

Effectiveness of commercial anti-graffiti treatments in two granites of different texture and mineralogy.

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ABSTRACT

This paper presents a study of the efficiency of two chemically different anti-graffiti coatings (sacrificial and permanent anti-graffiti products) on two different compositional and textural granitic stones, Rosa Porriño and Albero.

First, both uncoated and coated surfaces of the granites were characterized using stereomicroscopy and scanning electron microscopy, static contact angle measurements, colour spectrophotometry and gloss measurements. Results showed that both anti-graffiti products increased the static contact angle of the surfaces. The permanent anti-graffiti made them water-repellent without causing notable colour changes.

Second, effectiveness of the anti-graffiti products was evaluated by means of the removal of two different spray graffiti paints (blue and silver colours) on both granites protected with the above-mentioned anti-graffiti products. The cleaning procedures were those recommended by the manufacturers. Fourier Transform Infrared spectroscopy and the previously mentioned techniques were used to assess the cleaning efficiency of the coated surfaces by detecting or not the presence of graffiti remains. As a result, textural differences in the granites, chemical composition of the graffiti paints and removal time were found to be the key parameters controlling the effectiveness of graffiti removal. On Albero granite, more residues of paint were found in its fissure system. Blue graffiti based on alkyd and polyester resins was more readily removed than silver paint. In general terms, graffiti extraction was more effective 30 days after painting than 3 days after.

Keywords: anti-graffiti; granite; graffiti; stone protection; stone cleaning.

42 1. Introduction

43 Graffiti, perceived as vandalism, is a persistent problem around the world, especially in urban
44 areas where it can be found on public transportation, civil infrastructure, monuments and
45 buildings. Among the different graffiti cleaning procedures the most popular ones that involve
46 the use of detergents or solvents (chemical procedures) and/or pressure water (mechanical
47 procedures) are not always satisfactory [1] and can be quite expensive (e.g. the estimated cost
48 of cleaning graffiti in UK is over £1 billion a year [2]). Moreover, sometimes they may even be
49 counter-productive, especially on porous materials such as concrete and natural stone [3-7]. On
50 the one hand, chemicals can be retained in their pore systems (even after washing with
51 pressure water) and this contamination can result in the precipitation of salts [3-5]. On the
52 other hand, mechanical procedures can open or create fissures or cracks which would favour
53 water absorption and the adhesion of future graffiti paints [4-7]. For all those reasons and not
54 only for aesthetic impact, graffiti is a major threat particularly on built heritage materials. Even
55 the less aggressive cleaning methods with low pressure water (100-200 psi), which are less
56 efficient in cleaning graffiti, have associated hazards since excess of water can favour salt
57 migration as well as freeze-thaw deterioration [8].

58 Laser cleaning of graffiti, despite being expensive and time-consuming and still under
59 refinement, is the method recommended in situations where traditional procedures can be
60 harmful to the stone [1, 9]. This technique also has certain limitations; as occurs with traditional
61 cleaning methods, laser efficiency depends on the type of paint to be extracted [10]. The higher
62 the absorbance of the paints to laser radiation, the more efficient is their removal. This fact
63 explains the highest difficulty to remove metallic colours (gold, silver and bronze) that contain
64 high reflectance Al-rich particles [10, 11]. Occasionally, laser cleaning can cause colour
65 variations on the substrates because of migration of organic compounds from the graffiti into
66 their pores [12], the own interaction of the laser beam with the minerals of carbonate stones
67 causing the yellowing [13], the fading of the K-feldspar in pinkish granite [14] or changes in the

oxidation state of ferrous oxide compounds [9]. Even fusion of different granite forming minerals and the appearance of fractures have been reported [15, 16].

Despite granite being one of the most common building stone worldwide, research on the cleaning effectiveness of graffiti on granitic samples is scarcer than for carbonate stones [17-19]. Recent studies have compared the effectiveness of different (chemical, physical and laser) methods of graffiti removal on granites showing unsatisfactory results in spite of the low open porosity of the substrates examined (around 1%) [5, 15, 20]. All of the evaluated procedures produced harmful effects on the stones (chemical contamination, opening of fissures and alteration of rock-forming minerals) and even when graffiti was removed from the surfaces, graffiti still remained in fissures inaccessible to all the cleaning methods; e.g. after laser cleaning [10].

