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Origin of Gypsum-rich Coatings on Historic Buildings

J. Sanjurjo Sánchez · C. A. S. Alves ·
J. R. Vidal Romaní · D. Fernández Mosquera

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Abstract Gypsum-rich coatings found on buildings constructed with granitic rock ashlars have been studied, from both an urban and a rural area of the NW of Spain. Previous works have attributed gypsum to rock weathering by atmospheric pollution. Mineralogical, chemical, and physical data of coatings have allowed us to distinguish six different types of coatings formed in several ways. In most cases, they are originated by the deterioration calcium-rich plaster building materials. Sulfation of Ca-rich coatings, in situ gypsum dissolution and precipitation, and deposition of air pollution particles are the most important agents related to genesis of coatings. In fact, remains of plasters practically intact were found in some studied buildings. Also, data from coatings and rock ashlars suggest that gypsum-rich coatings are not formed by environment–rock interaction. Coatings located on different parts and façades of the buildings and submitted to different environmental conditions decay in a different way.

Keywords Air pollution · Gypsum crusts · Granite rocks · Heritage · Rock decay

1 Introduction

Rock coatings are accretions on rock surfaces whose constituents have been transported to these from a few microns or thousands of kilometers (Dorn 1998). The different types of existing coatings on rock surfaces have been generally classified according to their composition and attributed to different sources. Thus, several authors have differentiated case hardening, dust coatings, iron or heavy metal films, silica skins, and nitrate, gypsum, or halite salt crusts. Most of them are related to different processes, with a markedly autochthonous (weathering of the underlying rock) or allochthonous origin (transport and deposition/accretion of its components).

Dorn (1998) refers to "patina" as a term "generally used to designate a rock coating or a superficial alteration to stone" in archaeology. It is also clear from Dorn (1998) that the term has been frequently used (it is still used in papers published recently). The ICOMOS-ISCS online glossary (available online in 20/April/2008 in http://lrmh-ext.fr/icomos/consult/index.htm) defines patina as a "chromatic

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J. Sanjurjo Sánchez (✉) · J. R. Vidal Romaní ·
D. Fernández Mosquera
Instituto Universitario de Geología "Isidro Parga Pondal",
Campus de Elviña Universidade da Coruña,
15071 A Coruña, Spain
e-mail: jsanjurjo@udc.es

C. A. S. Alves
Centro de Investigação Geológica,
Ordenamento e Valorização de Recursos,
Campus de Gualtar Universidade do Minho,
4710-057 Braga, Portugal

modification of the material, generally resulting from natural or artificial aging and not involving visible surface deterioration," and in the presentation of subtypes, the expression "thin layer" is used. The term crust is defined in the ICOMOS-ISCS online glossary as a "coherent accumulation of materials on the surface. (...)" and is used in this sense in the present paper.

However, the incidence of both crusts and patinas is not the same on natural rock surfaces as rocks ashlars of Heritage buildings. In particular, salt crusts are very frequent on building stones, and gypsum coatings are commonly highlighted. Gypsum coatings have been found and studied in diverse Heritage buildings, on different rock types, and even other materials such as brick. Also, they have been identified from rural to urban areas in all climatic conditions.

To refer the gypsum coatings on Heritage buildings in urban areas, it is important to notice the differences between the studies on buildings constructed with siliceous and calcareous rocks. On the latter, both gypsum crusts and patinas are very common in urban environments. Because of the elevated air concentration of sulfur dioxide, Ca from calcium carbonate reacts with atmospheric sulfur to give crusts that deteriorate the rock surface.

Gypsum crusts are also common on monuments built with granitic rocks (Begonha et al. 1996; Schiavon 1993). Also in this case, they have been associated with air pollution but there is the problem of the source of Ca. Some authors have specifically postulated that these crusts are formed by combination of sulfates from air pollution and Ca from feldspars (Schiavon 1993). For others workers, gypsum crusts are produced in general by clay and soil airborne particles sulfation and nucleation (Del Monte and Sabbioni 1984) or by microorganisms involved in their formation (Blázquez et al. 1997). Some authors have attributed them to the oxidation of rock pyrites (Schiavon et al. 1994), although in most cases, the S is very low or absent in the rock. However, these processes cannot explain the formation of thick and compact crusts, due to both the low proportion of Ca of granitic rocks and the low crystallization of gypsum by nucleation, even in experiments under polluted atmospheres with high sulfate concentrations (Cultrone et al. 2000).

This limitation has encouraged other authors to propose alternative sources of calcium sulfate, as the sulfation of calcium from mortars (Smith et al. 1994). The mortars (joint and plaster) are very prone to sulfation, especially in urban environments with high sulfate air pollution because they are a huge source of easily soluble calcium and salts. Another alternative explanation is the use of gypsum plaster on the granite ashlars of the buildings. Their deterioration and blackening, by deposition of pollution particles, could explain his appearance as crusts (Sanjurjo Sánchez et al. 2004; Pavía and Caro 2006).

Therefore, the origin of gypsum in Heritage buildings constructed with granitic rocks is an issue that still must be solved. The aim of this paper is to contribute to define possible contributions to the origin of gypsum coatings on Heritage buildings built with Ca and S poor rocks (granitic rocks in this case). To that end, we have selected several important buildings in two localities in the NW coast of Spain (Fig. 1), placed at a distance of 20 km one to another: an urban area (A Coruña) and a rural village (Betanzos). The comparative study of the gypsum coatings in both areas has enabled to monitor the effect of some factors in their development. In fact, both sites correspond to two opposite cases in terms of air pollution: high pollution in the first one and lower in the other one. The effect of other potential factors such as the seaside spray influence or the contribution of the underlying rock to the development of coatings is very similar in both places.

1.1 Study Area

A Coruña is a city located on the NW coast of Spain, with approximately 250,000 inhabitants. Heritage buildings of the city have been constructed with two types of granitic rocks from local quarries: San Pedro leucogranite and Bregua granodiorite. The San Pedro leucogranite is white fine-grained granite, sometimes with feldspars slightly deformed and oriented. The Bregua granodiorite is a milky gray coarse-grain rock with biotite and muscovite (MAGNA 1994). The climate of the city is subhumid Mediterranean with Atlantic trend. The average annual temperature is 13.9°C, and the average annual rainfall is 1,000 mm (Carballeira et al. 1983). The prevailing wind direction is W–NE, although the resultant force of the winds is W–E direction. In winter, winds of 14–19 km/h are recorded an average of 3–4 days per month.

