Contents lists available at ScienceDirect





Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Effect of proteinaceous binder on pollution-induced sulfation of lime-based tempera paints



A. Herrera^a, C. Cardell^a, J.S. Pozo-Antonio^b, A. Burgos-Cara^{a,c}, K. Elert^{a,*}

^a Dept. of Mineralogy and Petrology, Faculty of Science, University of Granada, Campus Fuentenueva s/n, 18071, Granada, Spain

^c Sensient Colors UK Ltd., Oldmedow Road, King's Lynn, Norfolk, PE30 4LA, UK

ARTICLE INFO

Keywords: Paint dosimeter Calcite Gypsum Pigments Chemical weathering Pigment-binder interaction

ABSTRACT

Even though, atmospheric SO₂ contamination has been reduced over the last decades in Europe, practical experience has shown that sulfation of lime-based materials (i.e., lime-based tempera paint, lime mortar and plaster, as well as limestone) is still of importance, affecting monuments exposed to polluted air in urban centers. In order to evaluate the effect of organic binders (i.e., rabbit skin glue or egg yolk) on the chemical weathering resistance of lime-based materials, tempera paint dosimeters (i.e., paints containing calcite or mixtures of portlandite and calcite) were subjected to long-term outdoor exposure and accelerated SO₂-aging. SO₂-aging caused important morphological changes of the paint surface on the nano- and microscale. However, sulfation was significantly delayed in the presence of the organic binder. Furthermore, paints containing portlandite and calcite transformed faster into calcium sulfite hemihydrate and gypsum than paints containing only calcite. Calcium sulfite hemihydrate formation onto calcite always preceded non-epitaxial gypsum crystallization after dissolution of the sulfite precursor phase. These results suggest that a passivating product layer will not form onto calcite, and so sulfation will continue under suitable environmental conditions until all calcite is transformed into gypsum. Nevertheless, the organic binder strongly affected the mineralogical evolution of paints containing portlandite, resulting in the formation of organic-inorganic hybrid materials similar to biominerals. These hybrid materials generally have superior weathering resistance and might explain the absence of any clear signs of sulfation after prolonged outdoor exposure. The selection of lime-based tempera paints for conservation interventions must be made considering the prevailing exposure conditions. In polluted dry environments where carbonation of portlandite will be significantly delayed, the use of calcite-based tempera paints might be preferable, while tempera paints containing portlandite would be more suitable in humid climates where carbonation is fast, resulting in the formation of weather resistant hybrid materials.

1. Introduction

For decades atmospheric pollution has been recognized as one of the major threats to cultural heritage [1]. More recently, scientists have established that the damaging effects of pollution are enhanced by climate change, affecting a wide range of materials of the built heritage [2,3]. One of the classical examples of pollution-induced deterioration includes the formation of gypsum-rich black-crusts on limestone and lime mortars due to sulfation of calcite [4–7].

Even though, SO₂ concentration has been reduced drastically by ~75% since 1990 according to the European Environment agency [8], pollution-induced sulfation is still affecting monuments located in polluted metropolitan areas [9]. Actually, some experts suggest that there might not be any safe threshold and that resulfation of previously

cleaned monuments could occur relatively rapidly. The formation of gypsum crusts is well documented for many monuments and historic buildings in Granada (southern Spain) [4]. However, sulfation is not limited to building materials and also affects painting materials. Sayre et al. [10] detected large amounts of gypsum (CaSO₄·2H₂O) in decayed lime plaster from the Giotto frescoes in the Scrovegni Chapel, Italy, which they identified as a reaction product of calcium carbonate with atmospheric sulfur oxides (i.e., sulfur di- and trioxide) in the presence of moisture. While some research has been dedicated to the sulfation of pure lime in wall paintings [10,11], little is known on the effect of atmospheric SO₂ on lime-based binary systems, such as tempera paints, which contain an inorganic pigment and an organic binder.

Tempera paints applied in the fresco-secco technique have been extensively used in southern Spain and important examples include the

E-mail address: kelert@ugr.es (K. Elert).

https://doi.org/10.1016/j.porgcoat.2018.06.017

Received 26 February 2018; Received in revised form 8 June 2018; Accepted 24 June 2018 Available online 04 July 2018 0300-9440/ © 2018 Elsevier B.V. All rights reserved.

^b Dept. de Enxeñaría de Recursos Naturais e Medio Ambiente, Escola de Enxeñaría de Minas e Enerxía, University of Vigo, 36310, Vigo, Spain

^{*} Corresponding author.

wall paintings of the Hospital of "San Juan de Dios" located in semiopen courtyards or the mural paintings of the Alhambra and the Moorish quarter (Albaycin, Granada) [12,13]. These wall paintings are exposed to relatively high levels of atmospheric pollution [9,14]. The high porosity of tempera paints and the underlying mortars make wall paintings very vulnerable to pollution-induced chemical weathering. Common damage patterns observed upon crystallization of gypsum include disaggregation, microflaking, and the formation of surface bloom [15].

In order to get a better insight into SO₂-induced deterioration of lime-based tempera paints, paint dosimeters containing either rabbit skin glue or egg yolk were exposed outdoors for 40 months in the historic city center of Granada. A second set of dosimeters was exposed to an accelerated SO₂-aging test to further study mineralogical and morphological changes upon sulfation of lime-based pigments in the presence and absence of an organic binder. To this end a wide range of analytical techniques were applied, including x-ray diffraction (XRD), laser particle size analysis, nitrogen adsorption, field emission scanning electron microscopy (FESEM), Raman spectroscopy, and spectrophotometry. Analytical results revealed a significant effect of the organic binders on the mineralogical evolution of lime-based tempera paints and their susceptibility to sulfation. The outcome of this investigation furthers the understanding of the chemical weathering process of lime-based tempera paints and allows for recommendations regarding the selection and preparation of adequate materials, not only for paintings conservation but also for applications involving the use of lime mortars or plasters exposed to polluted urban air.

2. Materials and methods

2.1. Pigments and binders

Three different lime-based pigments of different grain size (see Table 1) were purchased from Kremer Pigment GmbH & Co. (Germany): *Bianco di San Giovanni* standard (Ref. 11,415) with a mean particle size of ~60 µm, *Bianco di San Giovanni* coarse (Ref. 11,416) with a mean particle size of ~120 µm, and extrafine calcite (Ref. 58,720) with mean particle size of ~25 µm [16]. Note that *Bianco di San Giovanni* has been historically prepared by sun-drying small "cakes" of slaked lime in order to obtain a partial carbonation of portlandite upon reaction with atmospheric CO₂ [17]. Consequently, these pigments contain a mixture

Table 1

Nomenclature of samples.

Pigments	Material
CA-EF BSG-ST BSG-C CaCO ₃ Ca(OH) ₂	Extrafine calcite Bianco di San Giovanni (standard) Bianco di San Giovanni (coarse) Analytical grade calcium carbonate (calcite) Analytical grade calcium hydroxide (portlandite)
Outdoor-exposed dosimeters and CA-EF-EY [*] BSG-ST-EY BSG-C-EY CA-EF-RG [*] BSG-ST-RG BSG-C-RG	Test duration 6, 12, 24, 36, 40 months
SO ₂ -aged dosimeters and Test du CA-EF-RG BSG-ST-RG BSG-C-RG CaCO ₃ -RG Ca(OH) ₂ -RG Ca(OH) ₂ -H ₂ O [°]	ration 5, 10, 34, 82 h

 * Paint dosimeters prepared with egg yolk (EY), rabbit skin glue (RG), or deionized water (H₂O).

of calcium carbonate (i.e. calcite, $CaCO_3$) and calcium hydroxide (i.e. portlandite, $Ca(OH)_2$). Pigments were mixed with two different organic binders: rabbit skin glue (Ref. 63028, Kremer Pigment GmbH & Co) or locally purchased egg yolk.