Considering the main drawbacks of laser and traditional cleaning procedures (chemicals retained in the pore systems, fusion of minerals and fractures), anti-graffiti coatings could be an alternative solution to optimize graffiti removal. These treatments hinder the adhesion of paint to the surface of the materials and so, make graffiti easier to remove with solvents and/or water with low pressure. In general, anti-graffiti products can be divided into two main groups. On the one hand, products based on waxes, polysaccharides and acrylates belong to the group of sacrificial anti-graffiti coatings which are removed together with graffiti. On the other hand, polyurethanes, siloxanes and epoxy resins are part of the permanent coatings group which can withstand various cleaning cycles without needing reapplication [21].

However, there have been published a few previous studies on such innovative treatments and their potential for use on built heritage where they provided an efficient protection with minimal modification of the historic substrate. Such studies have been mainly focussed on limestones and sandstones [6, 21-25] with uneven results. The effectiveness of these products on granites has been even less well explored. In two earlier works, Carmona-Quiroga et al. [26-27] found that the performance of two different permanent anti-graffiti coatings was more

satisfactory (less global colour changes after graffiti removal) in a limestone than in a granite due to their different finishes: smoother limestone was easier to clean than the rougher granite. To fill the knowledge gap on the cleaning effectiveness of graffiti on granitic stones, the evaluation of the application of permanent or sacrificial anti-graffiti coatings on granite could be an effective solution for graffiti removal, as opposed to traditional cleaning methods. As it is well known that textural peculiarities influence the response to different kinds of conservation interventions [28, 29], two renowned commercial quality granites with different porosities, mineralogy and texture (Rosa Porriño and Albero) were used in the current paper. Both granites were coated with a permanent and a sacrificial anti-graffiti products in order to test their effectiveness in the removing of two graffiti paint of different easiness of removal following a previous study [10]: an easier graffiti to be extracted (blue graffiti) and a more difficult one (silver graffiti). Their cleaning effectiveness was evaluated by means of microscopic and spectroscopic techniques. Prior to this evaluation, the surface properties of the granites were characterized after the application of both anti-graffiti coatings.

2. Materials and methods

2.1. Granitic samples, anti-graffiti coatings and graffiti paints

2.1.1. Granitic samples

Two commercially valuable granites from NW Iberian Peninsula, Rosa Porriño and Albero, were selected. Rosa Porriño is a post-Hercynian two-mica granite [30] with a panallotriomorphic heterogranular texture, composed of quartz (40%), potassium feldspar (27%), plagioclase (14%), biotite (8%), muscovite (2%) and chlorite and opaques as accessories minerals (5%). It is a coarse grained granite with crystals up to 10 mm (microcline) grains. Considering the physical properties, accessible porosity (AP) following [31] is 0.96 % (v/v), total porosity (TP, mercury injection, AutoporelV9500 porosimeter of Micrometrics) is 1.45% (v/v), water absorption coefficient (under pressure) is 0.48% (w/w) [32], water absorption coefficient (by capillarity) is 0.37% (w/w) [32] and apparent bulk density is 2605.00 kg.m⁻³ [33].

Albero is a pre-Hercynian equigranular medium grained granite [30] and it is composed by quartz (22%), K-feldspar (43%), plagioclase (23%), muscovite (4%), biotite (7 %) and apatite, zircon, rutile, chlorite and sillimanite as accessories minerals. It is a coarse grained granite with an average grain size of 5 mm. Therefore, Albero has a finer grain-size than Rosa Porriño. Regarding the physical properties, accessible porosity (AP) following [31] is 3.87 % (v/v), total porosity (TP, mercury injection, AutoporelV9500 porosimeter of Micrometrics) is 4.08% (v/v), water absorption coefficient (under pressure) following [31] is 1.52% (w/w), water absorption coefficient (by capillarity) following [34] is 1.32% (w/w) and apparent bulk density is 2541.47 kg.m⁻³ [35].

