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Comparative Study of Deterioration in Built Heritage in a Coastal Area: Barbanza Peninsula (Galicia, NW Spain)

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Abstract: The Barbanza Peninsula (Galicia, NW Spain) is located on the west coast of Galicia. It is a narrow tongue of terrain with an area of 416 km^2 and a high altitudinal gradient, with the top having a maximum height of more than 600 m at a distance of less than 5 Km from the sea. As a result of this, there is a significant rainfall gradient (from 900 to more than 3300 mm per year). In the peninsula, there are valuable historical buildings built with granite rock that show variable decay patterns. In this work, we have considered 14 of them, located in several parts of the peninsula, and we have studied their deterioration patterns. Some of them are close to the sea, with sea salt being a possible cause of decay, while for those located far from the sea, the high humidity and rainfall can be the most important cause of decay. A macroscopic study was carried out to determine the deterioration patterns. We have also analyzed the possible role of salts in the decay by using X-ray fluorescence as a screening technique to assess the presence of salts and the possible correlation of salts with the distance to the sea and using scanning electron microscopy to directly identify salts in some of the buildings. The most frequently reported decay is due to lichen growth (biological colonization). Depending on the proximity to the coast, the study area was divided into two zones: zone 1, closer to the sea (<1 km), with an important influence of sea salts and wind, and zone 2, further from the sea, with higher altitudes (center of the peninsula) and important rainfall, humidity, and therefore, biological colonization of stone surfaces. Crusts (to a lesser degree, because it is a mainly rural area) are more frequent in zone 1, but the state of conservation of stone in zone 1 is better than that in zone 2, possibly due to the concentration of urban centers in this zone and more interventions for cleaning stone surfaces. Finally, although we did not observe clear patterns in the appearance of salts in the buildings in agreement with the distance to the sea, we observed different patterns of salts in two of the buildings, one in each zone, which clearly show that, to some extent, salts are involved in decay.

Keywords: weathering; granite; built heritage; decay; salts; biological colonization

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1. Introduction

Although stone has been traditionally considered a resistant building material and has been commonly used in built heritage, it is well known that stone is subjected to deterioration processes that affect most historical buildings around the world (Siegesmund and Sneth) [1]. In Galicia (NW Spain), the most common historically used stone is granite, as it is the most abundant. Despite its high resistance to weathering and hardness, several weathering agents can accelerate its decay in buildings, as occurs with other rock types due to both natural and anthropic-related factors [2–4]. Indeed, the rock type, climate, and pollutants are referred to as the most important factors for assessing decay rates and types, due to the water pathways within buildings and stones [5–9].

Among decay processes, salt growth in the pore systems of building stone has been highlighted as the most damaging process [6,9–15]. The effect of salts depends on the stone porosity and absorption capacity, water sources, salt composition, and volumetric coefficients that determine whether salts crystallize on the surface of the rock ashlars (as efflorescences) or within the pore system (as sub-efflorescences) [5,6,11,13,15,16]. However, the complex pore system of most rocks and the poorly known distribution of moisture in buildings complicate the understanding of the mechanisms related to the migration, dissolution, and crystallization of salts [6,9,13,15–17].

Salts can come from several sources that are decisive for the type of salt [7,10,13,17–19]. Building materials, including stone and mortars, are a possible source of salts such as chlorides, sulfates, nitrates, and carbonates [2–4], as occurs with the use of incompatible materials such as Portland cement [20,21]. Sulfates of calcium, sodium, and magnesium are the most common among soluble salts in rocks [22,23]. Indeed, the origin of salts in building rock has also been observed in quarries [7]. Salts also can come from capillary rise from groundwater, which is considered as an ample source of salts because the waters in soil are dilute salt solutions [15,17]. The solutions contain chloride, sulfate, nitrate, carbonate, magnesium, calcium, sodium, potassium, and ammonium. Organic and biogenic sources of pollutants from human activities or organisms can produce phosphates and nitrates or even chlorides such as NaCl and $CaCl_2$ [3,4,24–27].

Because of the air pollution in urban environments, the deposition of atmospheric particles and gaseous pollutants, such as sulfur dioxide and nitrogen oxides, and acids, such as sulfuric, nitric, and hydrochloric acids, contributes to salt weathering, and both dry deposition and rainfall are well-known source of salts [3,4,6,13,15,19,28], although chloride is reduced relative to sulfates, nitrates, and carbonates [15]. The effect of atmospheric compounds includes the sea salts in coastal environments, which are considered as the greatest contributor of salts. Water droplets introduce salts, of which Na, Mg, Ca, and S are the most common [15]. In any case, water inputs and moisture changes cause salts to cyclically crystallize, hydrate, and dissolve, enhancing the deterioration role of salts.

In granites, despite their low porosity, severe damage has been reported, especially in coastal environments, because of the damage to feldspars and plagioclase that undergo salt-filling fracturing [29–33]. Also, in biotite, the opening of crystals by exfoliation planes is observed [7,34]. The ions dissolved in water that will form these salts are also considered to be a factor in chemical weathering. Solutions rich in sodium chloride, sodium carbonate, and sodium sulfate [35] result in the dissolution of Si from quartz precipitates as amorphous Si.

In this work, we considered 14 historical buildings of the Barbanza Peninsula (Western Galicia, in NW Spain). All of them have been built with granite ashlars. The Barbanza Peninsula is a rural area, with the studied buildings being located at several distances and heights from the seacoast. There is a significant humidity gradient that probably affects the seaside effect, causing several different degrees of salt weathering. This is a screening study that attempts to understand the possible effect of sea salts on the decay of historical buildings in the area, in an attempt to supply useful information to provide measures for the restoration and preservation of built heritage in the area.

2. Materials and Methods

2.1. Study Area

2.1.1. Geography

The Barbanza Peninsula is a well-defined and consolidated geographical area, being the northernmost of the peninsulas located on the western coast of Galicia. It is located specifically to the north of the Rías Baixas (SW of the province of A Coruña), between the Arousa (to the South) and Muros-Noia (to the North) estuaries (Figure 1). It has an area of 416 km^2 defined by its main geographical feature: the Sierra de Barbanza, a mountain chain formed at the end of the Tertiary, more than 6 km long, that runs longitudinally, in an NE–SW direction. Its average altitude is 500 m above sea level, and its highest part is made up of small plateaus, with Iroite being the highest peak of the peninsula (687 m), separated by hills and crossed by several small river valleys, among which the Pedra and Coroño are highlighted. Thus, two large groups are distinguished: on the one hand, the slopes (mostly with very pronounced and abrupt escarpments), and on the other hand, the coastal platforms, strips of altitude less than 200 m located to the north and southeast (with relief where smooth forms predominate), alternating beaches, sandbanks, and rocky cliffs behind which a narrow coastal plain extends (which expands in certain places).