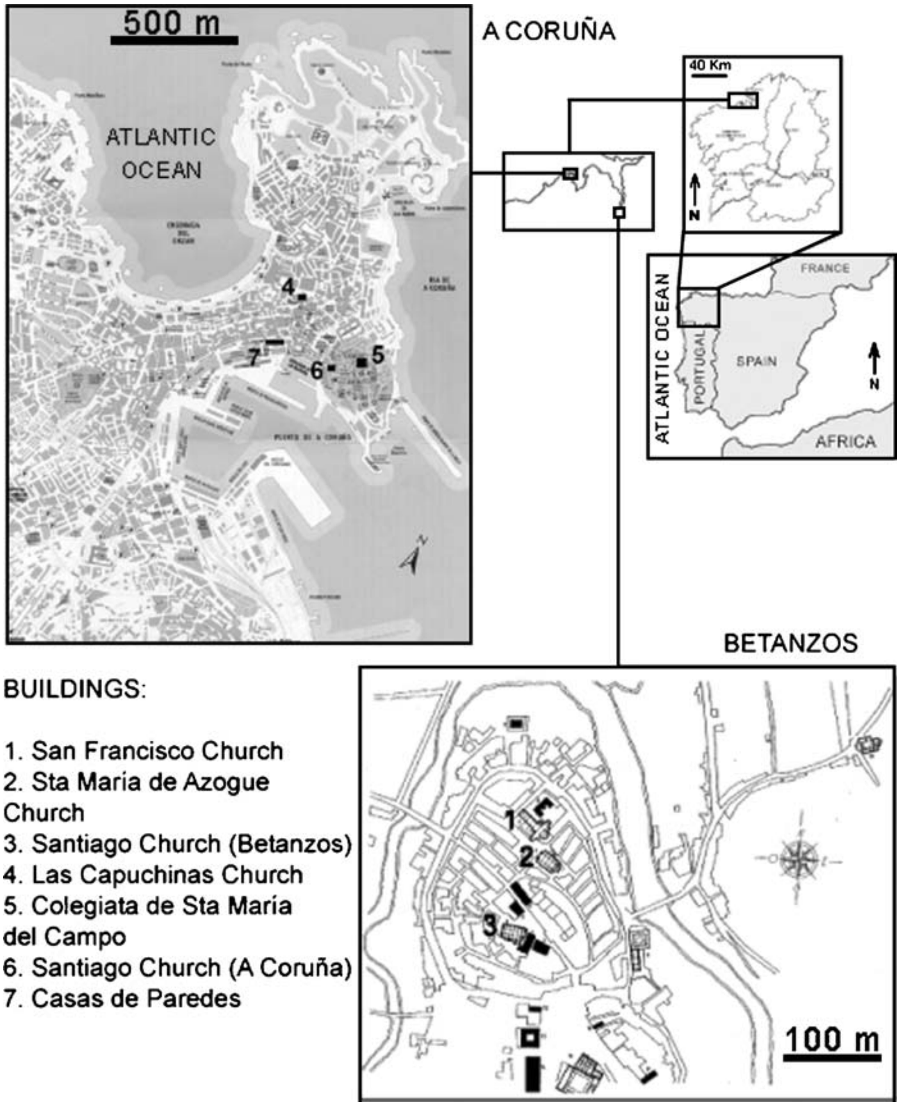


Fig. 1 Map of studied areas

Near the city of A Coruña (20 km east–southeast) is located the village of Betanzos. It has around 10,000 inhabitants and is located in the estuary of a river (Mandeo River) at the end of a bay (Ria of Betanzos) at a non-industrialized area. Thus, there is a significant seaside influence, but the air pollution is much lower in this area. The climatic conditions are very similar to A Coruña, with an average annual temperature of 12.3°C and an average annual precipitation of 900 mm, and both the direction and intensity of the wind are also the same (Carballeira et al. 1983). Betanzos was an important town in the Middle Ages. Because of its history, it has an important medieval old town. Heritage buildings have been constructed with granitic rocks of similar characteristics to those of A Coruña: the Parga leucogranite and granite. The former is white medium-fine grain granite, equigranular with biotite and muscovite. The latter is gray porphidic granite with megacrystals of K-feldspar, biotite, and muscovite (Aranguren Iriarte 1994). In this case, the leucogranite was only used in the construction of arcades of the façades, so that almost all ashlars are granite.

Data from air pollution in the area are not abundant. In A Coruña, the estimated average daily traffic is about 100,000 vehicles. In addition, in the outskirts of the city there are both a thermal power station (Sabón) and an oil refinery (situated 10 km W), which emit high amounts of sulfur to the atmosphere (see Table 1). These data have been used by some authors (Schiavon 1993) to justify the

Table 1 Gas and heavy metal emissions from thermal power stations and an oil refinery in A Coruña area (data from Varela Diaz, 2004)

Source	CO_2 (Tn)	SO_2 (Tn)	NO_x (Tn)	Cr (kg)	Ni (kg)	Pb (kg)	Cd (kg)	As (kg)
Sabón	10,558,000	7,900	800	411	5,754	213	164.4	82.2
Meirama	4,335,000	73,000	10,300	372.5	890.8	134.5	14.5	362.8
A Pontes	91,000	73,000	200	869	2,032	172.6	849.4	32.6
Refinery	1,340,809	18,821.5	2,501.1	–	–	–	–	–

formation of black crusts. However, prevailing winds indicate that industrial pollution should not affect both the city and other nearby locations. In addition, gypsum has not been detected, and very low S amounts have been found (0.18–0.08%) in recent studies of atmospheric dust depositions in urban and suburban areas of A Coruña (Moreda-Piñeiro et al. 2007). Also, there are two other thermal power stations in the area: one (Meirama) located approximately 20 km S from A Coruña and another about 60 km NE (As Pontes). Nevertheless, only little data have been published on both sulfate and other gas emissions for the year 2000 (see Table 1). Average annual atmospheric SO_2 concentration in the air from stations (average of five stations) located in the center of A Coruña attach 26 $\mu g/m^3$ for the years 1984–1985. Concentration for the same years near Betanzos (Monfero, 15 km NE) is 44.3 $\mu g/m^3$ (Casal Porto 1983).

1.2 Features of the Studied Buildings

Most of the façade buildings of A Coruña, built with one or both rock types (leucogranite and granodiorite) showed large covering of gypsum-rich patinas and crusts, most of them black crusts. By their situation in the city, the buildings are exposed to different seaside spray and road traffic air pollution conditions. This fact supports the suitability of the sampled buildings to study the processes involved in gypsum coating formation on building façades in urban environments. The studied buildings are Las Capuchinas Church, Church of Santiago, the Colegiata de Sta. Maria del Campo and the Houses of Paredes. The first one was built using only San Pedro leucogranite ashlars, while the last one was built with Bregua granodiorite. The other two buildings (the Church of Santiago and the Colegiata de Sta. Maria del Campo) were constructed using both rock types.

Exposure to some significant pollution sources, particularly from road traffic, varies from building to building. Las Capuchinas Church and Houses of Paredes are very exposed. They are located in areas of heavy traffic, and there are bus stops beside both façades. The other two buildings are located in areas of low traffic. Specifically, traffic is very low in the W side of the Church of Santiago and a little bit higher in the N one. In the N and W front of the Colegiata de Sta. Maria del Campo, there is no traffic, although there is low traffic intensity in the N and E façades.

Concerning the exposure to seaside spray, the Houses of Paredes and the Church of Santiago are located just 50 m from the coastline in N and NE direction, respectively (see Fig. 1). However, only the Houses of Paredes are located directly in front of the city's harbor. The Colegiata de Sta. Maria del Campo is surrounded by other buildings about 100 m E from the closest coastline, while Las Capuchinas Church is 150 m NW and 200 m S from the coastline.

The buildings studied in Betanzos are the Church of San Francisco, Church of Sta. Maria de Azogue, and the Church of Santiago. The three buildings are located at a high point of the village center, exposed to low road traffic, as this is a traffic-restricted area. Therefore, there is low air pollution from car emissions. Only the W and N (in its E corner) façades of the Church of San Francisco, the W façade of the Church of Sta. Mara de Azogue and N one of the Church of Santiago, are located on streets of very low intensity traffic. Exposure to seaside spray is similar for the three buildings, due to the frequent maritime fogs in the town (there is a frequent temperature inversion).