2.2. Preparation of paint dosimeters

Two sets of samples were prepared for testing. For long-term outdoor exposure, paint dosimeters were prepared following traditional recipes according to organoleptic parameters in order to mimic the egg yolk- and rabbit skin glue-based tempera paints used by medieval artists [18]. The binder content of paints with adequate consistency varied slightly, because binder demand depends on the pigments mineralogical composition and pigment particle size [16]. Note that the paints' consistency was found adequate when droplets formed at the tip of the brush would not fall off easily. In practice, 5 g of pigment were wetted with deionized water before adding fresh egg yolk or an 8 wt% aqueous rabbit glue solution. The organic binder content calculated based on thermogravimetric analysis was 16.6 \pm 3.3 wt% in the case of Bianco di San Giovanni-based paints and 9.5 \pm 1.5 wt% in extrafine calcite-based paint [19]. Freshly prepared paints were spread directly onto glass slides with a paintbrush. The paint was applied in several layers once the previous layer was completely dry. The paints' film thickness was 0.53 \pm 0.23 mm.

For the accelerated SO₂-aging test a second set of samples was prepared following the methodology above but with a fixed water/ pigment/rabbit skin glue ratio of 2:1:0.1 wt/wt. Paints prepared with analytical grade calcium hydroxide (Ca(OH)₂, Guinama S.L.U., Spain) and calcium carbonate (CaCO₃, Labkem, Spain) were included in this test as reference materials. The former was also prepared without the addition of rabbit skin glue, maintaining the same water-pigment ratio. Note that only samples prepared with rabbit skin glue were included in the accelerated SO₂-aging test because they can be expected to be more susceptible to chemical weathering than their egg yolk-based counterparts. All paint dosimeters were dried under laboratory conditions (20 \pm 5 °C and 40 \pm 10% RH) for 1 week before testing. Dosimeters were labeled by adding to the pigments label the letter EY for egg yolkbased paints, RG for rabbit skin glue-based paints, and H₂O for dosimeters prepared with water. See Table 1 for the complete nomenclature of samples.

2.3. Outdoor exposure test

Dosimeters were placed vertically in an exterior eave of the Hospital of San Juan de Dios in Granada which faces SW and is adjacent to a highly trafficked street. Samples were exposed for up to 40 months (i.e., from January 2014 to July 2017) to direct sunlight but partially protected from rain. Sunlight exposure was ~ 10 h in summer and ~ 5 h in winter, the maximum T being 40 $^{\circ}$ C in summer and the minimum T being -3 °C in winter. The climate in Granada is characterized by significant diurnal T and RH variations of 20 °C and 50%, respectively. Average RH is \sim 40% in summer and \sim 75% in winter [20]. Granada is a non-industrialized city surrounded by up to 3500 m high mountains. As a result of its topography, low wind speeds, heavy traffic and intensive construction work, O₃ and particulate matter frequently exceeded the threshold values set by the EU directive 2008/50EC and the World Health Organization (WHO) [9,21-24]. Even though, SO₂ concentration was below the limit established by the Directive 2008/50/EC it exceeded that recommended by the WHO in several occasions [21-23]. Moreover, based on the annual mean concentration (i.e., 11.85 μ g/m³ SO₂ in 2013), Granada is among the cities with the highest SO₂ contamination in Western Europe according to the European Environment Agency [24]. Data on average concentrations of atmospheric contaminants during the outdoor exposure test are reported in Table 2. Previous studies [4,9,14,25] showed that atmospheric particulate matter was primarily constituted of soil dust (quartz, calcite, dolomite,

A. Herrera et al.

Table 2

Average air contamination values (NO₂, O₃, SO₂, and particulate matter (PM₁₀ and PM_{2.5}) during the outdoor exposure of dosimeters in the city center of Granada [21–24].

Year	NO ₂		O ₃		SO ₂	PM ₁₀			PM _{2.5}		
	Annual		8 hours		8 hours	Daily value	Annual		Daily value	Annual	Daily value
	average		values		values		average			average	
	µg/m ⁻³		Nº days >120µg/m³		Nº days >100 µg/m³	Nº days >20 µg/m³	µg/m³		Nº days >50 µg./m³	µg/m³	Nº days >25 µg/m³
	Dir.*: max=40		Dir.: max=25		-	Dir.: max=35	Dir:: max=40		Dir.: max=35	Dir.: max=20	-
	WHO**:		-		WHO:	WHO:	WHO:		WHO:	WHO: max=10	WHO: max=3
	max=40				max=25	max=3	max=20		max=3		
2014		32		15	76	2		25	2	11	5
2015		36		17	85	17		33	8	15	16
2016		36		12	76	4		33	7	12	8

*Dir. = Directive 2008/50/EC.

**WHO = recommendations issued by the World Health Organizations (Grey color indicates values which exceed the threshold values set by the WHO).

gypsum, phyllosilicates, iron oxides/hydroxides), antropogenic black and organic carbon, metallic particles from fossil fuels, and sea salt.

2.4. Accelerated SO₂-aging test

Currently, no specific normative for accelerated SO₂-aging tests of pictorial samples is available. For this reason a test method used for the determination of the resistance of natural stone to SO₂-induced aging under high humidity conditions [26] was adapted. To this end, samples were enclosed in a hermetically sealed plastic container (7.5 l) together with diluted sulfurous acid (1.35 wt% SO₂, 104 ml) to generate a saturated SO₂ atmosphere and ~100% RH. The container was maintained at a 45° angle during testing in order to facilitate the run-off of condensation droplets accumulating at the container ceiling, which would otherwise have impacted the paint dosimeters. Samples were placed on a grid above the diluted acid and kept in the container for a total of 82 h. The mineralogical evolution was monitored by XRD after 5, 10, 34, and 82 h. Each time the container was opened the acid solution was replaced to assure a saturated SO₂ atmosphere.

2.5. Analytical techniques

X-ray diffraction (X'Pert PRO PANalytical B.V.) was used to determine the mineralogical composition of blank dosimeters and to identify compositional changes in outdoor-exposed/SO₂-aged samples. Analyses were performed using Cu-K α radiation, Ni filter, 45 kV voltage, 40 mA intensity and spinner. The exploration range was 3–60 °2 θ and goniometer speed 0.05°2 θ s⁻¹. Identification and semi-quantification (\pm 5 wt%) of minerals were carried out using Xpowder software [27].

Nitrogen sorption isotherms of powdered pigment samples were obtained at 77 K on a TriStar 3000 (Micromeritics) and the specific surface area was determined applying the BET method [28]. About 0.2 g of sample was degassed at 80 °C for 24 h prior to analysis using a sample degas system (VacPrep 061, Micrometrics).

Textural changes were studied using an optical microscope (Leica DVM2000) with $50-400 \times \text{lens}$. The data were processed using the Leica Application Suite v3.8.0 (Leica Microsystems[®]).

Color parameters of blanks and dosimeters exposed outdoors for 1, 6, 12, 24, and 40 months were measured with a Minolta CM-700d portable spectrophotometer using a 10° observer, 8 mm measuring aperture, and standard daylight illuminant D65 (color temperature: 6504 K). Data were expressed in CIEL*a*b* and CIEL*C*h color spaces, where L* is luminosity or lightness (black = 0 and white = 100); a* from + a* (red) to $-a^*$ (green), b* from + b* (yellow) to -b* (blue), C* is chroma and h is hue. Color changes were expressed as ΔL^* , Δa^* , Δb^* , ΔC^* , Δh , and ΔE^* ($\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$ [29]. Average values based on two measurements are reported. Note that ΔE^* higher than

three units is considered the threshold of perceptible detection for the human eye [30].