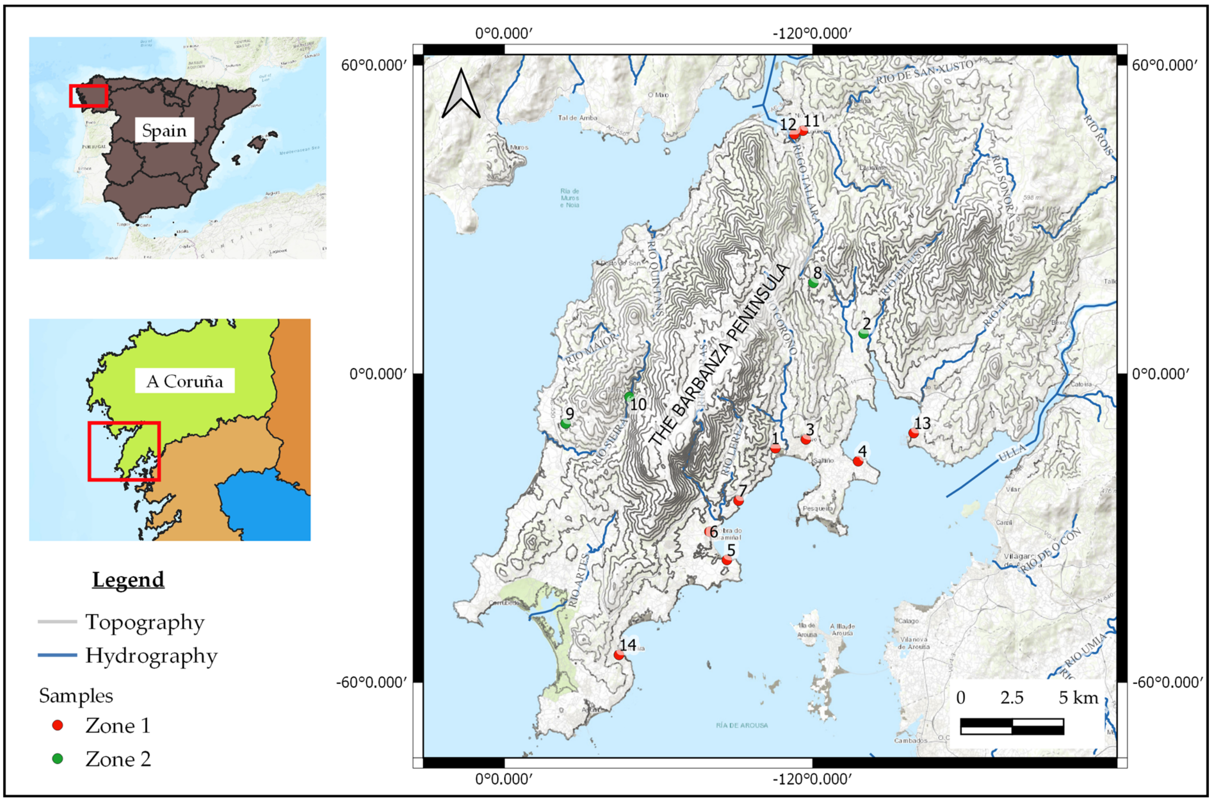

Figure 1. Location of the studied buildings on a topographic map of the Barbanza Peninsula (Galicia, Spain).

2.1.2. Climatological Setting

The Barbanza Peninsula belongs to the humid oceanic climate domain [36], characterized by a small annual thermal oscillation and abundant rainfall (above all in winter), although with some tendency towards summer aridity.

The range of annual precipitation is just under 900 mm in the coastal area and up to more than 3300 mm recorded on the top of Barbanza mountains, with a significant precipitation gradient versus altitude and topographic position. Indeed, in Ribeira (the most populated location in the outer part of the Ria), the annual precipitation is around 1250 mm, while in Boiro (the most populated location in the inner part of the Ria), the annual precipitation is about 2000 mm. The distribution of rainfall throughout the year is very irregular, but rainfall is more abundant during the three winter months (about 40% of the annual total) [37].

The average temperature ranges between 18.5 °C in summer and 9.5 °C in winter (typical of temperate climates in a humid oceanic domain) with a significant altitudinal gradient, especially noticeable in the duration of the seasons. The differences between the area closer to the sea (coastal platform) and elevated areas (slopes) are significant, for instance, in the average annual frost days, which do not exist in the lower levels but occur in the high-level areas.

There are two prevailing winds, from the SW in winter, associated with storms, and from the N to NE in the summer, more moderate. The highest speeds are usually reached during the spring, when they tend to oscillate between 20 and 40 km/h, although sometimes (in autumn) they even reach 80 km/h.

In any case, despite the small area of the peninsula, the presence and orientation of the Sierra de Barbanza favor the existence of a significant climatic variability, reflected in the proportional increase in rainfall rates with respect to altitude and in the existence of higher temperatures in areas open to warm air from the ocean.

2.1.3. Geology

The geological setting of the Barbanza Peninsula, dominated by granite [38], has played a fundamental role in the construction of the buildings with their natural environment. In general, most of the churches and cultural monuments in Galicia are built with granite material, possibly extracted from quarries located in nearby areas.

The Barbanza Peninsula includes a lithological variety (Figure 2). Among the types of granites, the one with the greatest representation is a granite with two micas of medium–coarse grain, called the Barbanza type, the majority in the entire central sector. In the Corrubedo area (SW), this is transformed into a fine-grained variant. Examples of churches with Barbanza-type granite are the churches of San Xoán de Macenda or Santa Maria de Ribasieira (Figure 3).

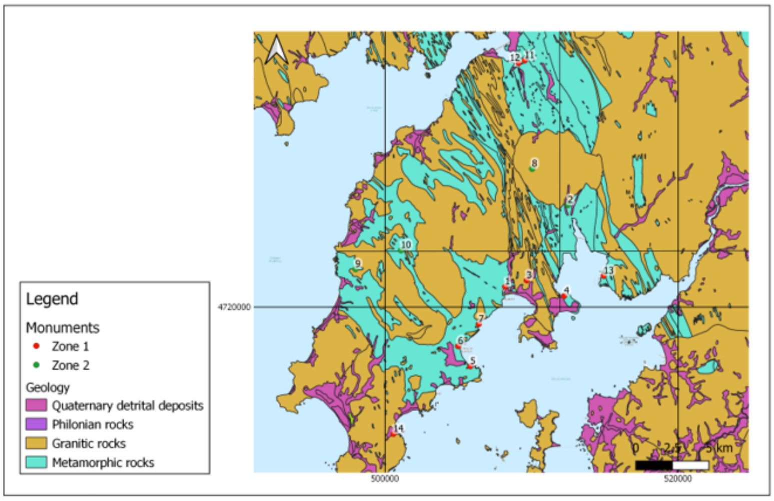

Figure 2. Location of the studied buildings on geological map of the Barbanza Peninsula.

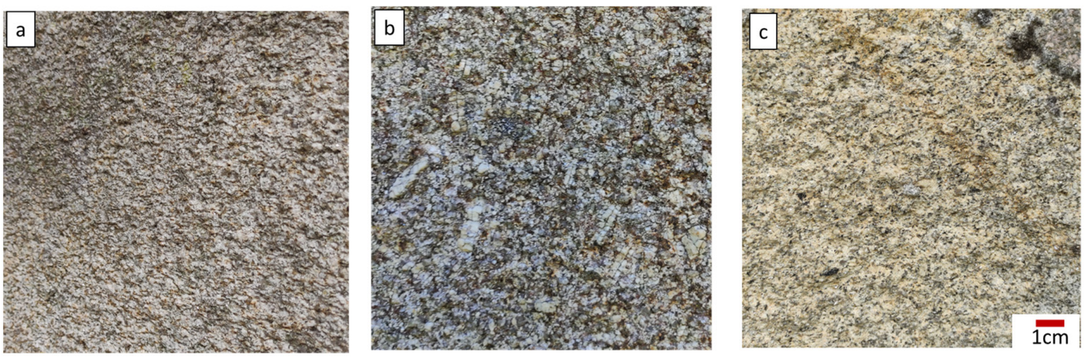

Figure 3. Different types of granite in walls of churches. (**a**) Granite with two micas of fine–medium grain in San Martiño de Noia Church. (**b**) Granite of two medium-grain micas in Church of San Xoan de Macenda; plagioclase phenocrysts are visible. (**c**) Fine-grained variant; Church of Santa Maria de Ribasieira.

Another type of granite forms part of the migmatitic domain: oriented, physical, and glandular granitic rocks that have undergone a process of migmitization and later metasomatism are distinguished. This type of oriented granite is visible in churches such as San Martiño de Noia (Figure 3). In the NE of the peninsula, the Noya Complex is found, which is formed by a granite of two medium-grain micas.

Other rock types present are shale, gneiss, and other metamorphic materials that make up the blastomylonitic pit. The structures of some of the churches and pazos studied include, in addition to granite, metamorphic rocks (such as Pazo da Merce).

Although less common, there are deposits of Quaternary origin, made up of materials of sedimentary origin and located mainly in coastal areas.

2.2. Description of Studied Buildings

This study was carried out on a total of 14 historical buildings distributed throughout the Barbanza Peninsula (Figure 1) and covering the communities of Boiro, Rianxo, Noia, Ribeira, Porto do Son, Lousame, and Pobla do Caramiñal. The types of monuments are mostly churches [39], chapels with significant historical value, and two country houses. The "pazos" represent admirable stately homes, a kind of small rural palace, typical of the Galician landscape and express a model of life based on country economic activities and the climate. However, in many cases, the abandonment of these constructions is notable, and there is little existing information related to the constructions and especially to their state of conservation. It is noteworthy that they were built in different centuries, so their state of conservation, style, and architectural features are very variable.