Most of the studied buildings were constructed at the same time period. The oldest ones are both the Colegiata de Sta. Maria del Campo and the Church of Santiago in A Coruña, and those located in Betanzos (fourteenth and fifteenth centuries). In some cases, the age varies from façade to façade or depending on the studied area of the building, due to reconstructions, as can be observed in Table 2. In fact, the W façade of the Colegiata de Sta. Maria del Campo and the E one

Table 2 Characteristics of studied buildings

Building	Locality	Façade	Rock type	Year	Seaside spray exposition	Traffic exposition
Capuchinas Church	A Coruña	S	SPL	1715	Low	High
Houses of Paredes	A Coruña	S	BG	1778	High	High
Colegiata de Sta. María del Campo	A Coruña	W	Both	1899	Low	No
		N	Both	1302–1899	Low	No
		E	Both	1302–1795	Low	Medium
		S	Both	1302–1899	Low	Medium
Church of Santiago	A Coruña	W	Both	1502	Med.–low	Medium
		N	Both	12th Century -1502	Medium	Medium
Church of San Francisco	Betanzos	W	Both	15th Century	Medium	Low
		S	Both	15th Century	Medium	Low
		E	PG		Medium	No
Church of Sta. María de Azogue	Betanzos	W	Both	15th Century	Medium	No
		S	Both	15th Century	Medium	Low
		E	PG	15th Century	Medium	No
		N	Both	15th Century	Medium	No
Church of Santiago	Betanzos	W	Both	15th Century	Medium	No
		N	Both	15th Century	Medium	Low
		E	PG	1900	Medium	No

Key: underlying rock: *SPL* San Pedro Leucogranite, *BG* Bregua Granodiorite, *PL* Parga Leucogranite, *PG* Parga Granite

of the Church of Santiago in Betanzos, were reconstructed in the late nineteenth century. Las Capuchinas church and the Houses of Paredes were built in the eighteenth century. Complete data from all building façades are presented in the Table 2.

2 Methods

Prior to the sample collection, a study based on the existing historical documentation about the buildings construction was conducted. Thus, information about reconstructions and façade modifications was collected. Also, information recorded about paintings, plasters, and mortars was compiled. From this documentation, it has been possible to know the data of both the construction years and modifications of the façades of each building. However, a few references to coatings, plasters, or paints on the buildings have been found. Only, it could be known that at the beginning of the nineteenth century, a “white paint” was applied in the arcades of the Church of Santiago in A Coruña (De Vedia y Gossens 1845).

Subsequently, fieldwork was performed, surveying the location and frequency of the coatings on all the studied façades. The aim of this field study was to observe the distribution patterns of the coatings, mapping their distribution and selecting the most appropriate and representative samples. Careful sampling was carried out to study the coatings composition, to cause the least possible damage to the façades.

About 65 coating samples were taken from façades. A little amount of every sample was taken carefully, to limit the impact on the ashlars, scraping off the ashlars surface, taking off the inner surface of the coatings. Also, samples of each rock type, used for the construction of buildings, were removed from scales of the ashlars. These rock samples were analyzed by powder X-ray diffraction (XRD) and X-ray fluorescence (XRF) to determine its exact mineralogical and chemical composition, respectively, and thus, establish any possible connection with the coatings found on its surface. Both methods (XRD and XRF) were also used to determine the mineralogical and chemical composition of coatings. For the XRD analysis, about 5 g of each sample was powdered and analyzed in a D5000 SIEMENS X-Ray diffractometer. In cases where sufficient sample amounts were available for the XRF, 30 g of sample was taken, and two 10 g aliquots for every sample were powdered and analyzed in a Fluorescence Spectrometer S4 Pioneer of wavelength dispersion Bruker-Nonius. Two other 5 g aliquots were calcined to 975°C to obtain loss on ignition (LOI). To study the components of the loss on ignition values found on XRF analyses, differential thermal analyses and thermogravimetric analyses (DTA-TGA) studies were carried out in a simultaneous DTA-TGA Thermal Analyzer SDT2960. Of each sample, 30–50 mg was crushed and heated to 1,050°C at a rate of 10°C/min under nitrogen purge.

For a detailed study of coatings by scanning electron microscopy (SEM), fragments of samples were dried and coated with gold. Both surface and polished cross-sections were prepared and observed in a JEOL JSM 6400 Scanning Electron Microscope at 16 keV. Also, electron dispersive spectroscopy analyses (EDS) were performed with an Oxford 200 Inca Energy EDS equipment.

3 Results

X-ray diffraction analyses of samples of the four rock types taken from ashlars were unable to detect the presence of sulfides such as pyrite (Table 5). In addition, chemical analyses, obtained by XRF, show that S amounts never exceeds 1% and that Ca percentage is very low (Fig. 2).

In most of the studied coatings, calcium sulfate is the predominant substance (usually as sheetlike gypsum crystals). The amount of other compounds (and/or minerals) is very variable (Fig. 3). The high number of samples studied and the variability of their macroscopic, microscopic, mineralogical, and chemical characteristics, allows establishing a typological classification of the coatings. In this way, two main criteria were adopted: the observed field features and both composition and structure. Among the field features, the color is the most useful. Although most gypsum coatings are black, there are grayish and brownish variations in some cases. Therefore, the surface texture (porous or compact, rough or smooth) has also been considered. Also, the surface morphology (regular or irregular surface, with or without nodules) contributes to their distinction. Lastly, distribution patterns on the façades are key data, as some of them are widely repeated.

Analyses of coatings have also helped to detect mineral or chemical components different to calcium sulfate, such as calcium carbonate layers underlying gypsum surface layers. Also, a great variability of minor and trace components has been observed. These other components have been used in the coatings typology. Based on these criteria, a classification of six types of coatings was established (Table 3). The occurrence of these coatings on the façades is detailed in Table 4.

A description of the main characteristics of the considered coating types, including field observations and analytical results from XRD (Table 5), XRF (Fig. 3), and TDA-TGA (Sanjurjo Sánchez et al. 2008) is reported below.

3.1 Type 1

Type 1 coatings are gypsum plasters (light yellow, up to 1 cm thick) located in niches and arcades (Fig. 4a), relatively sheltered from air pollution and rainwater. They have been found on San Pedro leucogranite because the use of this fine-grained rock to build these constructive features (on Las Capuchinas Church and both the N and S façades of Colegiata de Sta. María del Campo in A Coruña). A porous surface containing sand and calcium sulfate, mainly massive (without apparent crystalline forms) but also in tabular and sheetlike gypsum crystals in some areas have been observed by SEM. A few amounts of soil airborne particles, Ba-rich aggregates and fly-ash have been observed on the plaster surface. In the Colegiata de Sta. María del Campo, two layers have been noticed. The internal one (200 µm maximum thickness) is a C- and P-rich calcium sulfate layer, with clays and isolated Ba-, Ti-, Fe-, and Cr-rich particle aggregates on the surface. The external one is a 5- to 10-µm-thick Si-rich compact and fractured amorphous layer.

3.2 Type 2

They are calcium carbonate coatings with a blackened sulfated surface (Fig. 4b,c). A wide variety of colors among brown, gray, and black have been observed. They have been found on all rock types, independently of the façade orientation, at both localities.