Morphological features and chemical composition of blank and exposed dosimeters were studied by means of a Field Emission Scanning Electron Microscope (FESEM, Auriga, Carl Zeiss, Germany) working at 10^{-4} Pa vacuum and 3 kV in secondary electron imaging mode. Samples were carbon coated. Additionally, elemental mapping was performed using a Supra 40Vp (FESEM, Carl Zeiss-Germany equipped with an Aztec 3 EDX and X-Max 50 mm detector). The working conditions were: 40–66 Pa vacuum, 15–20 kV beam accelerating voltage. High-resolution X-ray maps (1024 × 768 pixels) from selected areas of uncoated samples were obtained using 100 frames, a dwell time of 10 ms (2.5 h acquisition), 3 nA filament current, and 20 eV/ch resolution.

Micro-Raman analysis was performed using a Jasco NRS-5100 confocal Raman spectrometer in order to detect possible compositional changes in paint dosimeters upon outdoor exposure and accelerated SO₂-aging. Spectra were recorded by placing the samples on the OLYMPUS microscope stage and observing them with a $20 \times$ objective. Samples were excited with a solid state Torsana Starbright laser (785 nm). A series of recorded spectra (n = 6–10) were collected from each sample spot and averaged, with exposure times from 60 to 90 s (100% power). The Raman signal was collected in a 180° backscattering geometry by a Charge Coupled Device (CCD) after having passed through a 50 µm entrance slit. The Raman spectra were recorded in the $3000-100 \text{ cm}^{-1}$ range with a spectral resolution of 1.6 cm^{-1} . The Raman spectra were processed using JASCO Spectra Manager[™] II software.

3. Results and discussion

3.1. XRD analysis of pigments and dosimeters before and after outdoor exposure and accelerated SO_2 -aging test

3.1.1. Pigments

Semiquantitative XRD analyses showed that BSG pigments contained ~15 wt% calcite and ~85 wt% portlandite. The analytical grade Ca(OH)₂ contained > 95 wt% portlandite and a small amount of calcite (< 5 wt%). The CA-EF pigment contained mainly calcite and ~10 wt% dolomite (CaMg(CO₃)₂), while analytical grade calcite revealed no detectable impurities.

3.1.2. Paint dosimeters

The mineralogical composition of BSG-based paints did not change significantly upon mixing with either egg yolk or rabbit skin glue (i.e., the amount of newly formed calcite due to the carbonation of portlandite was below the detection limit (\sim 5 wt%) of this technique, and the possible formation of amorphous calcium carbonate cannot be



Fig. 1. XRD patterns of outdoor-exposed paints; a) BSG-ST-RG dosimeter before and after 6-month exposure; b) CA-EF-RG paint exposed for 40 months. Inset shows detail of the 020 reflection of gypsum. Por = portlandite, Cal = calcite, Gp = gypsum, Ms = unspecified mica, and Qz = quartz. See Table 1 for acronyms.

detected with XRD. Paint dosimeters recently prepared with analytical grade $Ca(OH)_2$ and dried for 2 days under laboratory conditions contained 70 wt% calcite and 30 wt% portlandite in the absence of rabbit skin glue, and only 15 wt% calcite and 85 wt% portlandite in its presence. The later results indicate that the presence of rabbit skin glue resulted in an important delay in carbonation by the formation of a superficial film around portlandite particles, which hindered the diffusion of ambient CO_2 to the carbonation front (Fig. 1a and b, Supplementary materials) [16]. CA-EF-based paints only contained calcite and dolomite, which underwent only minor dissolution/reprecipitation upon paint preparation. Consequently, no mineralogical changes were detected upon paint preparation.

3.1.3. Outdoor exposure

During outdoor exposure, BSG-based paints suffered important compositional changes. In samples prepared with rabbit skin glue an almost complete carbonation was observed after 6 months, and only trace amounts of portlandite were detected (Fig. 1a). Egg yolk binder, on the other hand, partially inhibited carbonation, and BSG-ST-EY and BSG-C-EY dosimeters still contained 45 and 30 wt% portlandite, respectively. Apparently, the egg yolk was more efficient in forming a long lasting superficial film around portlandite particles and impeded the diffusion of ambient CO₂ as compared to the more water soluble rabbit skin glue (Fig. 1c and d, Supplementary materials). It is known that egg yolk transforms into a fairly water- and weathering resistant binder over time due to photochemical reactions, while animal glue has a higher photostability and still swells in contact with water even after prolonged aging [31,32]. In contrast to animal glue which contains principally proteins (i.e. amino acids), egg yolk additionally contains lipids. These lipids can form peroxy radicals upon photo-oxidation and facilitate the denaturation of proteins (i.e., polymerization of proteins and/or crosslinking of peptide chains) [32]. According to Smith et al. [33], the lipid-protein interactions cause a decrease in protein solubility, which explains the lower water solubility of egg yolk.

After 1-year exposure of the BSG-based paints carbonation was generally completed with the exception of paints prepared with BSG-ST and egg yolk, where a trace amount of portlandite was still present. After 2 years of outdoor exposure, however, portlandite was no longer detected in any of the tempera paint samples. The presence of portlandite has an important effect on the susceptibility of these paints towards sulfation as revealed by accelerated SO₂-aging test results, increasing the rate of transformation (see below). CA-EF-based paints, in contrast, showed only small mineralogical changes over the course of the outdoor exposure (Fig. 1b).

In the majority of outdoor exposed paint dosimeters small amounts of quartz, dolomite, and clay minerals (note that CA-EF originally contained dolomite as an impurity) were detected, which originated from the deposition of atmospheric particulate matter and increased in concentration over time (Fig. 1b). The concentration of gypsum was generally below the XRD detection limit. Only in CA-EF-EY a small amount of gypsum was detected, which might either originate from the deposition of particulate matter (i.e., gypsum being part of the soil dust) or from sulfation of the calcite-based pigment by atmospheric SO₂.

3.1.4. Accelerated SO₂-aging test

Results of the accelerated SO₂-aging test evidenced the important role of the mineralogical composition of lime-based tempera paints on the susceptibility to sulfation (Table 3; Fig. 2, Supplementary Materials). Paints originally containing 85 wt% portlandite and 15 wt% calcite (i.e., BSG-ST- and BSG-C-based paints) suffered a more rapid sulfation as compared to paints only containing calcite (Table 3). Note that CaCO3-RG paint followed the same trend as CA-EF-RG paint, and only data for the later sample are shown here as a representative example. During the first stage of sulfation only calcium sulfite hemihydrate (CaSO₃·0.5H₂O) was detected in all dosimeters. Note that calcium sulfite has long been recognized as an intermediate product during sulfation, eventually transforming into gypsum [34]. After 82 h of exposure, gypsum was indeed observed additional to calcium sulfite hydrate in BSG-based paints. In these paints only trace amounts of portlandite and calcite remained (Table 3). In both calcite-based paints, in contrast, gypsum was not detected after 82 h. The relative broadness of the calcium sulfite hemihydrate Bragg peaks suggests its low crystallinity (Fig. 2, Supplementary Materials), which is in agreement with FESEM observation showing its nanogranular morphology (see below). At the end of the test calcite-based paints still contained ~80 wt% calcite. This result is not surprising because portlandite is much more hygroscopic and soluble than calcite and, thus, reacts more readily with ambient SO₂ to form calcium sulfite/sulfate; a reaction which only occurs in the presence of water or sufficiently high relative humidity levels [35,36]. Cultrone et al. [7] already recognized the important role of portlandite in the fixation of SO₂ as sulfates. According to these authors, the high pH created by the dissolution of portlandite facilitates SO₂ absorption and hydrolysis, leading to the formation of sulfite and subsequent oxidation to sulfate ions, which react with Ca²⁺ and, ultimately, precipitate as gypsum.