Table 1 summarizes the most important data, including the construction period of the selected monuments, considering the factors that may contribute in different ways to the degree of deterioration: rock type, altitude, and distance from the sea. It is important to note that even though metamorphic rocks (schists and gneiss) have been found in some bases and other reconstructed walls, this study just focuses on the granite façades.

Table 1. Description of the monuments studied.

No.	Name of the Monument	Location	Lithology	Distance from the Sea (Km)	Altitude (m)	Categories of Populated Places	Construction Age (Century)	Zone
1	Pazo de Goians (with Chapel)	Boiro	Granite (medium–coarse grain)	0.5	20	Hamlet	XVIII *	Zone 1
2	Church of San Pedro de Bealo	Boiro	Granite (medium–coarse grain)	3	30	Hamlet	XIII *	Zone 2
3	Church of Santa Baia de Boiro	Boiro	Granite (medium–coarse grain)	0.9	40	Village	XII *	Zone 1
4	Church of San Cristovo de Abanqueiro	Boiro	Granite (Fine–medium grain)	0.2	15	Hamlet	XVIII	Zone 1
5	Church of Santa Maria de Jobre	Puebla del Caramiñal	Granite (medium grain)	0.5	7	Hamlet	XVIII	Zone 1
6	Church of Santiago da Pobra do Daen	Puebla del Caramiñal	Granite (medium–coarse grain)	0.2	20	Village	XVI	Zona 1
7	Pazo da Merce	Puebla del Caramiñal	Granite (medium–coarse grain)	0	18	Hamlet	XV	Zone 1

Table 1. *Cont.*

No.	Name of the Monument	Location	Lithology	Distance from the Sea (Km)	Altitude (m)	Categories of Populated Places	Construction Age (Century)	Zone
8	Church of San Xoan de Macenda	Boiro	Granite (fine–medium grain)	7.3	245	Hamlet	XVIII	Zone 2
9	Church of Santa Maria de Caamaño	Porto Son	Granite (medium–coarse grain)	1.5	57	Hamlet	XII*	Zone 2
10	Church of Santa Maria de Ribasieira	Porto Son	Granite (medium–coarse grain)	4.5	167	Hamlet	XVIII	Zone 2
11	Church of Santa Maria a Nova	Noia	Granite (Fine–medium grain)	0.1	9	Village	XIV	Zone 1
12	Church of San Martiño de Noia	Noia	Granite (two types)	0.1	9	Village	XV	Zone 1
13	Pazo de Mortelo	Rianxo	Granite (fine–medium grain)	0.1	11	Village	XVII	Zone 1
14	Church of Santa Uxia de Ribeira	Ribeira	Granite (fine–medium grain)	0.2	5	City	XIX	Zone 1

Note: (*) Heritage has been exposed to renovations over time.

The monuments were divided into two distinguishable zones (Figure 1):

- Zone 1: Monuments located on the coastal platform, closer to the sea (<1 km). According to the natural conditions described in Section 2.1, the influence of sea salts and wind on the decay of stone is expected, but also there is more human activity in this area because it is the area with the highest concentration of people in the peninsula.
- Zone 2: Monuments located on the slopes of the Sierra de Barbanza, with higher altitudes and higher precipitation (more than 3300 mm collected) and humidity.

2.3. Fieldwork and Laboratory Methods

The 14 monuments were studied during the summer season of 2021, as indicated in Table 1. A careful macroscopic characterization was carried out to identify decay patterns on the stone blocks used for their construction. Location and geology maps were built using QGIS version 3.12. Samples of stone fragments taken from the surface of some granite blocks were taken for elemental analyses. As sampling is very restricted in heritage buildings, it was not possible to obtain samples of all of them. As the purpose of this work was to screen the possible effect of salts on the stone, the analyses focused on elements that usually form salts in stone-built monuments.

2.3.1. Chemical Analyses

Elemental analyses of the samples were performed using a Bruker-Nonius wavelength-dispersion S4 Pioneer fluorescence spectrometer under helium purge. Samples were previously crushed and milled into powder. The elements considered that usually form salts are Na, K, Mg, Ca, Cl, S, and P. All XRF analyses were performed on three aliquots per sample.

2.3.2. Scanning Electron Microscopy (SEM) Coupled with Energy Dispersive X-ray Spectrometry (EDS)

The surfaces of two churches of each zone (1 and 2) were analyzed by scanning electron microscopy (SEM) for the comparison of macroscopic observations carried out and elemental analyses with these observations. These churches are the church of Santa Baia de Boiro (zone 1), located in the center of Boiro, and the church of Santa Maria de Ribasieira (zone 2).

Analyses were performed with a scanning electron microscope (Cambridge Instruments, version 360 Stereoscan, UK, Cambridge) equipped with a microanalyzer for energy dispersive spectrometry (EDS) (EDAX model) with an ultrathin (UHT) window in order to ensure the detection of light elements. The operating conditions were set at an accelerating voltage of 20 kV, beam current of 0.2 mA, acquisition time of 100 s, and dead time of 30–35%.

Chemical elemental analyses were carried out according to standard mode and normalized by weight (%). The detection limit for the EDS system was approximately 0.1% weight. The accuracy of the analysis was periodically tested on standard USGS samples. Chemical analyses of the crust surfaces were performed in raster mode.

3. Results and Discussion

3.1. Macroscopic Observations

The in situ observations of the studied buildings reveal different patterns of deterioration, as expected [40]. Damages ranging from just aesthetic to structural damages have been identified. In general, the most frequent decay consists of biological colonization, discoloration, coating, and detachment, but dark crusts and salt efflorescences are also observed in some cases (Table 2), in agreement with the most common decay patterns observed in other monuments previously studied in the NW Iberian Peninsula [18,19]. The comparison did not include the façade orientation, which could be important for assessing climatic and seaside effects. It seems that biological colonization exhibited trends of exponential abundance with altitude (Figure 4).

Table 2. Patterns of deterioration observed in monuments (abundance: +++ high, ++ medium, + low).

No.	Name of the Monument	Patterns of Deterioration					
		Zone	Biological Colonization	Discoloration	Physical Damage	Efflorescence	Others
1	Pazo de Goians (with Chapel)	Zone 1	++	+	++		
2	Church of San Pedro de Bealo	Zone 2	++		+		
3	Church of Santa Baia de Boiro	Zone 1	+	++	+		
4	Church of San Cristovo de Abanqueiro	Zone 1	++	++	++	+	
5	Church of Santa Maria de Jobre	Zone 1	++	+	+	+	
6	Church of Santiago da Pobra do Daen	Zona 1	++	++	+		Dark crust; graffiti
7	Pazo da Merce	Zone 1	+++	+	+++		
8	Church of San Xoan de Macenda	Zone 2	+++	+			
9	Church of Santa Maria de Caamaño	Zone 2	++	++	+		

Table 2. *Cont.*

No.	Name of the Monument	Patterns of Deterioration					
		Zone	**Biological Colonization**	**Discoloration**	**Physical Damage**	**Efflorescence**	**Others**
10	Church of Santa Maria de Ribasieira	Zone 2	+++	+	++		Dark crust
11	Church of Santa Maria a Nova	Zone 1	++	+	+		
12	Church of San Martiño de Noia	Zone 1	+	++	+	+	Graffiti
13	Pazo de Mortelo	Zone 1	++	+	+		
14	Church of Santa Uxia de Ribeira	Zone 1	+				

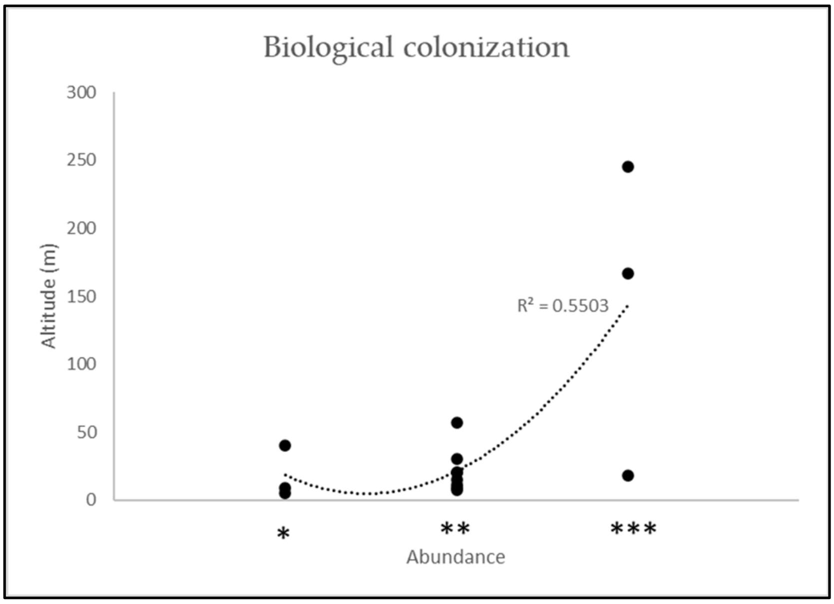

Figure 4. Biological colonization vs. altitude.