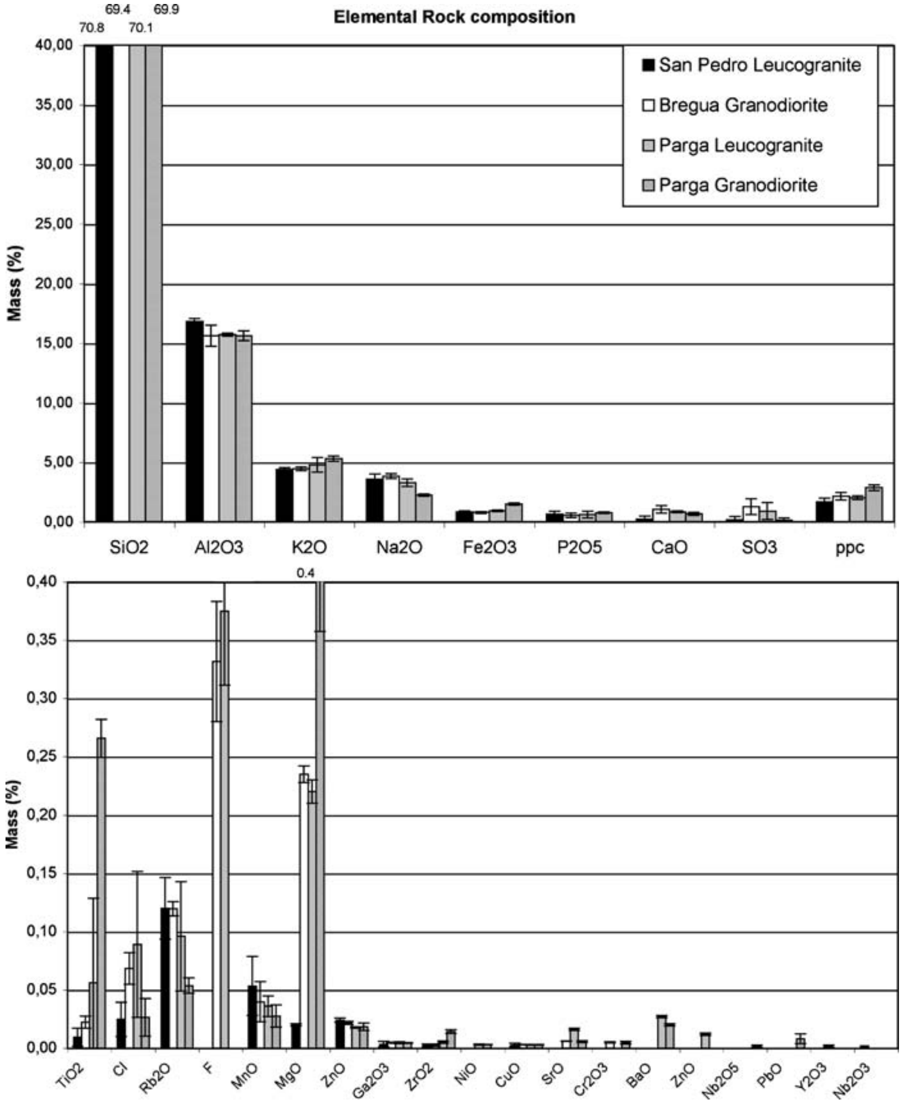


Fig. 2 XRF data from underlying granitic rock ashlars expressed as percent amounts (*bar height*). Observe the low SO_3 values

However, the surface calcium sulfate layers are thicker in samples from the Houses of Paredes, N façade of the Church of Santiago, and S of the Colegiata de Santa María del Campo (in A Coruña). A porous surface layer of calcium sulfate (10 to 400 μm) with sheetlike gypsum crystals (Fig. 5a,b) is observed. Also, soil airborne particles, fly-ash, halite, and C-, P-, Fe-, Mg-, Pb-, Ba-, and Cr-rich particle aggregates, and sometimes Ti, Zn, and Br particles have been detected, due to a paint coat found sometimes on the surface layer. The inner layer (up to 1 cm thick) is a compact calcium carbonate layer with minor gypsum and sand (Fig. 5c). XRD results have shown greater proportion of calcite and minor gypsum and other minerals (quartz, albite, and microcline). In some samples, a thin surface layer of paint is found with quartz, microcline, albite muscovite, biotite, dolomite, hematite, magnetite, and clinochlore. The XRF data have indicated that Ca is the main component (the SO_3:CaO ratio is about 0.3), and minor proportions of Si, S, and Al have been found. High Mg and Pb traces are also remarkable (0.75% and 0.07%, respectively). These data support the hypothesis that they are lime plasters sulfated by air pollution. High losses on ignition (25.4%) have been investigated by TDA-TGA analyses (see Sanjurjo Sánchez et al. 2008). They showed that these losses are due to two factors: loss of hydration water and CO_2 losses from calcium carbonate (endothermic peaks at 160°C and 700–800°C, respectively).