Albero is slightly more porous than Rosa Porriño, both in terms of accessible porosity and total mercury intrusion porosity. Comparing accessible porosity and total porosity by mercury injection (AP/TP), Rosa Porriño shows a lower percentage of accessible voids to mercury that are also accessible to water. However, Albero shows a higher level of communication among voids. Both granites have a pore size distribution characterized by the presence of typical trans-granular, inter-granular and intra-granular fissures [28]. 11 saw cutting-finished slabs of 6 cm x 6 cm x 2 cm for each granite were used.

2.1.2. Anti-graffiti products

Both granites were coated with two commercial anti-graffiti products: a permanent water based fluoralkyl siloxane (AGr1) and a sacrificial water based crystalline micro wax (AGr2). Two coats of each product were sprayed onto the surface of the materials on consecutive days. In total for both types of granite, 10 slabs were coated (5 with AGr1 and 5 with AGr2) and 1 slab per granite was left uncoated as a reference sample. Coated samples were dried at room temperature (18±5 °C, 50±10% RH) until constant mass. The flow of the current research can be consulted in Fig. 1.

2.1.3. Graffiti paints

Two spray paints, Blue Ultramarine and Silver Chrome from Montana Colors S.L. (<http://www.montanacolors.com>) were selected. Following a previous study [10], these graffiti paints showed different behaviour during cleaning, being blue graffiti the easiest to remove. As reported in [10] Blue Ultramarine is composed of alkyd and polyester resins, while Silver Chrome showed a predominance of polyethylene-type polymers. In Table 1, the composition of these two graffiti paints by X-ray Fluorescence (XRF, Siemens SRS 300) and Elemental analyser (CHNS, Fisons EA-1108) is shown. XRF was used to determine the chemical composition of the major and trace elements. For this analysis, the paint was applied to nitrocellulose supports and measurement was made directly, with the results expressed as oxide after subtraction of the signal from the nitrocellulose support. **An elemental analysis** (CHNS determination) was made of the residue scraped from the paints on an aluminium support.

For each granite, four slabs coated with the same anti-graffiti product were covered with each graffiti paint (Fig. 1). A sample coated with each anti-graffiti was left unpainted for use it as a reference. The graffiti paints were sprayed once on half of each specimen from a distance of 10 cm during 10 seconds.

INSERT TABLE 1

2.2. Cleaning procedure

The removal of the graffiti was performed at two different moments: after 3 days of drying at laboratory conditions (18 ± 5 °C, $50\pm10\%$ RH) and after 30 days of drying under laboratory conditions, in order to simulate immediate or delayed cleaning procedures respectively (Fig. 1).

On the surfaces coated with AGr1, the graffiti paints were removed with a suitable cleaner (designed for surfaces treated with AGr1) that was spread onto the surfaces and allowed to work for 15 minutes to dissolve the paints then washed away with water. This procedure was carried out twice. On the granites coated with AGr2, paints were removed together with the (sacrificial) anti-graffiti coating with a high pressure hot water spray (110 °C and 90 bars) as recommended by the coating manufacturer.

2.3. Analytical techniques

2.3.1. Characterization of the anti-graffiti coated surfaces

In order to assess the anti-graffiti product consumption, the active residue for each product in each granitic stone was calculated by the difference of mass (expressed in g.m^{-2}) between the mass before anti-graffiti application and the constant mass achieved after application.

The surfaces were evaluated after the application of the anti-graffiti products with stereomicroscopy (Nikon Eclipse800) to detect possible physical changes due to the product application. Also, the C-sputtered surfaces were characterized under scanning electron microscopy (SEM) with energy-dispersive x-ray spectroscopy (EDS) (Philips XL30) in both Secondary Electron (SE) and Back Scattered Electron (BSE) modes in order to observe the distribution of the product on the surface and in fissures.

The water-repellency of the substrates was determined by measuring the static contact angle (θ°) with an IT Concept Tracker. The water-rock contact angles of three drops of 5 μL were measured per area of 6x 6 cm (sample surface), applying the Laplace-Young equation to fit the drop profile. Measurements were taken before the application of the coatings and at 2 weeks and 10 weeks before the application of the coatings (samples kept under laboratory conditions).