From macroscopic observations, it is clear that biological colonization is the most important effect on the studied buildings. Bacteria, cyanobacteria, algae, fungi, lichens, and plants were observed, as has been previously reported for this type of rock in Galicia [41–44]. In this area, lichen growth on granite blocks is the most common effect on stone monuments. Lichens form biofilms with variable color, texture, and thickness. The majority of them form white spots, but green, yellow, black, red, and orange spots have been found also, and sometimes they do not cover the whole stone surface. The common appearance is that of crustose lichens, and foliose lichens appear less frequently. In several cases, although lichen species were not identified, it is clear that there is no predominance of one species, but the species are mixed (Figure 5a). Other organisms present are the same ones that grow in preferably horizontal and shady areas where more humidity is observed [45–47]. In addition, higher plants that usually appear between cracks or on roofs are also present. Depending on the state of abandonment, they can invade the entire monument, as is the case of the Pazo de la Merced (Figure 5b) or the Chapel of Pazo de Goians. Due to the fact that biological colonization is usually associated with the presence of water [47], it is expected that the wetness regime and the characteristics of the stone material will be correlated with these growths in the Barbanza Peninsula, with the climate variability of the area being very important. They not only affect the different parts of the monument but also elements such as tombstones, statues, and plaques (Figure 5c,d). However, differences in the distribution and abundance of colonization can be distinguished considering four issues: (1) the highest areas of the peninsula (zone 2) with respect to the lowest (zone 1), (2) the marine environment in zone 1, (3) the humidity (ascending, descending, or localized), and (4) the orientation and distribution of the façades. These issues are described as follows:

- Location of the building in the peninsula: In the highest parts of the peninsula (zone 2) precipitation is significantly more abundant, and there is more forest cover; this is a more humid area than zone 1. Therefore, these monuments exhibit a higher level of biological colonization (Figure 5e). An example is the Church of Ribasieria (PU3), one of the most recent and with great deterioration due to biological action.
- Marine environment: Zone 1 is directly exposed to marine spray. The accumulation of salts also allows the proliferation of certain biological communities, such as nitrophilous lichens (Figure 6a). In this zone, in the vicinity of the ground, the typical communities are usually *Aspicilia Calcarea* [48]. Likewise, the areas of higher condensation and poor wind exposure will also allow biological colonization. There are several reviews on the processes of salt weathering of rocks and stones and the factors that control their impact [13,49–53].
- Climatic effect: Both the relative humidity and the precipitation gradient in Barbanza cause there to be moist areas and biofilm growth on areas of building façades (Figure 6a,b,e) because rainwater runoff promotes the development of lichens. Another more local form of damage is caused by water leaks through pipes that could form biofilms with a limited extent (Figure 6d). Lastly, the rising of water from underground due to capillarity [54] is also very noticeable, also causing areas of darkening, and its amplitude depends on the characteristics of the material (Figure 6c) of the walls and foundations and the composition of the ground on which the monument sits.
- Orientation of façades: It is generally observed that the combined action of wind (means of transport of lichens and substances that help their proliferation) and rain and the degree of sun exposure is influenced by the façade orientation (Figure 6f). In this case, most of the monuments presented greater alteration on the principal façade or portico (oriented NW, W, or SW) and the least alteration on that exposed to the E. The buildings that surround the monument can also affect the luminosity (especially in zone 1, where population centers are concentrated).

Moreover, there are monuments that show chromatic alterations due to discoloration. The chromatic alterations and coatings observed on these monuments are closely associated with the chemical process of weathering of the minerals, and they are localized in specific areas of some façades exposed to this process. Moreover, there is extrinsic metallic staining in other materials and structures due to corrosion, especially that of iron, copper, and alloys (Figure 7a,b).

Soluble salts may also be responsible for the deterioration of the stone used in the studied buildings [55–59], coming from several possible sources such as sea spray (main source in zone 1), anthropogenic air pollution (more abundant in zone 1 where the most populated villages are concentrated), organic sources, and other construction materials.

In addition, soluble salts usually cause the development of different types of coatings [4,54]. The most common coating is the so-called black crust that forms from polluting gases [55] and has been reported in numerous modern constructions [58]. However, due to the rural context of the Barbanza Peninsula and climatic factors, black crusts are less visible in this location than on other studied monuments; otherwise, they are found in sheltered areas (Figure 8a). Another recognized process was marine efflorescence (Figure 8b,c); however, it rarely appeared on the outer surface of façades, being more common inside the monuments. In fact, [58] reported that salt growth is sporadically observable on the outer surface of buildings and more commonly detected on indoor surfaces because salts are highly soluble when directly exposed to rainfall.

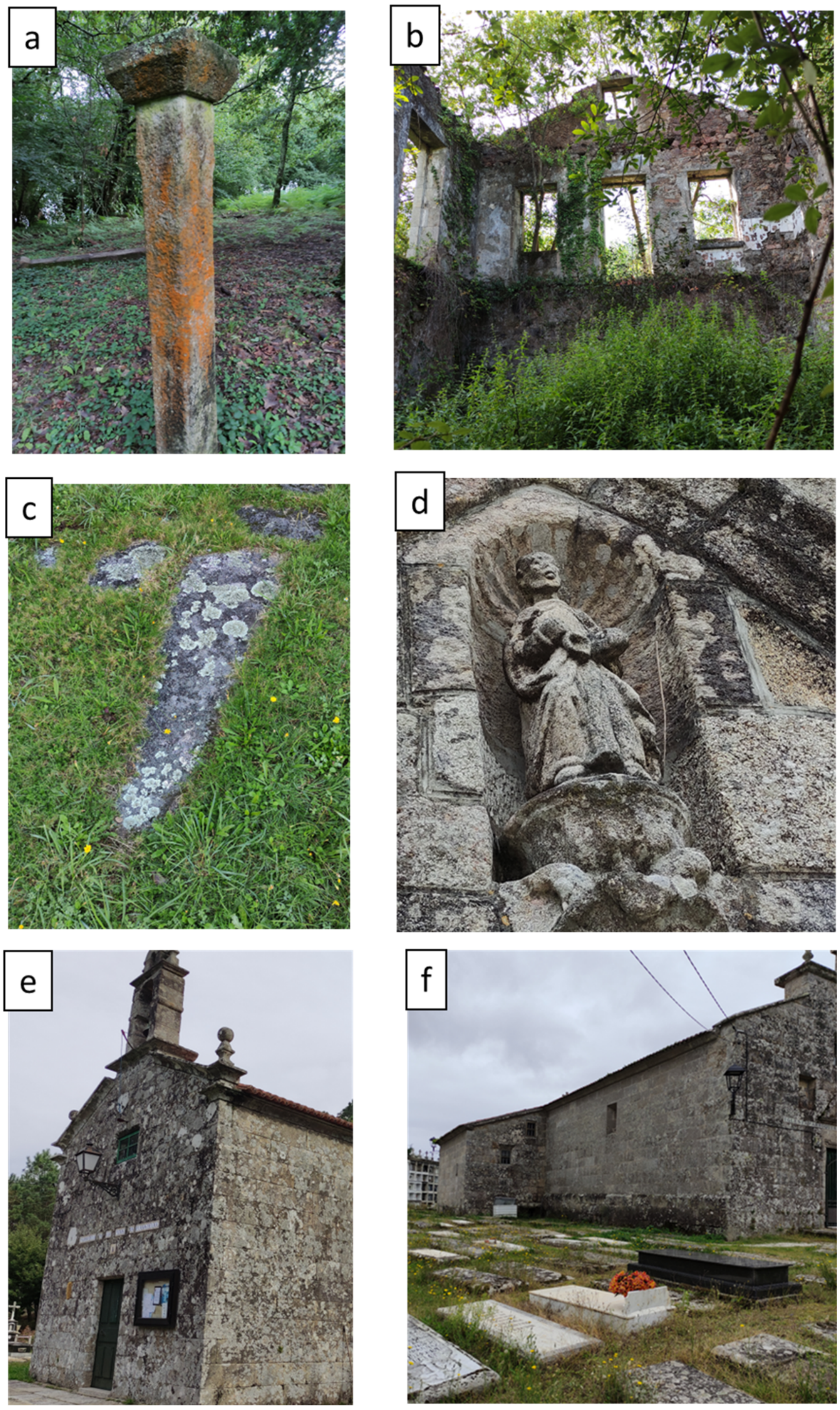

Figure 5. (**a**) Different communities of lichens in Pazo de Goians. (**b**) Plant invasion in Pazo de la Merced. (**c**) Lichens on tombstone of San Xoan de Macenda and (**d**) on the statue of San Pedro de Bealo. (**e**) All façades of Church Santa Maria de Ribaseira. (**f**) Local zones depending on humidity on Church of Santa Maria del Jobre.

