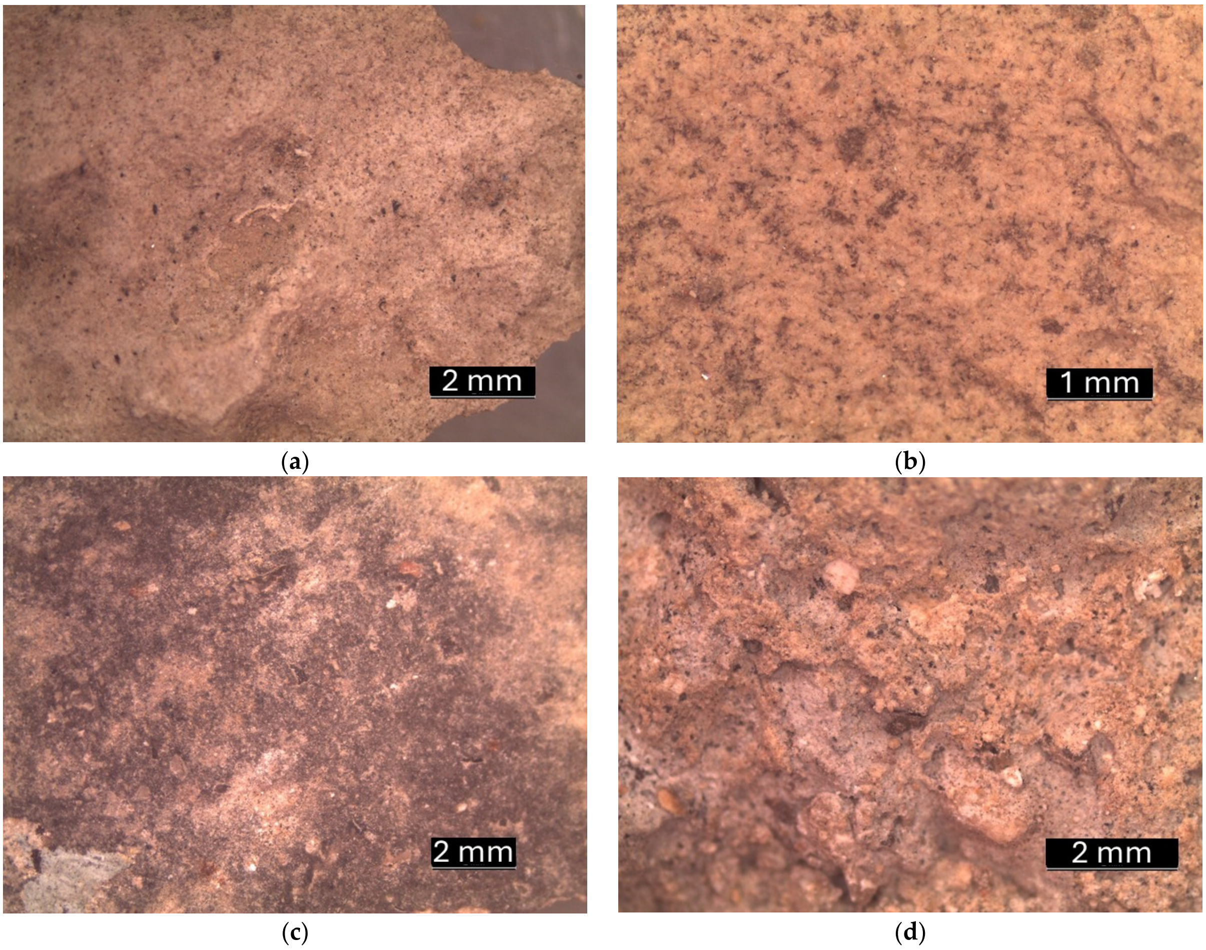


Figure 7. *Cont.*