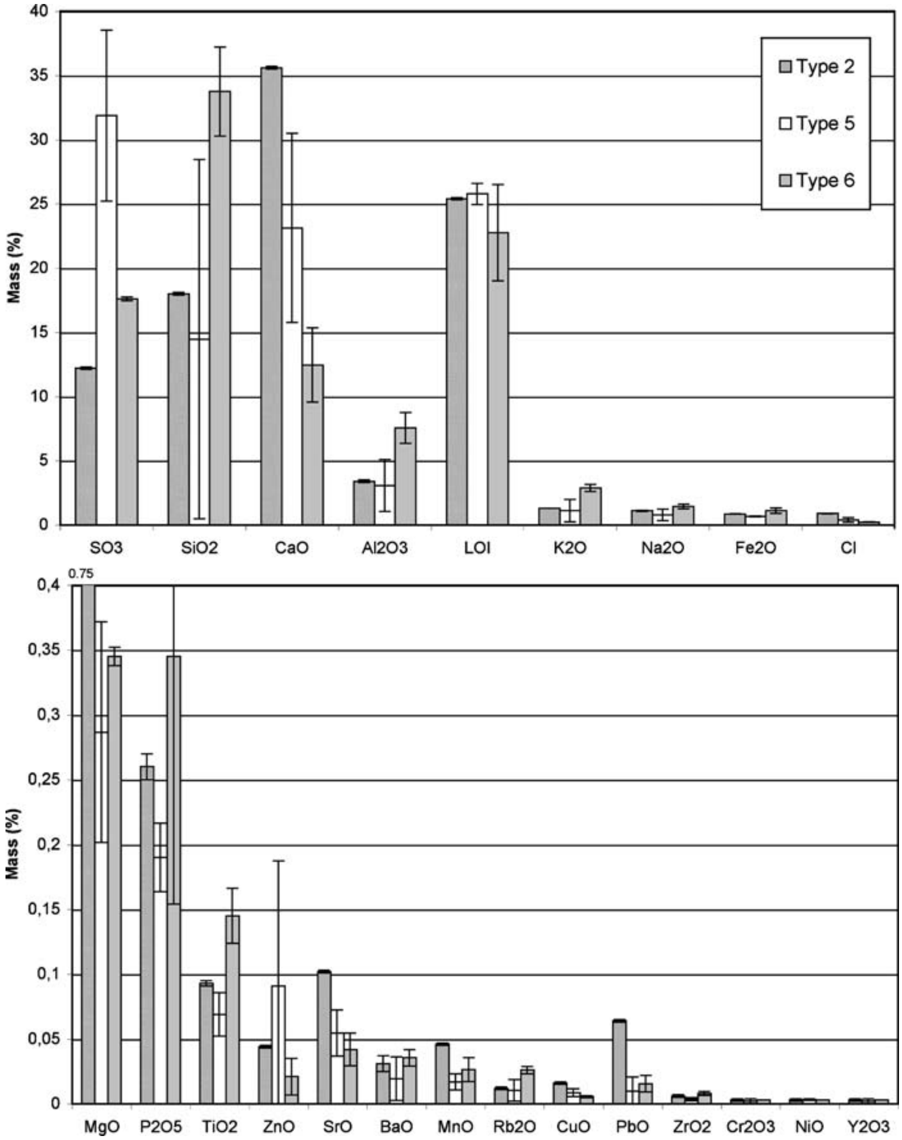


Fig. 3 XRF data from coatings. Remark amount differences of both SO_3 and CaO with rock ashlars. CaO/SO_3 ratios differ from type 2 to both 5 and 6 coatings. Also, SO_3 and CaO amounts are higher in the type 5 coatings (in situ developed from gypsum coatings). Higher MgO values in the type 2 samples could due to dolomite grains (detected by XRD)

3.3 Type 3

Type 3 are dark-black brown coatings, with variable textural characteristics that cover a large surface of the ashlars on the N (not exposed to traffic pollution) and S (moderately exposed) façades of the Colegiata de Sta. María del Campo, on both rock types (Fig. 4d). They are heterogeneous and distributed as runoff

Table 3 Coating types

Number of samples, underlying rock and short description of coatings. Underlying rock key: *SPL* San Pedro Leucogranite, *BG* Bregua Granodiorite, *PL* Parga Leucogranite, *PG* Parga Granite

Coating	Number of samples	Rock	Short description
Type 1	7	SPL	Gypsum plaster
Type 2	24	SPL, BG, PL, PG	Sulfated carbonate calcium plaster
Type 3	12	SPL, BG	Blackened gypsum plaster
Type 4	8	SPL, BG	Black crust
Type 5	7	SPL, BG	Black crust with nodules
Type 6	7	SPL, BG, GP	Gray-black run-off gypsum coating

Table 4 Distribution, occurrence, and frequency of coatings on the studied building façades

		Coating type											
		1		2		3		4		5		6	
	Rock type	L	G	L	G	L	G	L	G	L	G	L	G
Building	Façade												
LCC	S	+						+++		+		+	
HOP	S				+++				+		++		++
CMC	W												
	N	+		+	+	+	+	++				+	+
	E							+	+			++	++
	S	+		++	++	++	++	++				++	++
CSC	W							++				+	+
	N			++	++			++				+	+
CSF	W				+								
	S				+							+	
	E				++								
SMA	W												
	S				++								
	E				+								+
	N				+								
CSB	W												
	N			+	+								
	E				+								+

Buildings key: *LCC* Las Capuchinas Church, *HOP* Houses of Paredes, *CMC* Colegiata de Sta. María del Campo, *CSC* Church of Santiago in A Coruña, *CSF* Church of San Francisco, *CSMA* Church of Sta, María de Azogue, *CSB* Church of Santiago in Betanzos. Surface covered area key: low (+), medium (++), high (+++). Rock key: *L* leucogranite, *G* granodiorite or granite

Table 5 XRD analyses results

Coating or rock	Gp	Cal	Qtz	Ab	Mc	mi	Dol	Hl
Type 1	+++	–	+	+	+	t	–	–
Type 2								
External layer	++	++	+	+	+	–	t	t
Internal layer	t	+++	+	+	+	–	–	–
Type 3	+++	+	+	+	+	+	–	+
Type 4	+++	–	++	–	+	–	–	–
Type 5	+++	–	+	+	+	–	–	–
Type 6	+++	–	+	+	+	+	–	–
SPL	–	–	+++	+	+	t	–	–
BG	–	–	++	+	+	t	–	–
PL	–	–	+++	+	+	t	–	–
PG	–	–	++	+	+	t	–	–

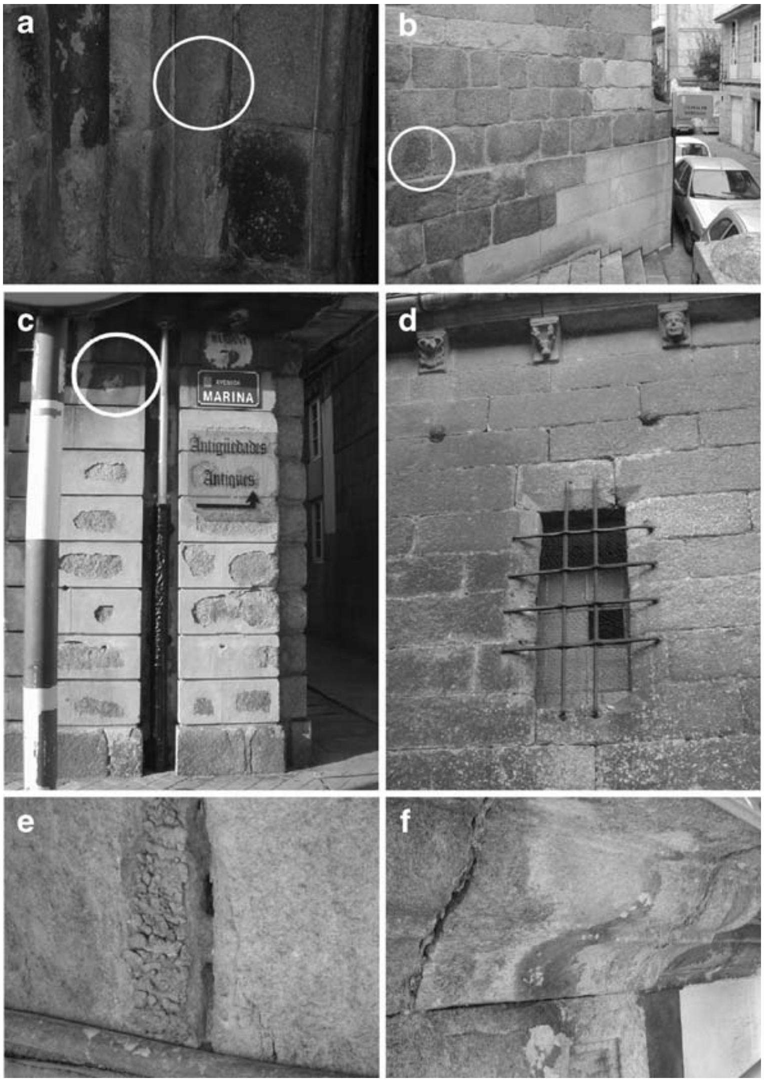
Minerals: *Gp* gypsum, *Cal* calcite, *Qtz* quartz, *Ab* albite, *Mc* microline, *mi* mica, *Hl* halite, *Dol* dolomite. Mineralogical content by abundance (excluding amorphous phases): +++ (abundant >40%), ++ (subsidiary 15–40%), + (minor 7–15%), t (trace <7%). Rock samples: *SPL* San Pedro Leucogranite, *BG* Bregua Granodiorite, *PL* Parga Leucogranite, *PG* Parga Granite

patches or as apparently in situ well-developed coatings on the façades. Thickness is low but highly variable (20–600 µm). Two layers are usually observed: an external compact and S, Ca and C-rich one (Fig. 5d), and an internal porous layer with higher amounts of C and little calcium sulfate and sand, both of highly variable thickness. Also, the surface of the coating is heterogeneous and has been partly eroded. Gypsum, halite, and soil airborne particles aggregates, and isolated Ba-, Ti-, Fe-, Pb- and Cr-rich particles were detected on the surface layer. A XRD analyses have shown high gypsum amounts and also quartz, microcline, albite, calcite, micas, and halite. Unfortunately, the low thickness of this coating did not allow analyzing the separated surface and inner layers, as sample enough to perform separate XRD measurements was not obtained.