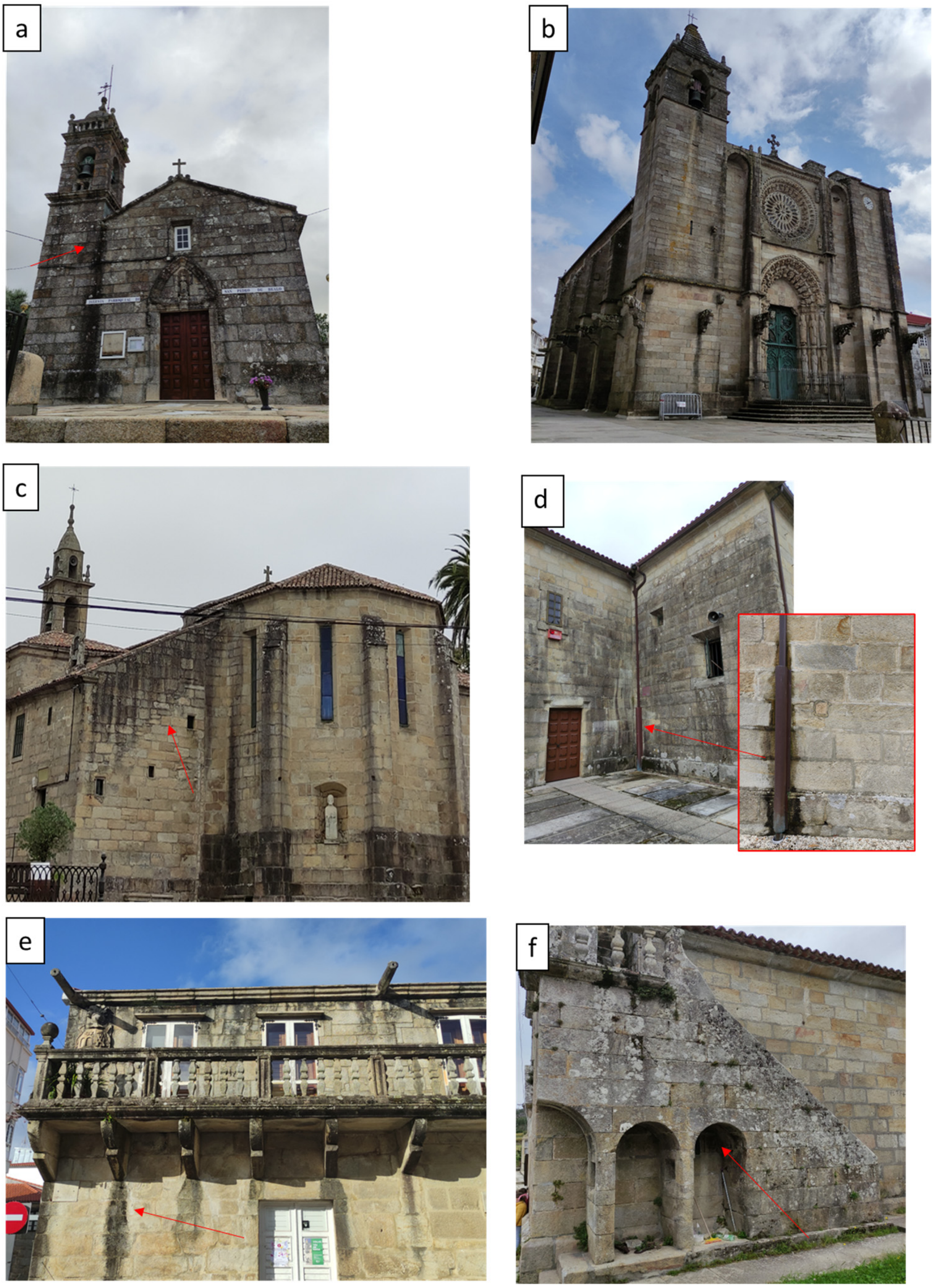

Figure 6. High descending humidity traces: (**a**) Church of San Pedro de Bealo, (**b**) Church of San Matiño de Noia, and (**c**) Church of Santiago da Pobra do Daen. (**d**) Leaks through pipes in Church of Santa Baia de Boiro. (**e**) Descending humidity in Pazo de Mortelo. (**f**) Different zones affected by biofilms (red arrow) on Church of Santa Maria de Caamaño.

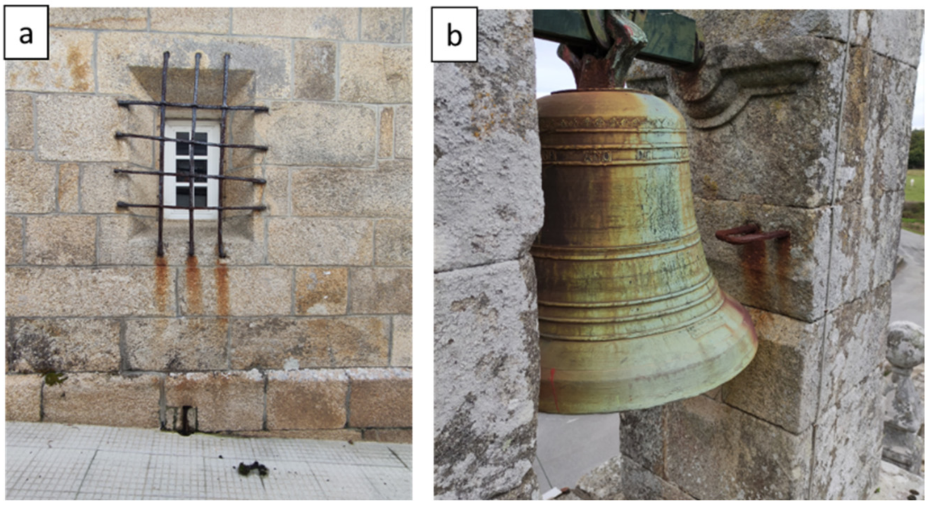

Figure 7. Chromatic alteration: (**a**) Church of Santa Maria de Bealo and (**b**) Church of Santa Maria de Caamaño.

Figure 8. (**a**) Black crust in the entrance of the Church of Santa Maria a Nova, (**b**) efflorescence on the exterior of the Church of Santa Uxia de Ribeira (red oval), and (**c**) efflorescence inside the Church of San Martiño de Noia.

Other worrisome decay patterns are those that cause physical damage that in the long term causes a significant loss of heritage value such as cracks (Figure 9a,b); deformation (Figure 9c); differential erosion (Figure 9d); and detachments (more often identified in this study), which include perforation gaps (Figure 9d,e), crumbling, and delamination (Figure 9f). Cracking may be due to weathering, flaws in the stone, static problems, rusting dowels, and too-hard repointing mortar [40]. On the other hand, crumbling was visible in several coarse-grained monuments, which exhibited granular disintegration. For example, in the Church of San Cristovo de Abanqueiro, this characteristic was present on all the façades but more pronounced at the entrance of the church and inside. Granular disintegration may be due to thermal stress [40] and the physical–chemical properties of the rocks. Damage due to erosive processes affects the surface of walls; statues; shields; figures; letters; and elements of aesthetic, ornamental, and/or cultural value, which can imply great destruction (e.g., Pazo da Merced).