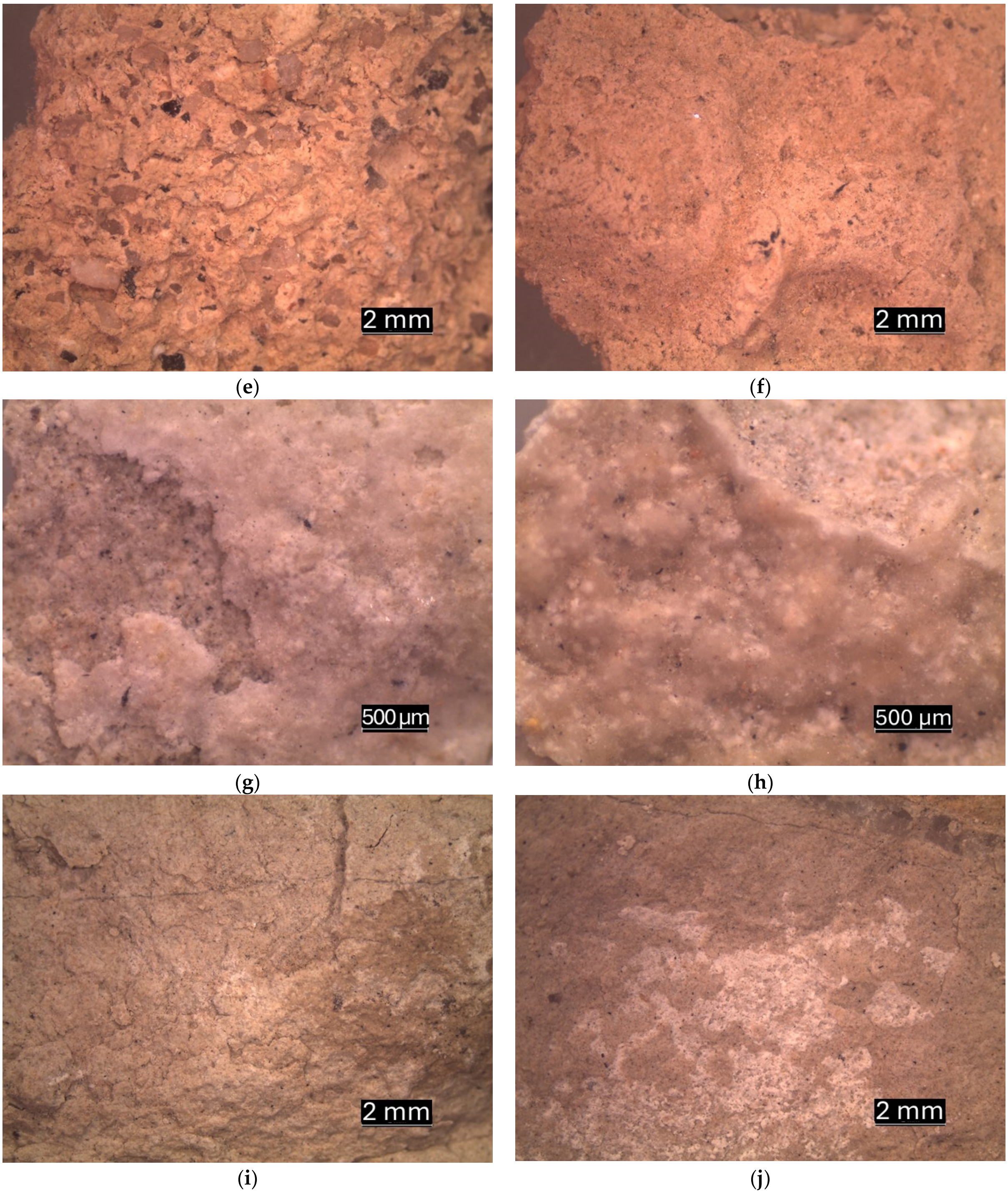
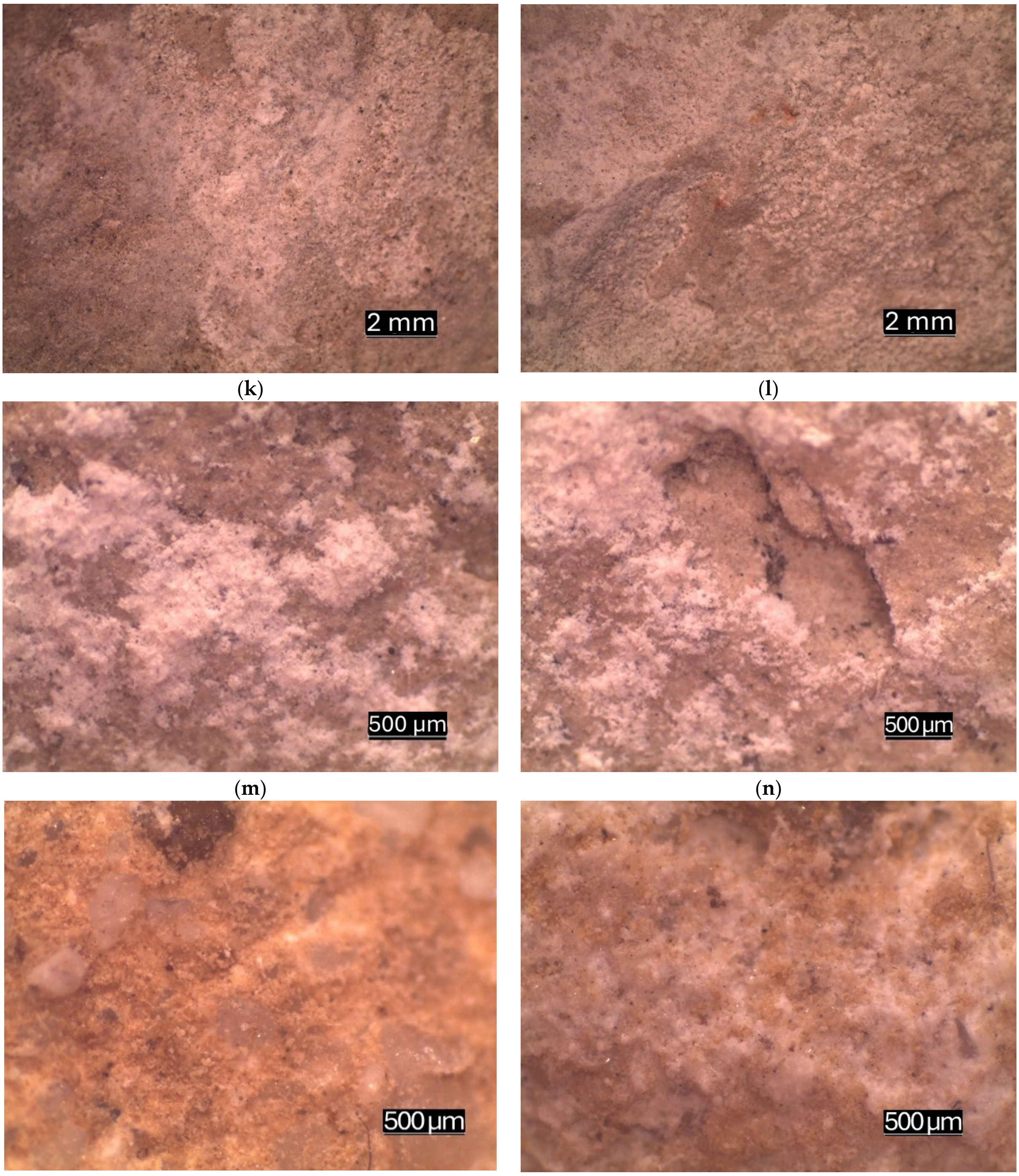