Experimental results also revealed the important influence of the organic binder on the susceptibility to sulfation. In the presence of rabbit skin glue, ~ 50 wt% of portlandite transformed into 25 wt% calcium sulfite hemihydrate and 25 wt% calcite after 34 h SO₂-aging, in the case of the sample prepared with analytical grade Ca(OH)₂ (Table 3). In the absence of rabbit skin glue, in contrast, only 20 wt% of calcite remained and portlandite completely transformed into calcium

Table 3

Mineralogical evolution	(wt%) based on semi	uantitative XRD analy	vsis of paint	dosimeters during	accelerated SO ₂ -agin	g (See Table 1	for acronyms).
		1	J F		2.0	0	

Sample	Mineral phase and JCPDS* card number							
	Calcite (721652)	Portlandite (892779)	Dolomite (841208)	Calcium sulfite hemihydrate (840962)	Gypsum (741905)			
BSG-ST-RG	15	85	-	_	-			
BSG-ST-RG-34 h	20	60	-	20	-			
BSG-ST-RG-82 h	Tr	Tr	-	40	60			
BSG-C-RG	15	85		-	-			
BSG-C-RG-34 h	35	50	-	15	-			
BSG-C-RG-82 h	Tr	Tr	-	35	65			
CA-EF-RG	90	-	10	-	-			
CA-EF-RG-34 h	80	-	10	10	-			
CA-EF-RG-82 h	80	-	5	15	-			
Ca(OH)2-RG	15	85	-	-	-			
Ca(OH)2-RG-34 h	25	50	-	25	-			
Ca(OH)2-RG-82 h	5	-	-	95	-			
Ca(OH)2-H2O	70	30	-	-	-			
Ca(OH)2-H2O-34 h	20	-	-	80	-			
Ca(OH) ₂ -H ₂ O-82 h	5	-	-	85	10			

JCPDS = Joint Committee on Powder Diffraction Standards.

Tr = trace.

sulfite hemihydrate. After 82 h, the sample Ca(OH)₂-H₂O contained $\sim 10 \text{ wt\%}$ gypsum additional to 85 wt% calcium sulfite hemihydrate and 5 wt% calcite, whereas gypsum had not formed in the Ca(OH)₂-RG sample (Table 3). Note that the blank Ca(OH)₂-RG sample contained 85 wt% portlandite at the beginning of the accelerated SO₂-aging test and, based on its mineralogical composition, should have been more susceptible to sulfation than the corresponding sample mixed with water (Ca(OH)2-H2O), which contained 70 wt% calcite at the start of the ageing test. However, the organic binder acted as a barrier by creating a superficial film around pigment particles, which hindered the access of water and SO₂ to the calcite and/or portlandite surfaces (Fig. 1, Supplementary materials). For sulfation to take place, water in direct contact with the calcite/portlandite surface is needed to induce the absorption and hydrolysis (and oxidation) of SO₂, and the dissolution of the substrate (i.e., source of Ca ions), in order to reach supersaturation with respect to calcium sulfite hemihydrate and/or gypsum. Over time, the rabbit skin glue suffered hydrolysis and dissolution as a result of the atmosphere's high RH and high SO₂ concentration, and was no longer effective as a barrier [37]. Consequently, sulfation could progress at a faster rate (Table 3).

3.2. Optical microscope study of blank and outdoor exposed dosimeters

Microscopic observations of blank dosimeters showed the influence of the pigment particle size on the surface roughness, coarser pigments leading to rougher, more irregular surfaces (Fig. 2). In paints prepared with the finest pigment (CA-EF) some large circular pockmarks were observed on the paint surface, which were relics of air bubbles (arrows in Fig. 2a and c). Generally, paints prepared with egg yolk had a more yellowish tint due to the strong yellow color of the binder.

On the surface of all outdoor-exposed dosimeters a large amount of dark brownish and yellowish particles was observed, which originated from deposited atmospheric particulate matter after 40 months of exposure. Elemental x-ray mapping allowed the identification of deposited particles as quartz, aluminosilicates, iron-bearing oxides/hydroxides, and dolomite (see below). The amount of deposited particles depended on the paint's surface roughness, a larger amount of deposited particles accumulating on rougher surfaces. Charola and Ware [36] also recognized the relationship between surface roughness and amount of deposited pollutants (i.e., gases and particles). They further stated that deposition would be facilitated by a high surface moisture content. Actually, surface moisture will be higher in BSG-based paints, containing an important amount of portlandite, which is more hygroscopic than calcite [38]. Deposited particulate matter plays an important role in the acid-induced degradation of carbonate material such as limestone, lime mortar, and lime-based tempera paints. On the one hand, carbonaceous particles contribute to the dry deposition of SO₂ as a result of their high surface area [36]. On the other hand, metallic particles (especially iron oxides/hydroxide) facilitate catalytic oxidation of SO₂ in the presence of humidity, resulting in the formation of sulfuric acid. The acid, in turn, will react with the calcium carbonate in the substrate and lead to the formation of calcium sulfates [4].

The paint sample prepared with CA-EF suffered severe material loss after 24 months regardless of binder type due to the periodic impact of rain (Fig. 2b and d), whereas paints prepared with BSG pigments appeared intact (Fig. 2f, h, j, and l). It has been demonstrated previously [16] that in the case of tempera paints prepared with BSG pigments (i.e., pigments containing ~85 wt% portlandite), pigment-binder interactions during carbonation lead to the formation of an organic-inorganic hybrid material similar to biominerals with high weathering resistance. In calcite-based paints (CA-EF), in contrast, no such pigment-binder interactions occurred and the paint disintegrated upon dissolution and leaching of the organic binder impacted by rain. As a consequence, part of the deposited particulate matter was also washed away and hardly any yellowish and brownish particles were observed (Fig. 2b and d).

3.3. Color measurements of blank, outdoor-exposed, and SO_2 -aged dosimeters

Spectrophotometry results revealed that L* was lower in paints prepared with CA-EF as compared to BSG-based paints regardless of binder type (Table 4). This can be explained by the substantial amount of dolomite in this pigment; dolomite absorbing more light in the visible spectrum as compared to calcite [39]. Color measurements were in agreement with optical microscopy observations, showing that paint prepared with egg yolk were more greenish-yellowish than rabbit skin glue-based paints as indicated by lower a* and higher b* values. Chroma and hue were significantly higher in egg-yolk based samples as compared to their rabbit skin glue-based counterparts. However, a direct relation between these parameters and the paints' mineralogical composition could not be established (Table 4).