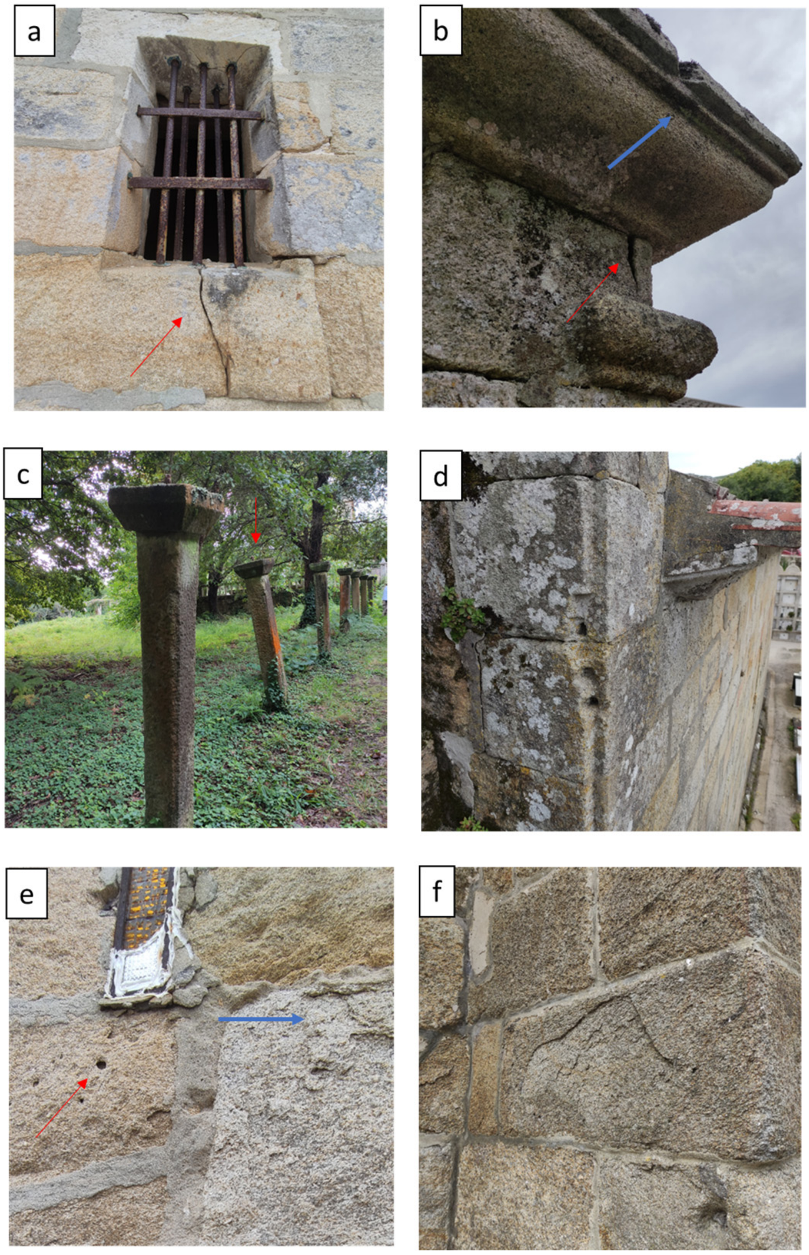

Figure 9. (**a**) Cracking in Church of San Cristovo de Abanqueiro; (**b**) crack (red arrow) and missing part (blue arrow) in Church of Santa Maria de Caamaño; (**c**) deformation in exterior columns of Pazo de Goians; (**d**) gaps (red arrow) and differential erosion (blue arrow) in Church of San Cristovo de Abanqueiro; (**e**) delamination in Church of San Martiño de Noia; (**f**) gaps in Church of Santa Maria de Caamaño.

Finally, graffiti (Figure 10a), which is considered a form of aesthetic deterioration caused by anthropogenic action, was also observed very locally in some churches (like San Martiño de Noia or Santiago da Pobra do Dean). However, the effort to recover cultural heritage was also observed in some monuments such as the Pazo de Goians (Figure 10b,c); here, the tower and main building have undergone maintenance in the last three years, and the recovery work on the chapel (currently in ruins) and rest of zones are future proposals projected in the medium–short term.

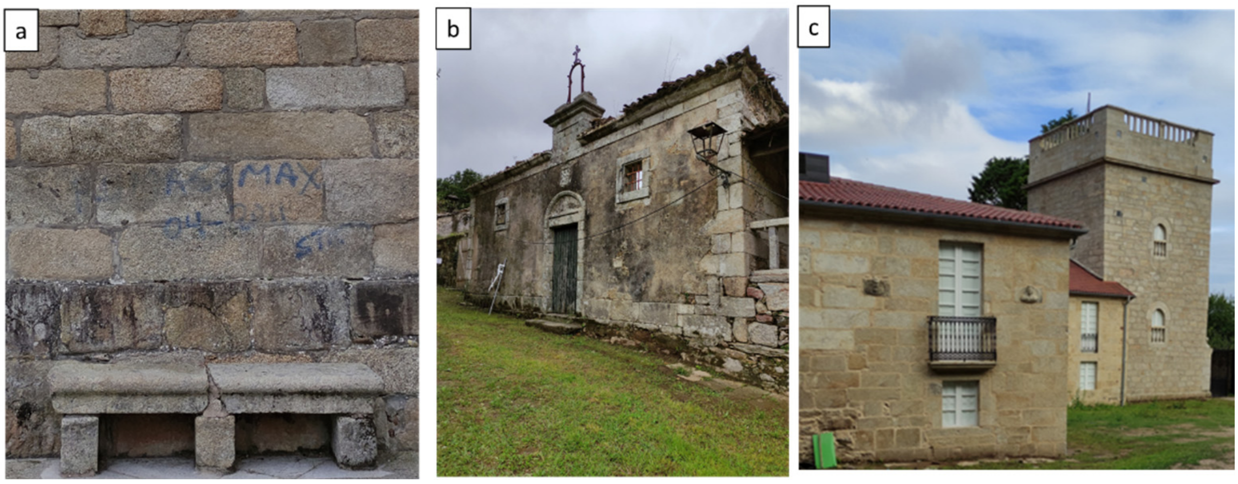

Figure 10. (**a**) Graffiti on Santiago da Pobra do Deán; (**b**) Chapel of Pazo de Goians in ruins; (**c**) Torre de Goins and the principal reconstructed building.

3.2. Elemental Analysis

A comparison was made between elements (as oxides) that usually form salts [10,15] measured by XRF (Table 3), including loss on ignition (LOI) versus the distance to the sea of the monuments studied, with the aim of assessing the possible effect of the sea salts on decay. Given the altitudinal and rainfall gradient of the Barbanza Peninsula, we also compared altitude with the presence of the same salts. For both comparisons, Pearson's linear correlation coefficient was used. Figure 11 shows the position of the studied buildings as a function of their distance from the sea and their altitude.

Table 3. Concentration (%) of salts analyzed by XRF.

Name of the Monument	K_2O	Na_2O	CaO	MgO	P_2O_5	SO_3	LOI	Distance from the Sea (Km)	Altitude (m)
Church of Santiago da Pobra do Daen	5.0	5.2	0.51	<0.005	<0.005	<0.030	0.6	0.2	20
Church of San Xoan de Macenda	5.8	5.3	0.78	0.36	0.14	<0.030	1.1	7.3	245
Pazo de Goians (with Chapel)	6.2	5.1	0.41	0.26	0.40	<0.030	1.3	0.5	20
Church of San Martiño de Noia	4.8	4.5	0.54	0.23	0.28	<0.030	1.4	0.1	9
Church of Santa Maria de Ribasieira	5.5	3.7	0.40	0.45	0.36	<0.030	2.2	4.5	167
Pazo da Merce	5.5	3.7	0.56	0.45	0.46	<0.030	2.4	0	18
Church of San Cristovo de Abanqueiro	5.8	3.2	0.37	0.32	0.45	<0.030	2.1	0.2	15

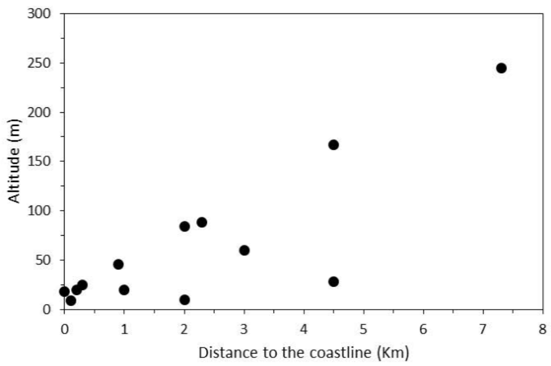

Figure 11. Relationship between the distance to the coastline (in km) and the altitude (in m) of the studied buildings.