Figure 7. *Cont.*



(k) (l) (m) (n) (o) (p)

Figure 7. *Cont.*

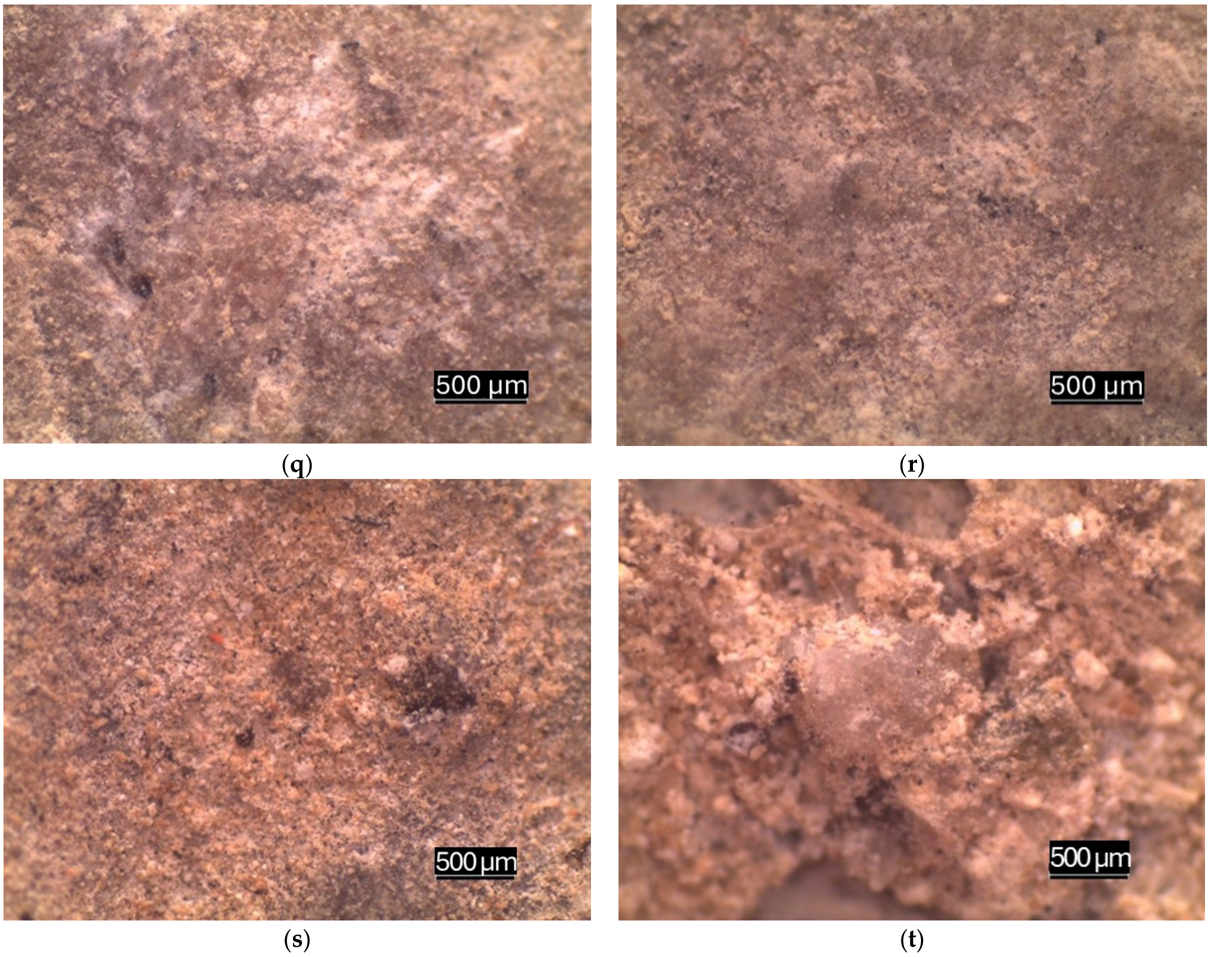


Figure 7. Visual analysis of the topography of the samples: (**a**) PEE—top face; (**b**) PEE—bottom face; (**c**) PEt—top face; (**d**) PEt—bottom face; (**e**) PPch—top face; (**f**) PPch—bottom face; (**g**) PEch—top face; (**h**) PEch—bottom face; (**i**) PEC—top face; (**j**) PEC—bottom face; (**k**) PER—top face; (**l**) PER—bottom face; (**m**) PES—top face; (**n**) PES—bottom face; (**o**) PLE—top face; (**p**) PLE—bottom face; (**q**) PE1—top face; (**r**) PE1—bottom face; (**s**) P3P—top face; (**t**) P3P—bottom face.

The chromatic properties of the materials are primarily influenced by their composition, particularly the presence of trace elements such as iron or manganese oxide. However, these properties are also impacted by textural variations, including pore size and the presence of banding [32].