Generally, a* increased slightly upon outdoor exposure, indicating a change towards a more reddish color. This change was more pronounced in the egg yolk-based samples (Fig. 3a). Remarkably, b* values generally diminished upon outdoor exposure for up to 12 months,



Fig. 2. Optical microscopy images of blank dosimeters and dosimeters exposed outdoors during 40 months. Arrows indicate pockmarks, being relics of air bubbles. See Table 1 for acronyms.

especially in the case of egg yolk-based paints (Fig. 3b). The reason for this decrease is twofold. On the one hand, it is known that egg yolk loses part of its yellow color upon exposure to light and/or heat [32,40]. On the other hand, partial binder loss, especially in the case of paints prepared with CA-EF, was responsible for the observed reduction in b^{*}. However, after 12 months of outdoor exposure b^{*} generally increased again and L^{*} decreased in dosimeters prepared with BSG, indicating a color change towards yellow, which might be attributed to the deposition of yellowish/brownish atmospheric dust particles. The amount of deposited particles increased over time, resulting in a reduction of L* of up to 8 units at the end of the outdoor exposure (Fig. 3c). Additionally, sunlight-induced degradation of the organic binder, which turned more yellowish especially in the case of rabbit skin glue-based paints, also had an important contribution to the observed color change [16,41]. Overall, paint dosimeters suffered important color changes (ΔE^*), which were generally well above the established limit for human perception (i.e., $\Delta E^* \ge 3$ units [30]) after prolonged exposure (Fig. 3d). The very small amount of gypsum (i.e.,

Progress in Organic Coatings 123 (2018) 99-110

Sample	L*	a*	b*	C*	h
CA-EF-EY	88,74 ± 0,07	$-1,31 \pm 0,01$	7,40 ± 0,31	$7,52 \pm 0,30$	100,1 ± 0,49
BSG-ST-EY	94,62 ± 0,13	$-1,68 \pm 0,04$	8,70 ± 0,22	8,88 ± 0,22	$101,0 \pm 0,54$
BSG-C-EY	95,68 ± 0,21	$-1,05 \pm 0,07$	$6,52 \pm 0,66$	6,60 ± 0,65	99,2 ± 1,19
CA-EF-RG	$90,32 \pm 0,40$	$-0,41 \pm 0,10$	$3,51 \pm 0,10$	$3,57 \pm 0,10$	96,7 ± 0,63
BSG-ST-RG	96,08 ± 0,09	$-0,53 \pm 0,02$	$3,42 \pm 0,03$	$3,46 \pm 0,03$	98,8 ± 0,35
BSG-C-RG	93,48 ± 0,38	$-0,35 \pm 0,03$	$5,77 \pm 0,18$	$5,78 \pm 0,17$	93,6 ± 0,42

 Table 4

 Color measurements of blank dosimeters. See Table 1 for acronyms

generally < 5 wt%) detected with XRD, Raman spectroscopy and SEM in outdoor-exposed dosimeters (see below) is not thought to be sufficient to contribute to any color change.

Exposure to SO₂ caused a decrease in L* and a generally important increase in b*, while changes in a* were very small (Table 5). These findings are in agreement with data presented by Grossi et al. [42], showing a similar effect of accelerated SO₂-aging on ornamental limestone, which became slightly darker and more yellowish. Changes in hue did not reveal any clear tendency in SO₂-aged paint dosimeters and the reason for the extreme color change in the case of CA-EF-RG has to be clarified in a future study.

3.4. FESEM analysis of pigments and paint dosimeters before and after outdoor exposure and accelerated SO_2 -aging test

3.4.1. Pigments

FESEM images of lime-based pigments show that CA-EF had a very distinct morphology as compared to BSG-ST/C pigments (Fig. 4a and

d). The former was comprised of blocky calcite crystals $(10-100 \,\mu\text{m})$ with irregular edges and a fractured appearance, typical for pigments obtained by grinding of bigger lumps. These large crystals were accompanied by smaller crystals, $\leq 1 \,\mu\text{m}$ in size (Fig. 4a). Images of BSG pigments, in contrast, revealed the presence of aggregates formed by nano-sized portlandite/calcite crystals. The morphological differences have an important influence on the paints' susceptibility to pollution-induced deterioration; BSG pigments offering a much larger surface area (i.e., specific surface area of BSG-ST and BSG-C being 12.6 m²/g and 11.7 m²/g, respectively) for reaction with atmospheric contaminants as compared with the CA-EF pigment (i.e., specific surface area being 1.6 m²/g).

3.4.2. Outdoor exposure

After 40-month outdoor exposure only minor changes in the calcite crystal morphology could be detected in CA-EF-based paints regardless of binder type (Fig. 4b and c). The edges of larger crystals seemed slightly rounded, possibly due to dissolution processes. Occasionally,



Fig. 3. Color changes a) Δb^* , b) ΔL^* , and c) ΔE^* undergone by paint dosimeters during outdoor exposure for up to 40 months. Error bars are included. Note that errors were in most cases too small to be visualized in the graphs. See Table 1 for acronyms.

Га	ble	5	
10	DIC		

Color changes of dosimeters after 82 h of SO₂ exposure. See Table 1 for acronyms.

-		-				
Sample	ΔL^*	Δa^*	Δb^*	ΔC^*	Δh	ΔE^*
CA-EF-RG BSG-ST-RG Ca(OH) ₂ -RG Ca(OH) ₂ -H ₂ O Ca(O ₂ -RG	$\begin{array}{r} -6,06 \pm 0.25 \\ -1,49 \pm 0.19 \\ -0.95 \pm 0.26 \\ -0.98 \pm 0.40 \\ -2.70 \pm 0.77 \end{array}$	$\begin{array}{c} -0.93 \pm 0.11 \\ 013 \pm 0.02 \\ 0.28 \pm 0.05 \\ 0.02 \pm 0.10 \\ 0.33 \pm 0.05 \end{array}$	$14,31 \pm 0,94 \\ 4,90 \pm 0,09 \\ 4,09 \pm 0,24 \\ 4,78 \pm 0,10 \\ 0.51 \pm 0,63$	$14,31 \pm 0,94 4,77 \pm 0,09 4,09 \pm 0,24 4,77 \pm 0,17 0,48 \pm 0,62$	$\begin{array}{r} -3,27 \pm 0,43 \\ -6.51 \pm 0,54 \\ -2,78 \pm 0,39 \\ 2,60 \pm 0,76 \\ 6.89 \pm 1,08 \end{array}$	$14,91 \pm 0,96 \\ 5,13 \pm 0,13 \\ 4,21 \pm 0,22 \\ 4,88 \pm 0,18 \\ 2.85 \pm 0,63$
	, .,	, ,,,,,	, .,	, .,.	, ,	, -,

calcite crystals showed fractures, likely being induced by severe diurnal T changes (Fig. 4c, dashed line). Rodriguez-Navarro et al. [43] demonstrated that thermally-induced physical weathering of calcite is related to the mineral's anisotropic thermal expansion. Note that fracturing was no artifact of sample preparation because samples were not ground prior to FESEM analysis. BSG-based paints underwent important changes due to the dissolution and carbonation of portlandite (Fig. 4e and f). Samples mixed with rabbit skin glue showed nanogranular structures and rhombohedral calcite crystals, presenting in some cases

rounded edges (Fig. 4e, arrows). These morphological features have typically been observed upon calcite crystallization in the presence of organics, and are interpreted as evidence for the formation of an organic-inorganic hybrid material [16,44]. Note that if no direct attachment or adsorption of the organics on ledges of advancing steps of the growing calcite surface had occurred, there would be no rounding [45]. Furthermore, spherical or semispherical structures typical for vaterite were detected in BSG-based paints prepared with egg yolk (Fig. 4f). The presence of vaterite was confirmed by Raman spectroscopy (see below).



Fig. 4. FESEM images of a) CA-EF pigment; b) CA-EF-RG outdoor-exposed for 40 months; c) CA-EF-EY outdoor-exposed for 40 months; d) BSG-ST pigment; e) BSG-ST-RG outdoor-exposed for 40 months (arrows indicate nanogranular structures and calcite crystals with rounded edges); f) BSG-ST-EY outdoor-exposed for 40 months, Vtr = vaterite; g) Sulfur x-ray map of CA-EF-EY blank; h) Sulfur x-ray map of CA-EF-EY dosimeter outdoor-exposed for 40 months; and i) gypsum detected on CA-EF-EY dosimeter outdoor-exposed for 40 months (microanalysis in inset). See Table 1 for acronyms.

Vaterite is a metastable phase and normally transforms readily into calcite under most ambient conditions [46]. However, it has been demonstrated that the presence of organics may result in a kinetic stabilization of vaterite and prevent or delay its transformation into calcite [47–49]. Note that vaterite was detected with XRD and SEM in identical samples exposed to very similar environmental conditions [16].