3.4 Type 4

They are black crusts, observed only in A Coruña, with variable porosity (Fig. 4a). They have been

Fig. 4 Photos of studied coatings: **a** type 1 (see *circle*) and type 4 coatings (*black*); **b** and **c** type 2 coatings (see *circle*); **d** type 3 coating; **e** type 5 nodulated crust; **f** type 6 coating



found below cornices, arcades, or on large surface areas on different oriented and traffic pollution-exposed façades constructed with the two rock types studied in this city. These coatings are specifically well developed in Las Capuchinas Church, some areas of the Houses of Paredes, N and S arcades of the Colegiata de Sta. María del Campo, and N and W arcades of the Church of Santiago (façades exposed to high traffic air pollution). They are 0.5 mm thick on average, reaching a maximum thickness of 3 cm. A surface layer (100–200 μm thick) of calcium sulfate without apparently crystalline forms, significant amounts of C and P, and gypsum sheetlike crystals is observed. Also, soil airborne particles, fly ash, halite, and Pb-rich aggregates are detected on some surface areas (Fig. 6). Moreover, Ti-rich aggregates have been found on the Church of Santiago coatings. The inner layer (500–800 μm) is calcium sulfate with sheetlike gypsum crystals in pores, soil airborne particles, and Fe- and C-rich aggregates. The XRD data have showed abundant gypsum and quartz, and microcline.

3.5 Type 5

They are compact nodulated black crusts (Fig. 4e), found below cornices and moldings in buildings exposed to road traffic pollution: Las Capuchinas

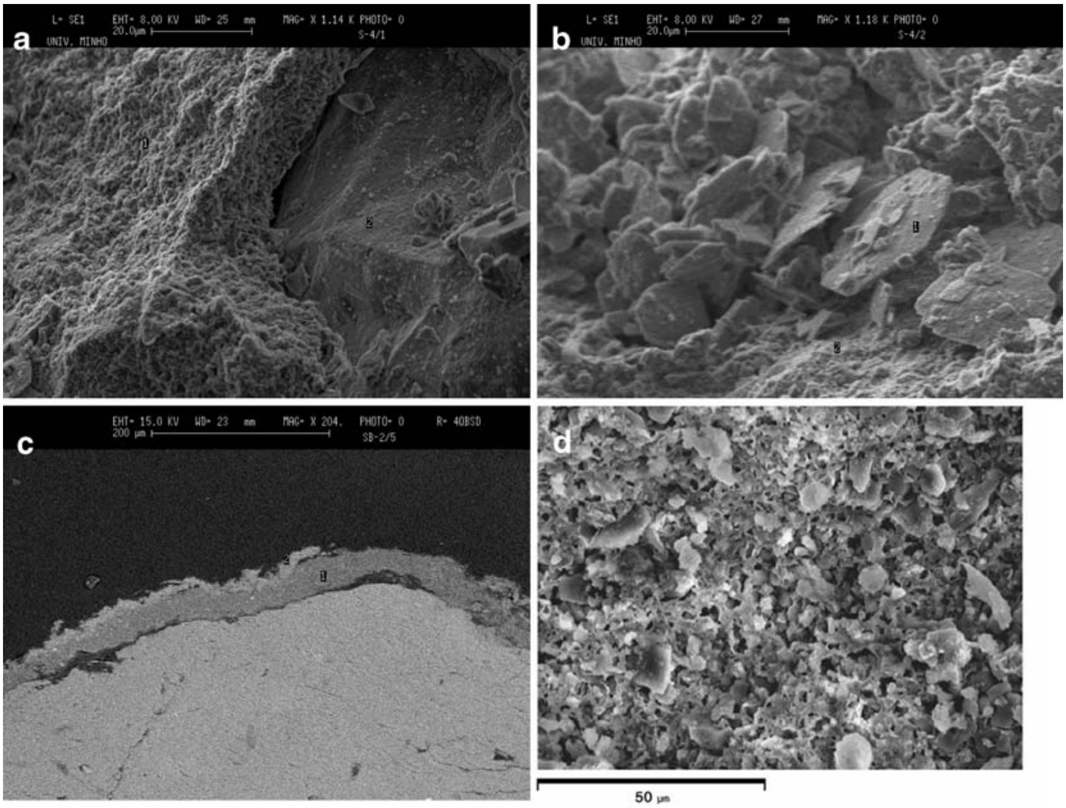


Fig. 5 SEM images of coatings: **a** surface view of a low sulfated type 2 coating; **b** detail of sheetlike gypsum crystals on type 2 coating surface; **c** cross-section of a well-developed gypsum surface layer of a type 2 coating (*1* carbonate calcium layer, *2* gypsum surface layer); **d** surface detail of a type 3 coating

Church and the Houses of Paredes, in A Coruña (on two rock types). Nodules are up to 1 cm in diameter. The surface layer (0.5–1 mm thick) is composed of gypsum sheetlike crystals of two different sizes: 10–50 and 2–5 µm (Fig. 7a), on a compact calcium sulfate matrix without apparently crystalline forms. Also, soil airborne particles, halite, and Fe-, Pb-, and C-rich aggregates have been detected on the surface layer. The inner layer, up to 3–4 mm thick, is very compact, S, Ca, C, P and sand-rich (Fig. 7b). The XRD data of the outer layer have revealed gypsum, quartz, albite, and microcline. The XRF results have shown that the coatings are Si (due to the high amounts of sand) and calcium sulfate-rich (note the SO_3:CaO ratio), with high loss on ignition (LOI). The ATD-ATG data suggest that these high losses are due to gypsum and silicates dehydration and organic matter (see Sanjurjo Sánchez et al. 2008).

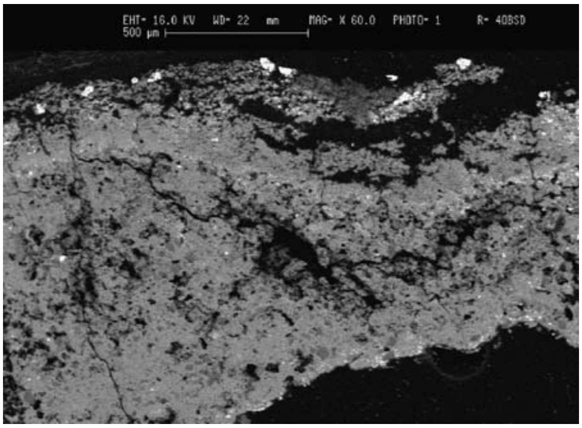


Fig. 6 SEM micrograph from a type 4 coating cross-section. The upper side is the surface layer, white particles are Pb-rich aggregates and black parts are resin-covered pores

3.6 Type 6

These coatings are gray or black porous patinas formed by runoff washing and precipitation (Fig. 4f). They are located below cornices or arranged as runoff patches on the façades. They have been