We determined some associated issues using the results obtained from the micrographs and the analysis performed with the colorimeter, particularly between the PER and PEC samples. These samples not only exhibit a very comparable appearance but also have a low ΔL (4.9), indicating that they are visually similar. The same result applies to the PEt and P3P samples—in this case, with a ΔL of 1.0. The results obtained for the colourimetric coordinates are consistent with those of a study conducted by Occhipinti et al. [33], which examined the colour properties of carbonate rocks from historic buildings in the city of Catania.

3.2. Mineralogical Analysis

The results obtained from the X-ray diffraction (XRD) analysis are summarized in Table 7 and Figure 8. These results provide information regarding the peaks associated with the mineralogical phases present in each sample, enabling categorization based on their specific characteristics.

Table 7. XRD results.

Samples	Mineralogical Peaks Identified	Categorization
PEch	Calcite	Efflorescence on limestone
	Gypsum	
	Nitre	
PES	Calcite	
	Nitre	
	Coquimbite	
	Rozenite	
	Gypsum	
	Huntite	
	Vaterite	
	Dolomite	
PE1	Calcite	Dolomitic limestone
	Dolomite	
	Quartz	
PLE	Calcite	
	Dolomite	
	Quartz (trace amounts)	
PEt	Quartz	Marlstone
	Calcite	
	Potassium feldspar	
	Plagioclase	
	Mica	
P3P	Quartz	
	Calcite	
	Potassium feldspar	
	Plagioclase	
	Dolomite	
	Mica	
PER	Calcite	Typical limestone
	Quartz	
	Kaolinite (trace amounts)	
PEE	Calcite	
	Quartz	
PEC	Calcite	
	Quartz	
PPch	Dolomite	Dolostone/Magnesian limestone
	Calcite	
	Quartz	
	Potassium feldspar	

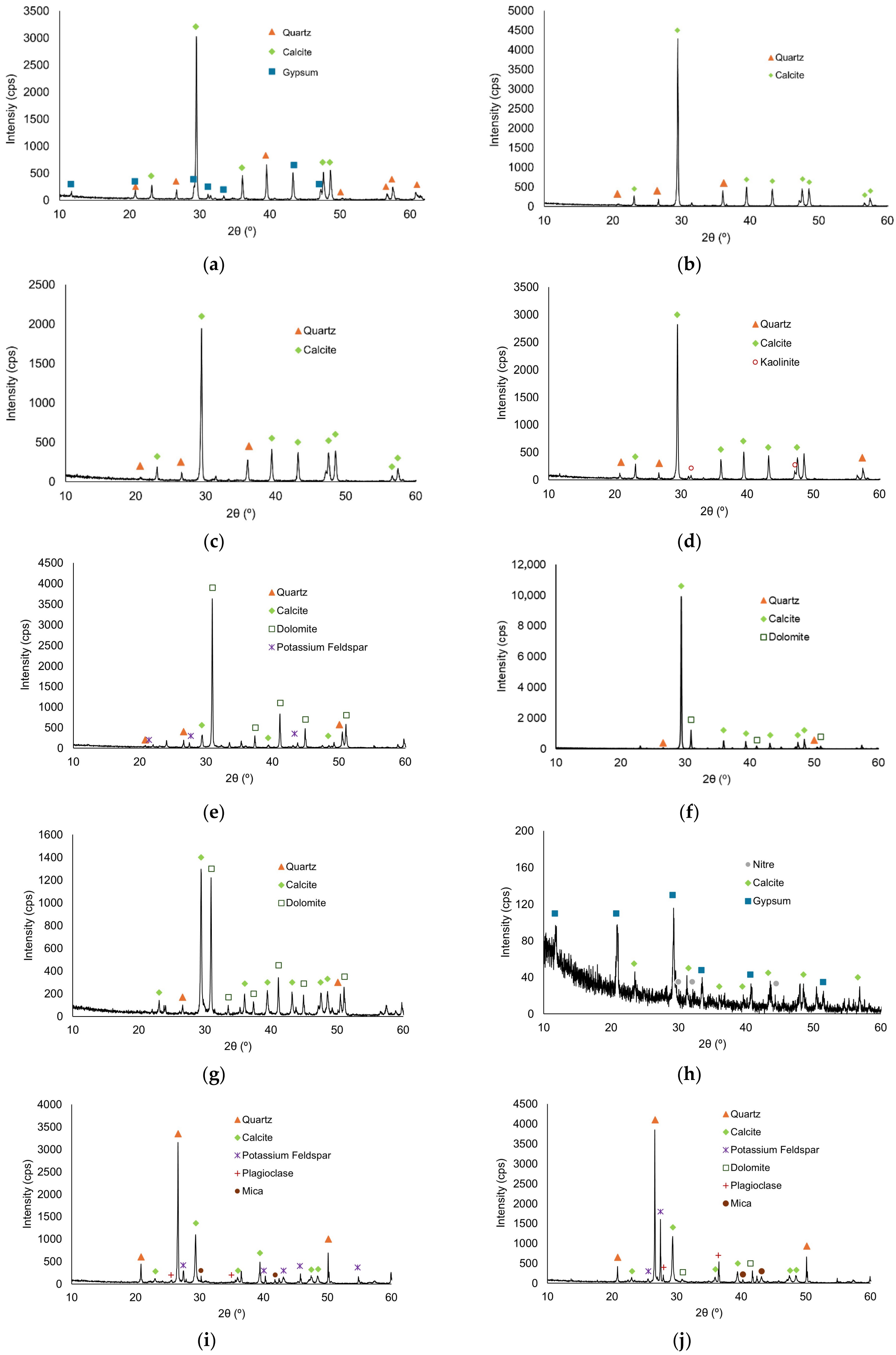


Figure 8. XRD graphs obtained: (**a**) PES; (**b**) PEC; (**c**) PEE; (**d**) PER; (**e**) PPch; (**f**) PLE; (**g**) PE1; (**h**) PEch (**i**) PEt; (**j**) P3P.