Firstly, the possible linear correlations between elements that most commonly form salts in monuments built with stone (10, 14–15, 59) are observed. The elements considered are Na, K, Mg, Ca, and P. Both S and Cl have been dismissed because their concentrations were below the detection limits of XRF in most samples. The possible correlation with LOI is included, given that some salts are hydrated, are usually related to porosity, or are eliminated during the calcination carried out to determine the LOI. For the data obtained, a clear linear correlation is only observed for Na vs. LOI (0.730, Figure 12A) and for K vs. Na (0.656, Figure 12B). Both elements have been related to salts present in buildings due to the sea spray effect.

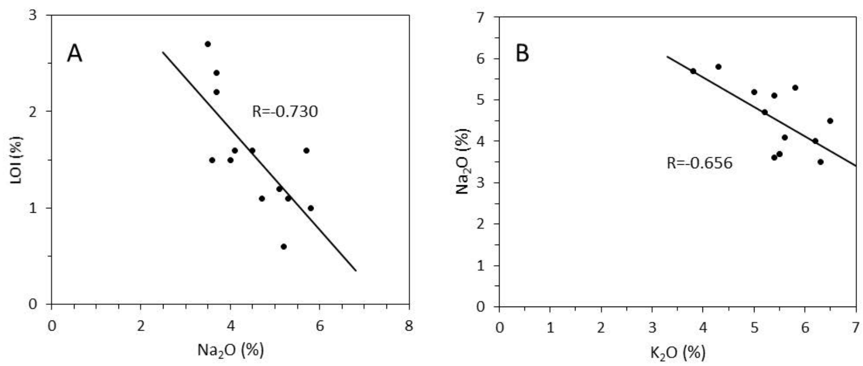

Figure 12. Linear correlation between some of the analyzed elements related to salts. Na vs. LOI (**A**) and for K vs. Na (**B**).

The comparison of elements from samples taken from buildings provides very low linear correlation coefficients, always well below 0.5 (Table 4). It is possible that this is due to the fact that beyond a minimum distance of a few hundred meters or 1 km from the coast, including a certain altitude, there is no correlation between distance or altitude and salts. In order to compare the data more precisely, the buildings studied are divided into two groups, considering those in zone 1 (<1 km from the coast) and zone 2 (>1 km from the coast). The linear correlation coefficients obtained for both LOI and K_2O are close to -0.5 (Figure 13a,b). Thus, there is a possible relationship between these salts and distance to the sea, with both decreasing the further the buildings are from the sea. There is also a positive correlation for Na_2O (Figure 13c), contrary to what would be expected, given that sea spray contributes Na (15, 32). As these correlations are weak, it would be necessary to explore them in more detail by analyzing a larger number of samples in these buildings. No other correlations are observed for zone 1 or zone 2 (Table 4), except in the case of P_2O_3 (Figure 13d), where a negative linear relationship of -0.600 is observed, indicating a possible correlation between P and distance to the sea. Since P is more related to human activities and organisms (14, 15) than to sea spray, this correlation also needs to be better studied.

Table 4. Pearson's linear relationship coefficient for different salts as a function of the distance to the sea and the altitude of the studied monuments.

	Zone 1 (<1 Km)	Zone 2 (>2 Km)	Altitude 1 (<30 m)
LOI	−0.443	0.151	−0.438
K_2O	−0.450	0.154	−0.160
Na_2O	0.470	0.290	0.257
MgO	0.149	0.101	0.116
CaO	0.333	0.384	0.191
P_2O_3	−0.200	−0.600	0.100

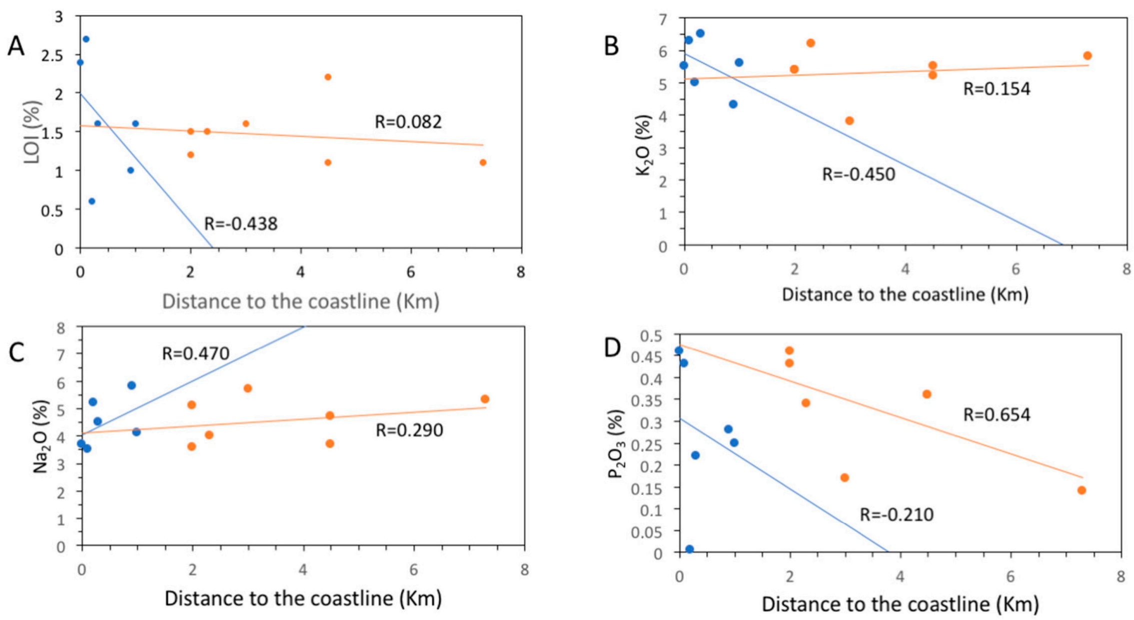

Figure 13. LOI (**A**) and concentrations of K_2O (**B**), Na_2O (**C**), and P_2O_3 (**D**) in relation to distance from the coast for buildings in the two areas considered in this study.

In the case of altitude, no obvious linear correlations are observed when all buildings are considered. If these are divided into two zones, namely Altitude 1 at a lower altitude above the sea (<30 m) and Altitude 2 at a higher altitude above the sea (>30 m), a certain negative linear correlation is observed for the LOI at Altitude 1 (Table 4). This correlation is similar to that observed for distance for buildings from the group Altitude 1. For buildings of the group Altitude 2, only a positive linear correlation is observed for K_2O greater than 0.5. This would indicate that the higher the altitude, the higher the abundance of K-salts from about 30 m upwards. Again, this possible correlation needs to be further explored by analyzing a larger number of samples per building.

3.3. Microscopic Observations

SEM micrographs of the granite surface of the Church of Santa Baia de Boiro displayed several deterioration features such as dissolution (Figure 14a), corrosion pits in the feldspar grains (Figure 14b), and salt precipitates (Figure 14c) covering the minerals that form this rock, quartz, plagioclase, feldspar, and micas.

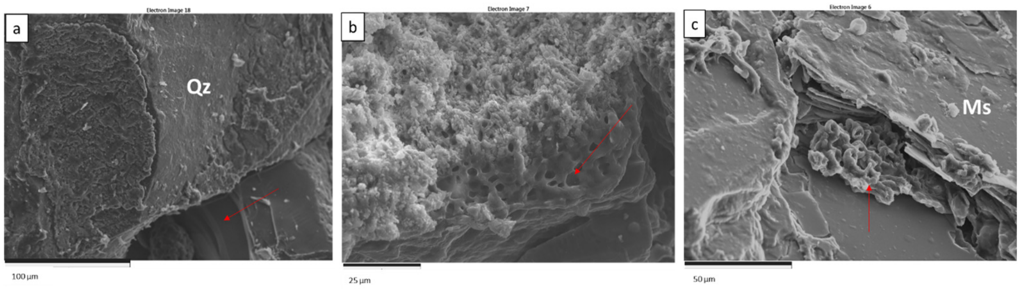

Figure 14. SEM photomicrographs showing the deterioration characteristics of the Church of Santa Baia de Boiro: (**a**) Quartz crystal with dissolution. The arrow points to the typical conchoidal fracture characteristic of quartz crystals. (**b**) Plagioclase crystal with pitches and crystallization of minerals and saline efflorescence. (**c**) Micas with amorphous calcite precipitation.