The comparison of elemental x-ray maps of blank and outdoor-exposed dosimeters revealed the appearance of isolated areas of high sulfur concentration upon prolonged exposure (Fig. 4g and h). All outdoor-exposed dosimeters showed these sulfur-rich areas but only the elemental map of CA-EF-EY is included here as a representative example. The observed sulfur signal in the blank CA-EF-EY dosimeter corresponded to background noise and no sulfur-rich impurities can be detected in this sample (Fig. 4g). Note that elemental mapping also disclosed the presence of Al, Si, Fe, K, and Mg on outdoor-exposed dosimeters, all elements likely being related with deposited atmospheric particulate matter such as quartz, aluminosilicates, iron-bearing oxides/hydroxides, and dolomite. FESEM imaging (Fig. 4i) in combination with microanalysis allowed the unambiguous identification of the sulfur-rich areas as gypsum aggregates, showing similar morphological features as those of authigenic gypsum (i.e., tabular-shaped crystals either isolated or forming small clusters), formed in tempera paint samples subjected to accelerated SO₂-aging (Fig. 5). However, solely based on FESEM results it was impossible to unambiguously determine the origin of gypsum crystals (i.e., deposited gypsum particles or sulfated calcite particles) because the very early stages of calcite/portlandite sulfation could not be detected. In many cases, gypsum crystals seemed to be deposited on the surface and a calcite/gypsum intergrowth was not observed. Even though direct evidence for sulfation was not detected in outdoor-exposed tempera paints, the presence of gypsum particles is of importance because they can act as templates for gypsum crystallization via self-epitaxy [4].

The lack of any clear sign of sulfation was unexpected. Especially, considering the relatively high SO₂ and particulate matter concentrations in Granada's urban air (Table 2). Moreover, Urosevic et al. [9] found relatively rapid gypsum formation on limestone samples exposed for 1 year to urban air in Granada's historic city center. Most likely, the organic binder in tempera paints hindered gypsum formation over the course of the 40-month outdoor exposure. First of all, the organic binder acted as a barrier by creating a film around the pigment particles as observed in the case of dosimeters exposed to accelerated SO₂-aging (Table 3; Fig. 2, Supplementary Materials). However, the thickness of the organic film will gradually be reduced during the outdoor exposure by the periodic impact of rain and photo-induced degradation. As a result, the film will no longer be effective as a protective barrier. In the case of BSG-based paints, portlandite almost completely carbonated in the presence of the organic binder during the first 6 months of the outdoor exposure (Fig. 1a), facilitating the formation of an organicinorganic hybrid material (Fig. 4e), where part of the organic binder is incorporated in the organic-inorganic calcite structure and cannot easily be leached out [16]. Recent studies demonstrated that these hybrid materials not only have higher mechanical resistance, but also show improved chemical weathering resistance, which would explain the lack of any clear sign of sulfation in this type of paints [50]. Obviously, in the case of calcite-based paints, the organic binder can not be incorporated into the calcite structure and organic-inorganic hybrid materials do not form. Actually, optical microscopy observations revealed the lower weathering resistance of this type of paints, suffering severe material loss (Fig. 2b and d). Considering the relatively high solubility of gypsum (solubility = 2.4 g/L at $20 \degree$ C) as compared to calcite (solubility = 0.013 g/L at 25 °C), it is possible that most of the sulfate weathering products together with part of the calcite-based paint have been washed away by the periodic impact of rain. In fact, gypsum formation is generally not detected on surfaces which are "washed" by the direct impact of rain [9,51].

3.4.3. Accelerated SO₂-aging test

The extreme conditions during the SO₂-aging test provoked significant morphological changes in lime-based tempera paints. Paint samples prepared by mixing reagent grade Ca(OH)₂ with water, which contained ~70 wt% calcite according to XRD analysis, originally showed calcite crystal bundles with the typical scalenohedral morphology of carbonated Ca(OH)₂ pastes [52]. After 82 h of SO₂ exposure, scalenohedral calcite crystals suffered severe dissolution and blocky gypsum crystals formed (Fig. 5b). However, it was not possible to unambiguously identify calcium sulfite hemihydrate in this sample based on morphological characteristics.

In the case of CA-EF-RG paint, the originally smooth surface of calcite crystals (Fig. 5c) was almost completely covered with a film of nanogranular calcium sulfite hemihydrate (according to XRD) after 82 h (Fig. 5d). The observed nanostructural features of the newly formed phases are in agreement with XRD results, which hinted a low crystalinity of calcium sulfite hemihydrate. The FESEM image shows that no crystallographic continuity exists between the dissolving calcite (Fig. 5d, arrow indicates dissolution-induced macro steps) and the newly formed sulfite product layer (which is separated from the calcite substrate by a gap). Although the produced sulfite grossly preserves the overall rhombohedral shape of calcite crystals (Fig. 3, Supplementary Materials), thereby pointing to a possible pseudomorphic replacement, there is no epitaxy between parent and product phases (Fig. 5d, dashed arrow). This implies that no passivation layer will form and the reaction would continue under adequate environmental conditions until all calcite is transformed [53].

BSG-based paints revealed a structure formed by aggregated nanosized particles (Fig. 5e). After 82 h of SO2 exposure, a massive formation of tabular-shaped gypsum clusters was observed, completely replacing portlandite and $\sim 90 \text{ wt\%}$ of the original calcite according to XRD data. Furthermore, spherical morphologies typical for vaterite were detected. Note that the corresponding blank dosimeters did not contain any vaterite and it can be ascertained that this phase formed during the SO₂ exposure. Actually, Fernández-Díaz et al. [54] were able to demonstrate that vaterite was stabilized in the presence of SO₄ over a relative long period of time (i.e., > 250 h). The presence of the metastable vaterite will add to the destabilization of tempera paints exposed to SO₂-aging. On the one hand, phase transition is accompanied by volume changes (i.e., transformation of portlandite into gypsum or vaterite, and calcite transformation into gypsum) (Table 6). Furthermore, vaterite will eventually transform into calcite, which again will result in a volume change. On the other hand, the spherical vaterite will have inferior mechanical strength as compared to scalenohedral calcite crystals, which forms an interlocked structure with higher cementing capacity [52].

3.5. Raman analysis

3.5.1. Outdoor exposure

Raman spectroscopy confirmed XRD and SEM data (see below), revealing the presence of gypsum in outdoor-exposed paint dosimeters, indicated by low intensity gypsum bands at 415 and 1013 cm⁻¹ (Fig. 6a). Note that only spectra of the BSG-ST-EY sample are included here as representative examples. Raman spectra also showed a decrease in portlandite content over time in BSG-based paints as a result of the reaction with atmospheric CO₂ (Fig. 6a), and allowed the detection of vaterite, which was not present in a sufficiently high concentration to be detected by XRD. In samples exposed to accelerated SO₂-aging, abundant amounts of gypsum and calcium sulfite hemihydrate were observed, the spectrum of the later being almost identical to hannebachite (2CaSO₃·(H₂O)) (Fig. 6b) [55]. Note that the presence of vaterite in SO₂-aged samples could not be confirmed unambiguously with this technique.



Fig. 5. FESEM images of a) $Ca(OH)_2$ -H₂O blank; b) $Ca(OH)_2$ -H₂O after 82 h SO₂-aging test, Gp = gypsum c) CA-EF-RG blank; d) CA-EF-RG after 82 h SO₂-aging test; e) BSG-C-RG blank (high magnification image in inset); and f) BSG-C-RG after 82 h SO₂-aging test (arrows indicate gypsum crystals). See Table 1 for acronyms.

Table 6

Molar volume (cm $^3\,{\rm mol}^{-1})$ of minerals and calculated volume change (%) upon phase transition.