The mineralogical analysis (Table 7 and Figure 8) yielded the typical composition of regional calcitic limestone (i.e., samples PER, PEE, and PEC) and dolomitic limestone (PE1 and PLE); however, one sample was more similar to a dolostone (sample PPch). As expected, the sampled efflorescence indicated the presence of sulphates such as gypsum (Ca sulphate), coquimbite (Fe and Al sulphate), and rozenite (Fe sulphate); nitrates such as nitre (K nitrate); and secondary carbonates such as vaterite (Ca carbonate) and huntite (Fe and Mg carbonate).

3.3. Chemical Analysis

A preliminary analysis was carried out on Ançã stone from the region for comparison with the new samples and those from the literature, followed by an analysis of the samples chosen from the Sé Velha cathedral. The results are presented in Table 8.

Table 8. Chemical composition data for the original Ançã stone supplied by the stone museum (LOI: Lost on Ignition).

	%Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Sr	LOI
A1	0.030	0.395	0.241	2.488	0.019	0.059	0.030	0.257	54.330	0.019	0.001	0.135	0.046	41.950
A2	0.129	0.533	0.298	4.236	0.032	0.135	0.194	0.423	51.595	0.015	0.002	0.145	0.044	42.200

Additionally, the mineralogical analysis revealed that both samples (A1 and A2) were nearly monomineralic, consisting primarily of calcite, with a very minor, almost vestigial, presence of quartz. This result indicates a highly pure and, therefore, soft limestone.

The results obtained from the X-ray fluorescence (XRF) analysis for the samples investigated in this study are summarized in Table 9. These results provide information on the quantification percentage of the chemical elements present in each sample.

Table 9. XRF results.

Elements (%)	PEE	PEt	PEch	PPch	PEC	PER	PE1	PLE	P3P	PES
Cl	0.25	0.86	-	0.53	0.05	0.20	0.61	0.09	1.00	0.17
Al	0.28	1.03	0.33	0.32	0.26	0.27	0.28	0.27	0.97	0.26
Ca	86.37	62.72	29.96	75.36	88.08	85.86	81.39	87.80	67.76	88.97
Cr	-	0.04	-	0.04	-	-	-	-	0.04	0.05
Cu	-	0.03	0.86	0.11	0.03	-	-	-	0.04	0.02
Fe	3.45	6.58	2.36	9.26	2.13	2.37	6.22	2.96	6.67	2.17
K	0.89	4.84	0.40	2.66	1.05	1.19	1.59	0.92	5.78	0.81
Mg	0.10	0.24	0.23	1.88	0.23	0.09	0.81	0.51	0.30	0.09
Mn	0.07	0.14	-	1.04	0.08	0.03	0.59	0.61	0.20	0.04
Ni	0.05	0.04	0.45	0.03	0.03	0.02	0.04	0.02	-	0.02
O	6.00	9.14	53.16	5.78	5.20	7.29	6.34	5.13	5.41	4.81
P	0.30	0.47	3.77	0.30	0.25	0.21	0.24	0.20	0.38	0.22
S	0.54	0.78	6.81	0.18	0.95	1.21	0.12	0.08	0.70	0.70
Si	1.24	12.01	1.43	2.12	1.27	0.83	1.25	1.12	9.76	1.20
Sr	0.16	0.10	0.06	0.04	0.14	0.17	0.10	0.02	0.12	0.14
Ti	0.24	0.55	-	0.21	0.20	0.21	0.23	0.18	0.49	0.25
Zn	0.03	0.08	-	0.01	0.01	0.02	0.06	0.05	0.10	0.02

The results obtained from the chemical analysis (Table 9) agree with the lithological and mineralogical features of the studied samples. These limestone-type samples were found to be extremely rich in Ca, whereas the more dolomitic samples presented slightly higher Mg and Fe values. The amounts of Al remained low, as expected for carbonate-rich rocks. The efflorescence results indicated some higher amounts of S, Fe, and Cl.

3.4. SEM/EDS Analysis

Figures 9 and 10 present the results obtained from the SEM/EDS analyses of the most representative samples of the different stones.