Thus, the results correlated with the chemical composition of this sample. In Figure 15, the SEM-EDX micrographs show the chemical composition of salt precipitates, mainly chlorides, ca-phosphates, sulfates, and carbonates (Figure 15a). The presence of these salts could be related to the marine influence that affects the study region, especially zone 1 (closer to the sea). In addition, the presence of Pb is detected, which may be related to local emissions (combustion), taking into account that Boiro is the second most populated parish in the Barbanza region, and the church is located in the center of this town, next to the main avenue.

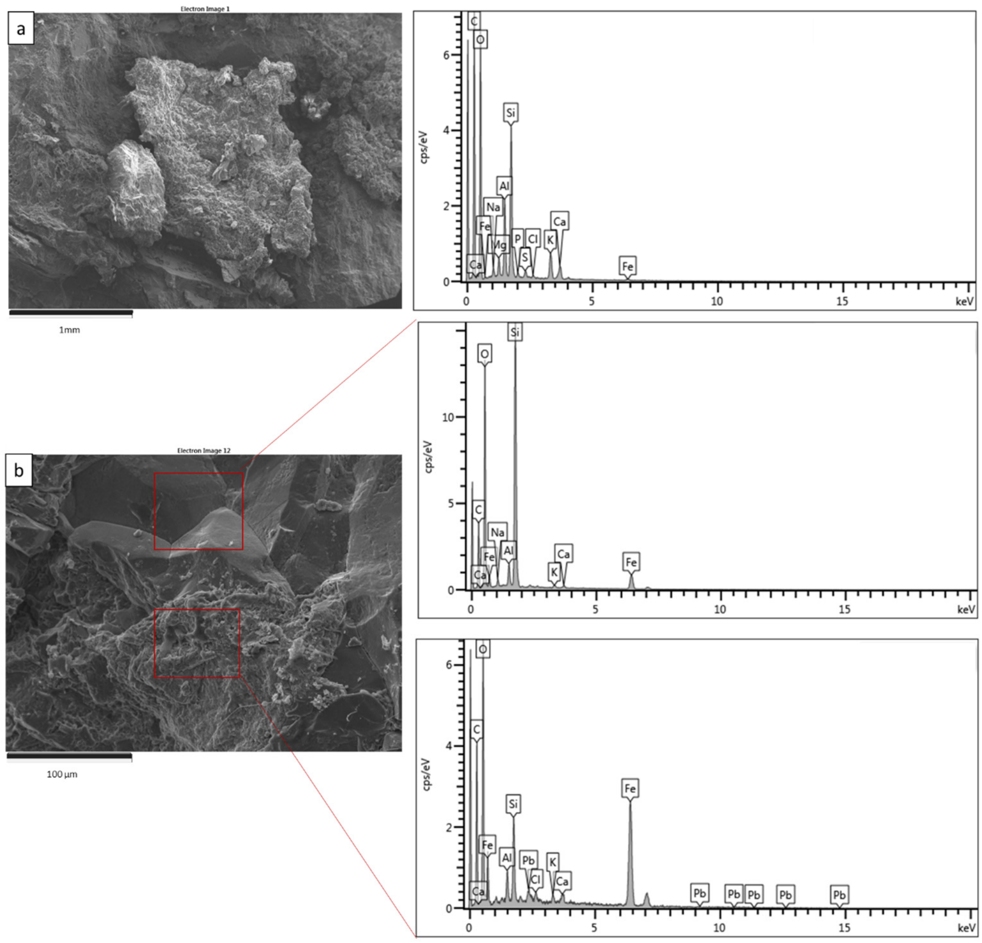

Figure 15. SEM-EDX of Church of Santa Baia de Boiro. (**a**) Weathered plagioclase crystal with precipitation of phosphates, sulfates, carbonates, and chlorides. (**b**) Weathered plagioclase crystal with chloride and carbonate crust. The presence of lead (Pb) is detected.

On the other hand, the sample corresponding to the Church of Santa María de Ribasieira (Figure 16) shows a greater predominance of calcium carbonate precipitation and biological colonization. Thus, the combined effect of physical, chemical, and biological weathering causes the mineral structure on the stone surface to disintegrate, the crystallization of salts, and the settlement of biological growth [60]. Thus, considering the macro and micro features, this sample is subjected to considerable biological colonization which induces its gradual destruction, in accordance with what is characterized in zone 2.

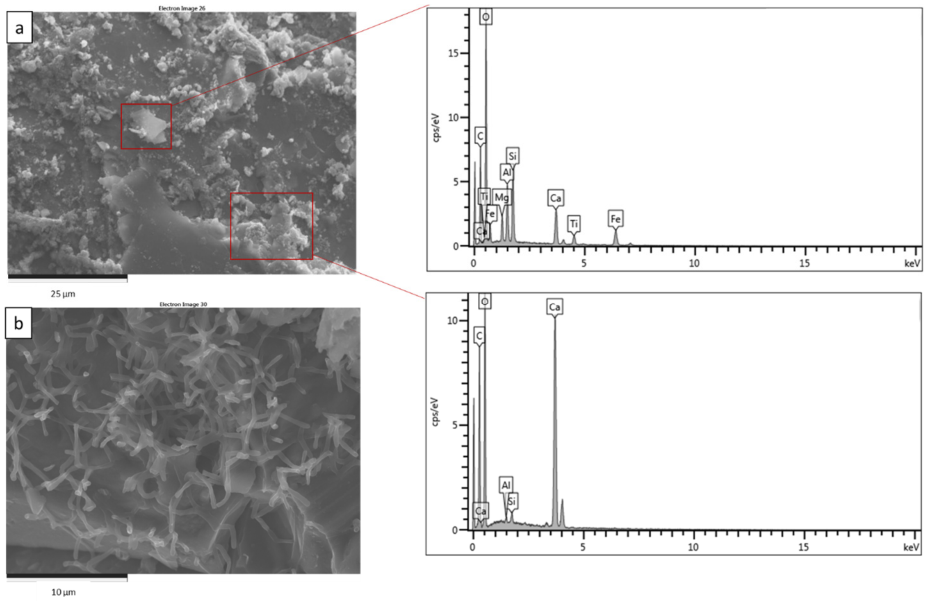

Figure 16. SEM-EDX of Church of Santa Maria de Ribasieira. (**a**) EDX above shows mica crystals with Fe-Ti oxide particles. On the other hand, calcium carbonate crusts are detected in the lower part. (**b**) SEM micrograph with presence of biological colonization.

4. Conclusions

A set of 14 historical buildings has been studied in the Barbanza Peninsula to assess the decay patterns and the possible role of environmental factors in such decay. The most frequently reported deterioration is caused by biological colonization, mainly by the growth of lichens. Depending on the proximity to the sea, the study area has been divided into two zones. It seems that this colonization is correlated with the studied area, depending on the rainfall and distance to the sea. Thus, the cultural heritage located mainly on the coast (zone 1) has certain characteristics that contrast with the heritage located at higher altitudes (zone 2). Crusts are most present in zone 1, but the state of conservation in zone 1 is better than that in zone 2, in part due to the concentration of urban centers on the coast. Meanwhile, in zone 2, the lack of conservation interventions can be also claimed as a cause of the higher biological colonization (mainly by lichens, algae, and even vascular plants). We have assessed the possible role of sea spray salts in the decay of the buildings located in zone 1, where they are expected to be more present and a cause of decay. Our screening analyses do not show any significant correlation between most elements that usually form salts, except a weak linear correlation of loss on ignition and K with distance to the sea. In addition, no significant correlations are observed for the possible effect of altitude (and rainfall) on the growth of salts. It is possible that these results are due to the scarce number of samples studied. However, the use of SEM observations for two buildings, one from each studied zone, indicates the presence of salt growths of marine origin in zone 1 and the presence of different salts in zone 2. Thus, despite the effect of rainfall on biological growth on the studied buildings, it is necessary to carry out more detailed studies, probably using SEM, to assess the role of sea salt in the decay of the historical buildings in the peninsula.

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