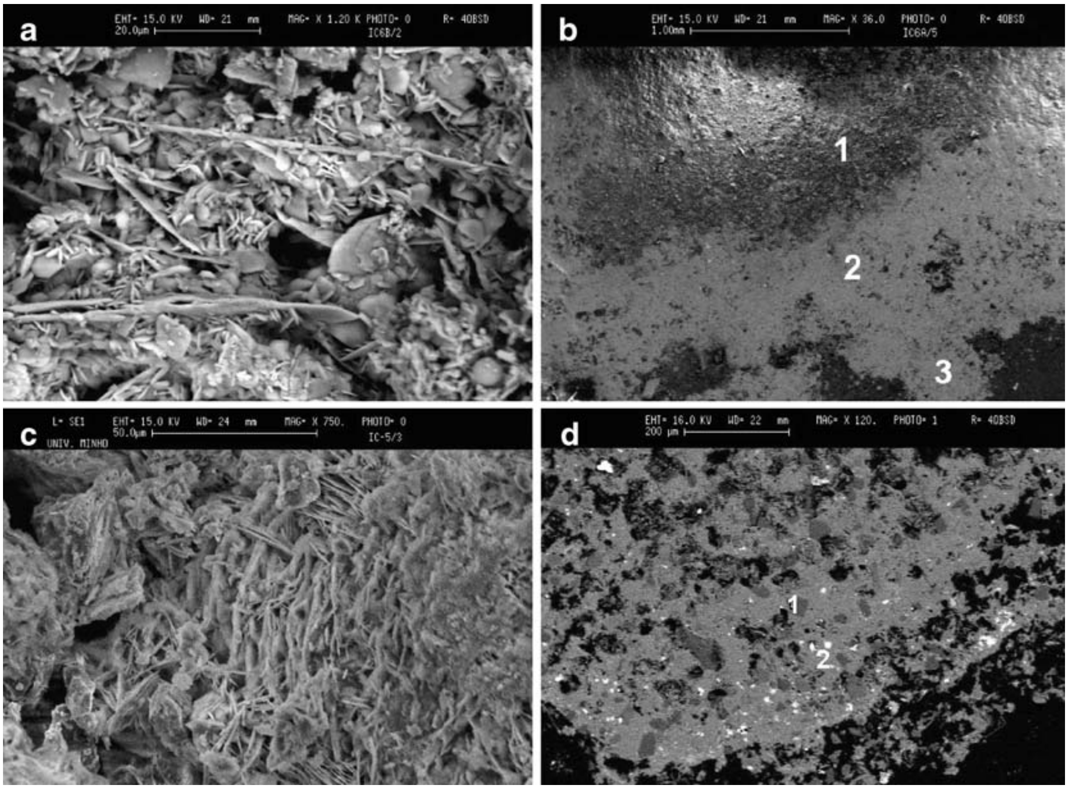


Fig. 7 SEM micrographs of coatings: **a** detail of gypsum sheetlike crystals of two different sizes on the surface of a type 5 coating sample; **b** cross-section of a type 5 coating with both internal (*1*) compact calcium sulfate C-rich layer, a surface porous gypsum layer (*2*) and surface nodules (*3*); **c** surface gypsum sheetlike crystal on a type 6 coating; **d** Cross-section of a type 6 coating with halite crystals (*1* light gray) and Fe-rich aggregates (*2* white)

found on all the studied building façades at both localities and on all rock types. However, they are much more frequent and well-developed (its thickness is greater) in A Coruña, especially in Las Capuchinas Church, Houses of Paredes, E and S façades of the Colegiata de Sta. María del Campo, and N façade of Church of Santiago. The surface is rough and porous of gypsum sheetlike crystals (Fig. 7c). Soil airborne particles, Fe- (up to 50 µm) and C-rich aggregates, halite (Fig. 7d), and fly-ash have also been found on the surface. In some cross-section areas, C-rich calcium sulfate without defined crystalline forms has been detected. Their thickness is variable (200 µm–2 mm), and soil airborne particles and Fe-rich oxides have been observed in the inner portions of the crust. The XRD results have shown gypsum, quartz, microcline, albite, and mica. The XRF data have revealed Si, S, Ca, Al, traces of many other elements and high losses on ignition.

4 Discussion

The performed study has allowed assessing the influence of two kinds of variables in the development of gypsum coatings on Heritage building façades constructed with granitic rocks. The first one is related to the coatings substrate characteristics of the coatings, including rock types (chemical and mineralogical composition), joint and plaster mortars, and architectural features. The second one concerns environmental factors: the influence of the seaside spray and the air pollution.

4.1 Influence of the Building Characteristics

No relationship between the different coatings and the underlying rock types have been found from field surveys. Analytical studies are in agreement with field observations, and evidences do not support the attribution of gypsum crusts to rock weathering processes. In this sense, Ca-release from feldspars dissolution or sulfate genesis related to pyrite alteration has not been observed, as some authors have suggested (Schiavon 1993). However, a relationship between coatings and both plaster and joint mortars has been noticed, in agreement with Smith et al. (1994).

S-rich surface layers evidences in situ sulfation of Ca-rich compounds from plaster mortars. Likewise, interaction with atmospheric pollution has modified gypsum mortar and plasters to form some gypsum coatings.

Regarding architectural, as has been previously observed, sheltering architectural features such as moldings, cornices, arcades, and niches provide façade areas not exposed to rainfall, thus allowing the calcium sulfate precipitation to form gypsum coatings.

4.2 Influence of Environmental Factors

Related to environmental factors, differences in proximity of the buildings to the coastline allow evaluating the influence of the seaside spray. Several authors have linked the development of gypsum coatings to this factor (Chavas and Lefèvre 1996; Van Grieken and Torfs 1996). To check this hypothesis, the halite on coatings has been relatively assessed. In this sense, halite should be detected at exposed to spray areas of the façades (Chavas and Jeannette 2001). However, any relationship between the halite occurrence and seaside spray has not been noticed. Ca-rich mortar sulfation is not greater in theoretically most sea-exposed areas of A Coruña, and significant proportions of halite have not been found on coatings of those most exposed façades. If detected, halite is always a minor component, and other factors such as exposure to rainwater easily wash it out.

An open discussion on the formation of gypsum coatings on building façades concerns the effects of air pollution. To assess this factor, the distribution of coatings, their characteristics, and the content of some typically atmospheric pollution particles are a good tool. In this sense, we can compare these characteristics to local and regional pollution.

At both localities, the effects of traffic pollution in the development of different coatings on the façades can be observed, taking into account the other factors considered (rock type, mortars, and influence of the seaside spray). The differences are obvious between the two localities. Atmospheric pollution by road traffic, heating systems, and industrial focuses, is much higher in A Coruña. Also, the situation of both areas is different regarding, at least, four major sources of air pollution: three thermal power stations, and an oil refinery.