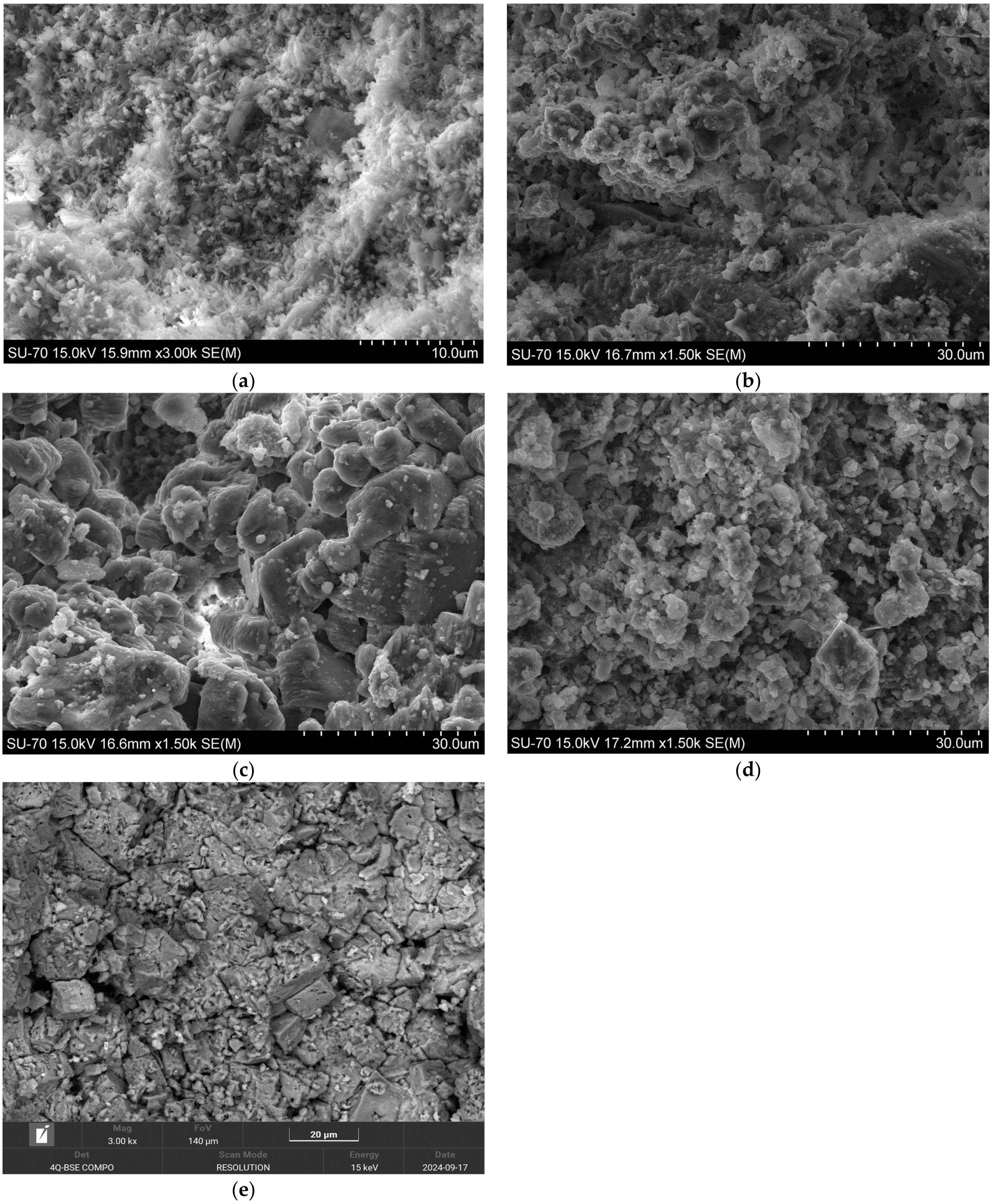


Figure 9. SEM images from the samples: (**a**) P3P; (**b**) PE1; (**c**) Pech; (**d**) PEE; (**e**) PPch.