Molar volume ($cm^3 mol^{-1}$)	Volume change (%)
33.2	19 (Por \rightarrow Vtr)
	11 (Por \rightarrow Cal)
	123 (Por \rightarrow Gp)
39.4	-6 (Vtr \rightarrow Cal)
36.9	111 (Cal \rightarrow Gp)
74.1	
	Molar volume (cm ³ mol ⁻¹) 33.2 39.4 36.9 74.1

Por = portlandite, Vtr = vaterite, Cal = calcite, Gp = gypsum.

4. Conclusions

Analytical results revealed the important influence of the pigment's mineralogical composition and specific surface area on the susceptibility towards sulfation; pigments containing portlandite showing faster sulfation than pigments containing only calcite. Furthermore, the organic binder delayed the reaction between lime-based paints and atmospheric SO₂. However, the presence of organic binder also slows down carbonation in the case of BSG-based paints and thus the possible formation of organic-inorganic hybrid materials. Future studies should be performed to determine the optimal binder content which would effectively delay sulfation without impeding a fast carbonation.



Fig. 6. Raman spectra a) BSG-ST-EY paint before and during outdoor exposure; b) BSG-C-RG and Ca(OH)₂-H₂O before and after accelerated SO₂-aging for 82 h T = torsion, Vtr = vaterite, Por = portlandite, Cal = calcite, Gp = gypsum, and CS = calcium sulfite hemihydrate. See Table 1 for acronyms.

Regardless of pigment composition, calcium sulfite hemihydrate was always detected as an intermediate phase on samples exposed to SO₂, forming a nanogranular film on the pigment particle's surface. Direct transformation of calcite into gypsum was not detected and the lack of crystallographic continuity of calcium sulfite hemihydrate with the underlying calcite implies that the sulfation process will not cease until complete sulfation is achieved. However, the sulfation reaction requires water and might halt under dry conditions (i.e., low RH and little or no precipitation) but resume as water becomes available.

Remarkably, no clear evidence for sulfation was detected in limebased tempera paints after 40-month outdoor exposure to polluted urban air. Several reasons might explain this result. On the one hand, carbonation of portlandite in the presence of organics (i.e., rabbit skin glue or egg yolk binder) might have promoted the formation of organicinorganic hybrid materials with high resistance towards chemical weathering in the case of BSG-based paints. On the other hand, periodic impact of rain might have washed off calcium sulfite/sulfate phases, especially in the case of calcite-based paints, which showed severe material loss after prolonged outdoor exposure.

The selection of lime-based paints for conservation interventions in polluted environments should be made considering the prevailing climate conditions. In dry climates where a severe delay in the carbonation reaction can be expected, the use of calcite-based paints might be advisable. In humid climates or under direct impact of rain, in contrast, BSG-based paints are preferable, which are able to form organic-inorganic hybrid materials with high resistance towards physical and chemical weathering. The use of organic additives such as rabbit skin glue might also be beneficial to improve the chemical weathering resistance of lime mortars and plasters. However, as pointed out before, the optimal organic content has to be established to allow for sufficiently fast carbonation.

Acknowledgements

Financial support was provided by the Spanish Government and the Junta de Andalucía (research projects AERIMPACT, CGL2012-30729 and EXPOAIR, P12-FQM-1889), the European Regional Development Fund (ERDF) and the Andalusian Research Groups RNM-179. Analyses were performed at the Scientific Instrumentation Center (CIC) of the University of Granada (Spain). J.A. Herrera Rubia is funded by a Spanish grant from the AERIMPACT Project (ref.BES-2013-065507). J.S. Pozo-Antonio was supported by a postdoctoral contract with the University of Vigo within the framework of the 2011–2015 Galician Plan for Research, Innovation and Growth (Plan I2C) for 2014. K. Elert is a post-doctoral fellow in the EXPOAIR Project. We thank C. Rodriguez-Navarro for comments and suggestions.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.porgcoat.2018.06.017.

References

- R.J. Schaffer, The Weathering of Natural Building Stones, DSIR, Building Research Special Report 18, Stationary Office, London, 1932.
- [2] B.J. Smith, M. Gomez-Heras, S. McCabe, Understanding the decay of stone-built cultural heritage, Prog. Phys. Geogr. 32 (2008) 439–461.
- [3] D. Patrón, H. Lyamani, G. Titos, J.A. Casquero-Vera, C. Cardell, G. Močnik, L. Alados-Arboledas, F.J. Olmo, Monumental heritage exposure to urban black carbon pollution, Atmos. Environ. 170 (2017) 22–32.
- [4] C. Rodriguez-Navarro, E. Sebastian, Role of particulate matter from vehicle exhaust on porous building stones (limestone) sulfation, Sci. Total Environ. 187 (1996) 79–91.
- [5] P. Maravelaki-Kalaitzaki, Black crusts and patinas on Pentelic marble from the Parthenon and Erechtheum (Acropolis, Athens): characterization and origin, Anal. Chim. Acta 532 (2005) 187–198.
- [6] Á. Török, Black crusts on travertine: factors controlling development and stability, Environ. Geol. 56 (2008) 583–594.
- [7] G. Cultrone, A. Arizzi, E. Sebastián, C. Rodriguez-Navarro, Sulfation of calcitic and dolomitic lime mortars in the presence of diesel particulate matter, Environ. Geol. 56 (2008) 741–752.
- [8] European Environment Agency, Air Pollution Fact Sheet 2013 Spain, European Environment Agency, Copenhagen, 2013.
- [9] M. Urosevic, A. Yebra-Rodríguez, E. Sebastián-Pardo, C. Cardell, Black soiling of an architectural limestone during two-year term exposure to urban air in the city of Granada (S Spain), Sci. Total Environ. 414 (2012) 564–575.
- [10] E.V. Sayre, L.J. Majewski II., Technical inestigation of the deterioration of the paintings, Stud. Conserv. 8 (1963) 42–54.
- [11] K. Zehnder, Gypsum efflorescences in the zone of rising damp. Monitoring of slow decay processes caused by crystallizing salts on wall paintings, in: J. Riederer (Ed.), Proc. 8th Inter. Congress on Deterioration and Conservation of Stone, Möller Druck, Berlin, 1996, pp. 1669–1678.
- [12] L.F. Capitán-Vallvey, E. Manzano, V.M. Flórez, Estudio de materiales de las pinturas murales de la Torre de las Damas (Granada) y estado de conservación, Al-Qantara 14 (1993) 177–203.
- [13] E. Manzano, A. García Bueno, A. González-Casado, M. Del Olmo, Mortars, pigments and binding media of wall paintings in the 'Carrera del Darro' in Granada, Spain, J. Cult. Herit. 1 (1999) 19–28.
- [14] V. Kontozova-Deutsch, C. Cardell, M. Urosevic, E. Ruiz-Agudo, F. Deutsch, R. Van Grieken, Characterization of indoor and outdoor atmospheric pollutants impacting architectural monuments: the case of San Jerónimo Monastery (Granada, Spain), Environ. Earth Sci. 63 (2011) 1433–1445.
- [15] M. Matteini, An Assessment of Florentine Methods of Wall Painting Conservation Based, in: The Conservation of Wall Paintings, The Getty Conservation Institute, Los Angeles, 1992, pp. 137–148.
- [16] K. Elert, A. Herrera, C. Cardell, Pigment-binder interactions in calcium-based tempera paints, Dyes Pigm. 148 (2018) 236–248.
- [17] C. Cennini, El libro del Arte, AKAL S.L., Madrid (Spain), 1988.