Considering the situation of these sources, a greater exposure of A Coruña is expected to three of them. However, data from air pollution stations do not reflect this difference, as can be seen on the 26 $\mu g/m^3$ annual average measured in the urban area (Casal Porto 1983). The prevailing W–E wind direction could explain the scarce influence of all these sources in both localities. If this is the main sulfate source, all buildings studied in A Coruña should have a similar occurrence and distribution of gypsum coatings, which is not observed. Therefore, the coating distribution patterns do not support the hypothesis of influence of industrial pollution sources in the development of the gypsum coatings in A Coruña, as suggested by some studies (Schiavon 1993). This also explains the differences among façades in the city, existing both low covered façades (and coatings with little amounts of pollution particles) and façades highly affected by pollution. In addition, coatings on façades of different orientation lead to dismiss this hypothesis. Theoretically, sulfate transport by wind from these industrial pollution sources, should involve a greater occurrence and development of gypsum coatings on the W-oriented façades (considering the WE wind direction), which is not observed.

Broadly speaking, Ca-rich mortar sulfation is widespread on the most exposed façades to traffic pollution in A Coruña (Las Capuchinas Church and the Houses of Paredes, both of S orientation) and on moderate exposure façades such as S and E façades of the Colegiata de Sta. María del Campo and the N of the Church of Santiago (A Coruña). In these cases, the surface calcium sulfate layers are the most developed on lime mortars (type 2). Also, this higher impact of traffic pollution is registered on the original plasters, observed as black crusts, with an important deposition of Pb-rich aggregates and fly-ash on the surface layers, but not at inner layers (types 2, 4, and 5). Moreover, there are more thick and compact crusts (type 3 and 5), and washing patinas which contain particles (type 6) on the façades of A Coruña. This correlation between traffic exposure, development of coatings and particle content, is particularly clear on Las Capuchinas Church and the Houses of Paredes (sites with higher road traffic). On other building fronts, affected by minor local vehicle traffic pollution, a smaller development of calcium sulfate surface layers (less thick and less particle content) has been observed.

At Betanzos, the variability of coating types observed is much lower. In fact, thick gypsum crusts (of the types 3, 4, and 5) have not been found. Only poorly developed and thin gypsum coatings, which cover a very small area on the façades, have been observed. Still, there are local variations front to front. Thus, façades located in areas without automobile traffic did not show calcium sulfate or gypsum-rich coatings. In contrast, the N façade of the Church of Santiago (Betanzos), the S of the Sta. Maria de Azogue, and the corner between the S and E façades of the Church of San Francisco (in a street with low traffic) have shown further development of gypsum coatings.

Regarding the effect of the rainwater dissolution on the coatings, it is difficult to assess the exposure of the façades. To that end, the best indicator is the sense of the prevailing winds (E–W). Thus, if rainwater dissolution would a major factor, W façades should show lower incidence of gypsum coatings or a lesser thickness of gypsum layers. Broadly, this trend is observed, and the W façades are the less covered in both localities (see Table 4). However, it should not exclude that in both areas, the W façades are located at low, very low, or closed to traffic streets or squares (see Table 2) because the trend in the area had been built the main façades of the churches in the W fronts of the buildings. For that reason, W façades are located at open spaces (usually squares or gardens).

4.3 Coatings Development

The genesis of gypsum coatings seems to be conditioned by the starting substrate conditions. In some cases, they are related to the presence of calcium-rich mortar, and the interaction of these substrates with the surrounding environmental conditions. On gypsum plasters, rainwater can cause erosion by dissolving and washing, as calcium sulfates are water-soluble. Thus, washing will be effective on rain-exposed areas of the façades, and water runoff could precipitate sulfates on protected areas (i.e., below ledges, cornices, arcades, etc).

Comparing the surface of both naked and coated ashlars on the façades, a clear difference in the deposition of particles is observed. In fact, blackening and deposition of particles on the granite ashlars is not observed. The only exception occurs on the Houses Paredes façades, on which a surface blackening (without gypsum or calcium sulfate aggregates) is observed because of its exposition to strong road traffic (Sanjurjo Sánchez et al. 2008). This fact indicates that the deposition and accumulation of atmospheric particles occurs due to the existence of a porous substrate. Our observations do not support the reverse process, to wit, the formation of gypsum crust due to particle nucleation directly on the rock ashlars, as other studies have proposed (Pye and Schiavon 1989; Cultrone et al. 2000). Furthermore, gypsum coatings of variable thickness, color, and particle content (generated on different building façades by pollution) contradict this last hypothesis, as can be concluded regarding both the original and blackened gypsum plasters. In addition, studies of atmospheric deposition in urban and suburban areas of A Coruña have not yielded gypsum aggregates, and the S detected has been smaller than 0.2% (Moreda-Piñeiro et al. 2007).

Regarding superficial sulfated Ca-rich mortars, these thin calcium sulfate surface layers could be indicative of less intense and slower sulfation processes. This can be seen on the façades of Betanzos (where the car traffic is much lower) and the less traffic exposed façades of A Coruña (considering that most buildings are of similar age in both locations). However, it should not be ruled out that these layers or isolated particles of calcium sulfate could be vestiges of previous eroded gypsum plasters in some cases. Also, generally, the particles found in the coatings (fly-ash, of Pb-, Fe-, Ba-, Cr-, etc. rich particle aggregates) are located on black or dark surface layers of the coatings.

5 Conclusions

In this paper, the impact of several factors related to environmental conditions and building material characteristics has been assessed through the study of the coating characteristics and their occurrence in an urban and a rural area.

Most of the coatings (designated in this study by 1, 4, and 5 type) are related to previous gypsum plasters. They have been formed by deterioration due to the interaction of environmental factors surrounding the façades of the studied buildings. The findings suggest a genetic pattern for the different types of gypsum coatings. In this sense, type 1 coatings are remnant gypsum plasters that were found intact on several buildings. Since type 1 coatings, type 4 coatings were formed by the deposition of particles on the surface. Type 5 coatings have been developed by re-precipitation of calcium sulfate dissolved on the surface from gypsum plasters or Ca-rich mortars of upper areas of the façades. The two calcium sulfate-rich layers reflect this process. The inner one contains abundant C and is very compact. On the contrary, the type coatings 6 patinas are formed by precipitated calcium sulfate, washed from upper areas of the façades, on the ashlars surface. Moreover, the type 2 coatings correspond to original lime mortar coating of, which have undergone in situ sulfation processes (not necessarily connected to runoff). This fact allows developing a calcium sulfate or gypsum surface layer of variable thickness. Also, the type 3 coatings come from mixed gypsum and calcium carbonate mortars. For this reason, they are heterogeneous, due to the variability of their constituents and the Ca sulfation processes, depending on the exposure of the façades to pollution sources and rainwater.

No evidences of interaction between the rock ashlars and the environmental factors in the surrounding area of the buildings have been found. However, there was a significant interaction with joint and plaster mortars on the façades, particularly those containing gypsum. In fact, there are only two situations in which black crusts are not associated with a prior gypsum coating substrate. The first one are the type 2 coatings (lime plasters). The other one are the type 6 coatings, although this one is not really a crust but a patina (smaller thickness). Despite this, the latter could be related to artificial gypsum coatings, since they are a possible source of S (though the patina is not developed on the gypsum mortar surface), and their formation is due to deposition of rainwater-washed materials deposited on the surface ashlars. The difference with other gypsum coatings is that the patina structure is homogeneous (they do not have both a surface and an inner layer), in addition to its smaller thickness.

Among the environmental factors, we were unable to observe differences on the effect of seaside spray in the coatings formation. However, a good correlation has been observed between the distribution and development of most coatings and exposure to road traffic air pollution. The effect of industrial sources of air pollution, located in the outskirts of both localities is not visible. Apart from this factor, the exposure of coatings to rainwater has the opposite effect, eroding and washing the coatings.

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