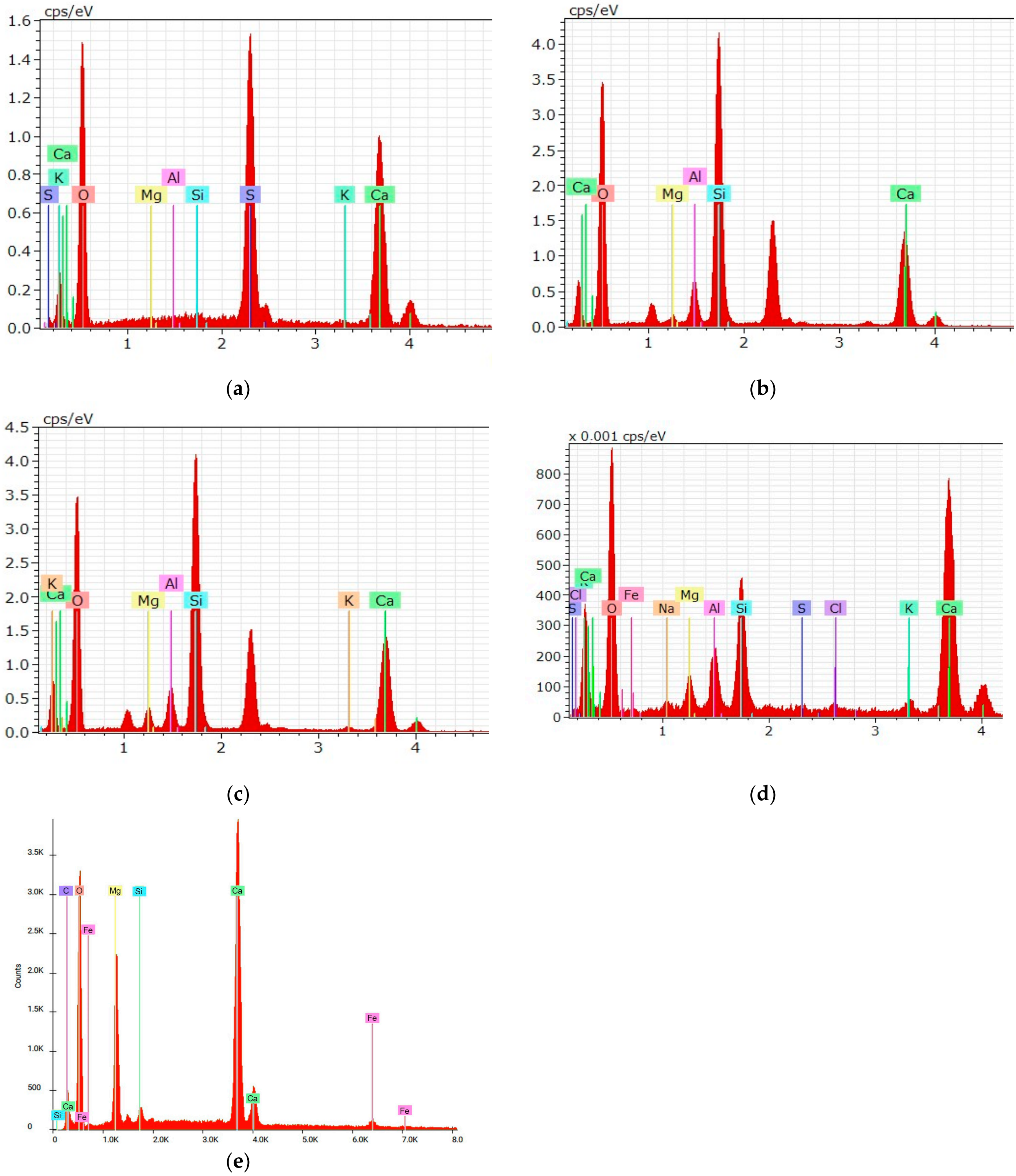


Figure 10. EDS analyses: (**a**) P3P; (**b**) PE1; (**c**) Pech; (**d**) PEE; (**e**) PPch.

SEM images show some textural differences between samples, but the main aspects are in the analysis results showing samples richer in Ca, such as PEE and PPch (the latter also in Mg), whereas others show more Si content (such as PE1 and Pech; P3P shows distinctive S presence).

4. Discussion

Previous studies focused more strongly on lower portions of the monument and the Porta Especiosa portal (separately), while analyses of the samples in the present investigation were taken from the internal faces of the wall facades and from the Porta Especiosa. These areas were defined for sampling due to their lower risk of contact with visitors and the resulting contamination. This approach enabled us to advance our understanding of this monument.

Previous studies indicated the presence of different types of carbonate rocks such as dolostone, calcitic dolostone, and Pedra de Ançã limestone (white to yellowish and marly to grey) at the Porta Especiosa portal, although this position did not achieve consensus and appears to depend upon the sampling location. Most of the results obtained from other sampling areas considered the use of dolostone, with the main body showing a dark patina that hides the yellowish colour of the dolostone used in the frames of windows.

Chemical and mineralogical analyses (Tables 7 and 9), as well as SEM/EDS results, clearly indicate the presence of different types of stone and efflorescence.

Four different types of stone were detected among the samples, based on their analysed mineralogical composition (via XRD) and chemical characteristics (via XRF and SEM/EDS, the latter just on selected samples).

The PER, PEE, and PEC samples composed primarily of calcite (calcium carbonate) with Ca contents higher than 80% corresponded to typical Ançã limestone, which agrees with the results from previous studies. PEE and PEC were both relatively pure in their mineralogical (only calcite and some quartz) and chemical composition (with around 1% of Si and predominant Ca). However, PER showed the presence of S, suggesting the additional presence of sulphates, which were likely not detected via XRD due to their amorphous structures.

The mineralogical composition of samples PE1 and PLE indicated the predominance of calcite but with a significant presence of dolomite (calcium and magnesium carbonate) and an increase in Mg content compared to that indicated via the chemical analyses. PE1 showed the presence of Fe, also suggesting the presence of iron oxides/hydroxites, which were likely not detected via XRD due to their amorphous structures. These samples corresponded to a variety of dolomitic limestone locally known as Outil Limestone.

Based on the chemical analysis, dolomite was predominant in the PPch sample, albeit with the presence of calcite due to an increase in Mg and a decrease in Ca contents. Therefore, this sample was a dolostone/magnesian limestone, which points to a carbonate rock that differs from common limestone due to being more dolomitic (instead of calcitic), which is locally designated as Portunhos Limestone.

This compositional substitution of calcite by dolomite, which is common in carbonate sedimentary deposits, usually occurs due to the effects of diagenesis over geological time, with practical consequences on the physicochemical behaviour of these rocks. Dolomite, which is a more magnesian stone, has greater chemical stability and, generally, offers higher mechanical resistance (in most of the parameters relevant to building materials, such as the compressive strength and elastic modulus), resulting in a “harder” stone [34]. Thus, in this case, the Ançã Limestone was found to be the most “vulnerable” to both chemical and physical degradation but also much more “workable” due to being “softer” (less “hard”), particularly when used for ornamental purposes.

It is possible to establish a sequence of increasing resistance (i.e., decreasing vulnerability) for Ançã Limestone (PER, PEE, and PEC)—Outil Limestone: PE1 and PLE samples—Portunhos Limestone (PPch sample), mainly containing dolomite (lower in Ançã and higher in Portunhos); in addition, dolomite generally shows higher mechanical resistance than calcite [35]. The greater vulnerability of the Ançã Limestone is well illustrated in the PES sample, which corresponds to its calcite-rich typology (Ançã Limestone) albeit with the occurrence of gypsum (hydrated calcium sulphate) and placement outdoors, leading to weathering and urban traffic.

These three types of limestone occur in the region of Coimbra and represent the main typologies of construction stone and ornamentation at the local and regional levels and are present in both historical and contemporary buildings.