A. Herrera et al.

- [18] F. Pacheco, El arte de la pintura, Cátedra, Madrid, 1990.
- [19] J.S. Pozo-Antonio, D. Barral, A. Herrera, K. Elert, T. Rivas, C. Cardell, Effect of tempera paint composition on their superficial physical properties-application of interferometric profilometry and hyperspectral imaging techniques, Prog. Org. Coat. 117 (2018) 56–68.
- [20] N. Velilla, Estación meteorológica Granada-Albayzín (España), (2017) (Accessed 07 October 2016), www.ugr.es/~velilla/meteo-albayzin/resumen.htm.
- [21] Ecologistas en acción, Informe La calidad del aire en el Estado español durante 2015 (2014), p. 104.
- [22] Ecologistas en acción, Informe La calidad del aire en el Estado español durante 2016 (2015), p. 110.
- [23] Ecologistas en acción, Informe La calidad del aire en el Estado español durante 2017 (2016), p. 119.
- [24] European Environment Agency, (2013) (Accessed 5 January 2017), http://www. eea.europa.eu/themes/air/interactive/so2.
- [25] B. Horemans, C. Cardell, L. Bencs, V. Kontozova-Deutsch, K. De Wael, R. Van Grieken, Evaluation of airborne particles at the Alhambra monument in Granada, Spain, Microchem. J. 99 (2011) 429–438.
- [26] AENOR, Natural Stone Test Methods. Determination of Resistance to Ageing by SO2 Action in the Presence of Humidity (UNE-EN 13919:2003, Madrid), (2003).
- [27] J.D. Martín-Ramos, Using XPowder: A Software Package for Powder X-Ray Diffraction Analysis (GR 1001/04. ISBN 84-609-1497-6), (2004).
- [28] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60 (1938) 309–319.
- [29] CIE S014-4/E:2007, Colorimetry Part 4: CIE 1976 L*A*b* Colour Space. Commission Internationale de l'eclairage, CIE Central Bureau, Vienna, 2007.
- [30] R.S. Berns, Principles of Color Technology, 3rd ed., Wiley-Blackwell, Hoboken, 2000.
- [31] H. Kühn, Erhaltung und Pflege von Kunstwerken und Antiquitäten 1, Keysersche Verlagsbuchhandlung, München, 1981.
- [32] A. Karpowicz, Ageing and deterioration of proteinaceous media, Stud. Conserv. 26 (1981) 153–160.
- [33] D.M. Smith, S.H. Noormarji, J.F. Price, M.R. Bennink, T.J. Herald, Effect of lipid oxidation on the functional and nutritional properties of washed chicken myofibrils stored at different water activities, J. Agric. Food Chem. 38 (1990) 1307–1312.
- [34] G. Amoroso, V. Fassina, Stone Decay and Conservation: Atmospheric Pollution, Cleaning, Consolidation and Protection, Elsevier, Amsterdam, 1983.
- [35] D. Camuffo, M. Del Monte, C. Sabbioni, Origin and growth of the sulfated crusts on urban limestone, Water Air Soil Pollut. 19 (1983) 351–359.
- [36] A.E. Charola, R. Ware, Acid depositon and the deterioration of stone: a brief review of a broad topic, in: S. Siegesmund, T. Weiss, A. Vollbrecht (Eds.), Natural Stone, Weathering Phenomena, Conservation Strategies and Case Studies. Geological Society Special Publication No. 205, London, 2002, pp. 393–406.
- [37] A. Tsugita, J.J. Scheffler, A rapid method for acid hydrolysis of protein with a mixture of trifluoroacetic acid and hydrochloric acid, Eur. J. Biochem. 124 (1982) 585–588.
- [38] D.T. Beruto, F. Barberis, R. Botter, Calcium carbonate binding mechanisms in the setting of calcium and calcium-magnesium putty limes, J. Cult. Herit. 6 (2005) 253–260.

- Progress in Organic Coatings 123 (2018) 99-110
- [39] S.J. Gaffey, Spectral reflectance of carbonate minerals in the visible and near infrared (0.35-2.55 microns): calcite, aragonite, and dolomite, J. Raman Spectrosc. 71 (1986) 151–162.
- [40] R. Mayer, S. Sheehan, The Artist's Handbook of Materials and Techniques, The Viking, New York, 1991.
- [41] K.J. Dilley, Loss of tryotophan associated with photo-polymerization and yellowing of proteins exposed to light over 300 nm, Biochem. J. 133 (1973) 821–826.
- [42] C.M. Grossi, P. Brimblecombe, R.M. Esbert, F.J. Alonso, Color changes in architectural limestones from pollution and cleaning, Color Res. Appl. 32 (2007) 320–331.
- [43] C. Rodriguez-Navarro, A. Rodriguez-Navarro, K. Elert, E. Sebastian, Role of marble microstructure in near-infrared laser-induced damage during laser cleaning, J. Appl. Phys. 95 (2004) 3350–3357.
- [44] C. Rodríguez-Navarro, E. Ruiz-Agudo, J. Harris, S.E. Wolf, Nonclassical crystallization in vivo et in vitro (II): nanogranular features in biomimetic minerals disclose a general colloid-mediated crystal growth mechanism, J. Struct. Biol. 196 (2016) 260–287.
- [45] H.H. Teng, P.M. Dove, C.A. Orme, J.J. De Yoreo, Thermodynamics of calcite growth: baseline for understanding biomineral formation, Science 282 (1998) 724–727.
- [46] C. Rodriguez-Navarro, C. Jimenez-Lopez, A. Rodriguez-Navarro, M.T. Gonzalez-Munoz, M. Rodriguez-Gallego, Bacterially mediated mineralization of vaterite, Geochim. Cosmochim. Acta 71 (2007) 1197–1213.
- [47] F. Manoli, J. Kanakis, P. Malkaj, E. Dalas, The effect of aminoacids on the crystal growth of calcium carbonate, J. Cryst. Growth 236 (2002) 363–370.
- [48] A.J. Xie, Y.H. Shen, C.Y. Zhang, Z.W. Yuan, X.M. Zhu, Y.M. Yang, Crystal growth of calcium carbonate with various morphologies in different amino acid systems, J. Cryst. Growth 285 (2005) 436–443.
- [49] C. Rodriguez-Navarro, A. Suzuki, E. Ruiz-Agudo, Alcohol dispersions of calcium hydroxide nanoparticles for stone conservation, Langmuir 29 (2013) 11457–11470.
- [50] F. Jroundi, M. Schiro, E. Ruiz-Agudo, K. Elert, I. Martin-Sanchez, M.T. Gonzalez-Munoz, C. Rodriguez-Navarro, Protection and consolidation of stone heritage by self-inoculation with indigenous carbonatogenic bacterial communities, Nat. Commun. 8 (2017) 279.
- [51] D. Camuffo, The influence of run-off on weathering of monuments, Atmos. Environ. 18 (1984) 2273–2275.
- [52] Ö. Cizer, C. Rodriguez-Navarro, E. Ruiz-Agudo, J. Elsen, D. Van Gemert, K. Van Balen, Phase and morphology evolution of calcium carbonate precipitation by carbonation of hydrated lime, J. Mater. Sci. 47 (2012) 6151–6165.
- [53] E. Ruiz-Agudo, P. Álvarez-Lloret, A. Ibañez-Velasco, M. Ortega-Huertas, Crystallographic control in the replacement of calcite by calcium sulfates, Cryst. Growth Des. 16 (2016) 4950–4959.
- [54] L. Fernández-Díaz, Á. Fernández-González, M. Prieto, The role of sulfate groups in controlling CaCO₃ polymorphism, Geochim. Cosmochim. Acta 74 (2010) 6064–6607.
- [55] R.L. Frost, E.C. Keeffe, Raman spectroscopic study of the sulfite-bearing minerals scotlandite, hannebachite and orschallite: implications for the desulfation of soils, J. Raman Spectrosc. 40 (2009) 244–248.