The PEt and P3P samples, on the other hand, were still carbonated but presented a different chemical–mineralogical composition compared with that of Ançã, Portunhos, and Outil limestone. With the significant presence of quartz and feldspars (both silicates), the calcite content decreased, whereas the Si, Al, K, and Fe contents increased. These features indicate marlstones, which are softer and chemically more vulnerable than the other three types of limestone previously described. These two samples were located (Figure 5) in a different part of the building, relatively far from the famous Porta Especiosa on one of its more monumental components, close to all other samples. These stones likely represent a "second-class" choice or a posterior replacement using stones of lesser quality.

P3P sample SEM/EDS analysis shows a distinctive S presence, pointing to the formation of efflorescences, not detected on XRD most probably due to their amorphous state.

Considering the efflorescence, gypsum (hydrated calcium sulphate) and nitre (hydrated potassium nitrate) were found in the PES and PEch samples. In the PEch samples, we found other compounds such as coquimbite (hydrated iron and aluminium sulphate) and rozenite (hydrated iron sulphate). Sulphates (gypsum) were most common in the PES samples, while nitrate (nitre) was most common in PEch, indicating different processes/causes of alteration, and, eventually, the influence of its position in the building. Moreover, the sulphate-rich PES sample was taken from the interior of the building, whereas the nitrate-rich PEch sample was taken from the exterior and exposed to much more traffic and bird droppings.

These results reveal the use of different types of carbonate stones in different parts of of the Sé Velha Cathedral, as presented in Figure 11.

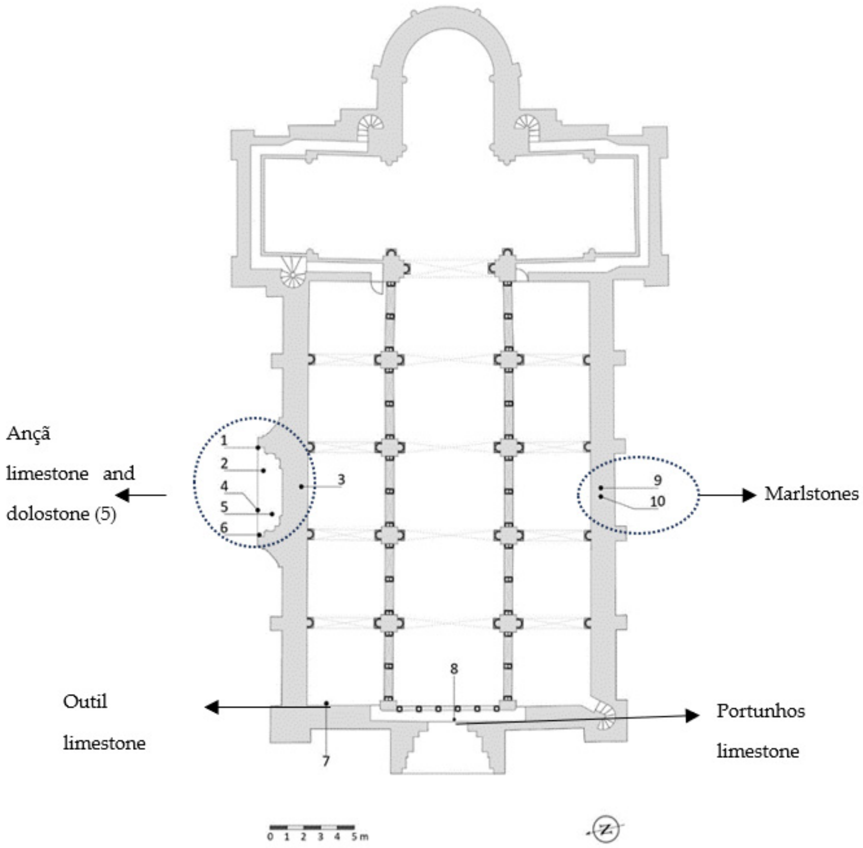


Figure 11. Distribution of carbonate stones (recorded from new data). 1—PEE; 2—PEch; 3—PES; 4—PEC; 5—PE1; 6—PER; 7—PLE; 8—PPch; 9—PEt; 10—P3P.

Lastly, the various chemical and mechanical characteristics of the different stones used in the construction of this cathedral explain the different damage patterns observed.

5. Conclusions

The present investigation analysed samples from different locations of the Sé Velha Cathedral (Coimbra) to identify the different types of limestone used in the cathedral's construction. On the upper floor of the cathedral, we identified four different types of carbonate stones. Based on the mineralogical and chemical analyses carried out, the use of Ançã limestone was apparently concentrated around the Porta Especiosa, along with dolostone. These conclusions agree with those from previous investigations by LNEC. However, other types of stone were used in other areas of the monument, namely near the large windows, which differ between the front (Portunhos limestone) and side facades (marlstones, Outil limestone). These data reveal the use of stone from different quarries in the Coimbra region for the upper floors of the cathedral, which has not yet been studied.

These results indicate that stones from different quarries were used in different stages of construction and alterations to the monument. In some cases, these stones are more vulnerable to the activities of atmospheric agents and pollution. Overall, the construction of the cathedral relied on different types of stones with different chemical and mechanical characteristics. Notably, the Porta Especiosa was constructed from more vulnerable types of stone and is already in an advanced state of degradation, making it impossible to remove it. Because this entryway faces north, it should be protected using a structure that allows one to control hygrothermal conditions.

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