The influence of the anti-graffiti products on granite aesthetics was evaluated through colour measurements in the CIELAB colour space and through gloss analysis. L^* (lightness), a^* (red/green hue) and b^* (yellow/blue hue) coordinates were recorded with a Minolta CM-700d spectrophotometer using a template. Nine measurements per slab were obtained in order to characterize the colour of these polymineralic rocks [36]. Colour data were obtained in the two measurements modes, SCI (Specular Component Included) and SCE (Specular Component Excluded), with a spot area of 8 mm of diameter (MAV), using illuminant D65 and at an observer angle of 10° . Global colour changes, ΔE^*_{ab} , were also determined taking the original colour of the stones as the reference value ($\Delta E^*_{ab} = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$) [37].

Also, the variation of the gloss (ΔG) of the treated surfaces at a reflection angle of 85° [38] was determined with a TQC glossmeter, taken 3 measurements per slab.

2.3.2. Graffiti cleaning effectiveness

To evaluate the protective effectiveness of each anti-graffiti product, granite slabs were examined by stereomicroscopy after graffiti cleaning procedures to detect any remains of blue and silver spray paints on their surface including superficial fissures. Also, SEM-EDS and Fourier Transform Infrared Spectroscopy (FTIR) data were collected (Fig. 1); the latter in micro mode using a FTIR Thermo Nicolet® Continuum and identifying the presence or absence of paint remains on the surfaces through the characterization of the functional groups of both spray paints. Furthermore, changes in colour, gloss and contact angle were assessed 3 days and 30 days after the cleaning of the graffiti.

INSERT FIGURE 1

3. Results

3.1 Characterization of the anti-graffiti coated surfaces

Regarding the product consumption, Albero absorbed more of both anti-graffiti products than Rosa Porriño. Considering standard deviations, the amount of active residue of both anti-graffiti was similar in Rosa Porriño granite, whereas, in Albero, the active matter obtained for AGr1 was higher than that obtained for AGr2 (Table 2).

Regarding the influence of each anti-graffiti product on the granitic surfaces, on Rosa Porriño treated with both anti-graffiti products a more intense pinkish colour was detected in some of the K-feldspar grains (Fig. 2B, C). However, on Albero surfaces, the changes were even less detectable (Fig. 2H, I). In this regard, ΔE^*_{ab} suffered by both granites after being coated with AGr1 was higher than ΔE^*_{ab} of both granites coated with AGr2. L^* decreased in all cases, a^* increased for the Rosa Porriño with both anti-graffiti coatings, and b^* increased in all cases.

Although the same procedure was used to cut the slabs of each granite, the surfaces of both materials exhibited different gloss: semi-matt for Rosa Porriño (gloss >10 at 85° ; [39]) and matt

for Albero (gloss <10 at 85°; [39]). For the surface of Rosa Porriño with the sacrificial AGr2 and the surfaces of Albero coated with both anti-graffiti coatings, the gloss variations were less than 2 units. However, for the semi-matt Rosa Porriño with AGr1, the gloss decreased by 10 units. SEM-EDS analysis allowed to find that for the surfaces coated with AGr1, the product was mainly located in fractures and cracks (Rosa Porriño: Fig. 2E; Albero: Fig. 2K). Fluorine signal in the EDS spectra was used to track AGr1 as shown in Fig. 2E and Fig. 2K. In the fissures mainly, the permanent anti-graffiti showed cracked features (Fig. 2K). The sacrificial anti-graffiti, AGr2, detected as very low contrast deposits rich in C, was mainly found on the surfaces of the forming minerals (Fig. 2F depicts AGr2 on the Rosa Porriño surface; Fig. 2L shows AGr2 deposits on quartz grains whose appearance without anti-graffiti is showed in Fig. 2J). Note that none of the anti-graffiti products formed a homogeneous layer on the surfaces.

Finally, changes in the water-repellency of granites were assessed. Water-rock static contact angle (θ°) values after 2 weeks of treatment revealed that AGr1 made water-repellent the surfaces of both granites, since the θ° was higher than 90° [40]. AGr1 increased the water-stone static contact angles on both granites up to values of around 116°. Considering the standard deviations, these values slightly increased after 10 weeks. Conversely, AGr2 did not confer hydrophobic behaviour to the rocks, since the contact angles did not exceed 90° [40], except in Albero granite after 10 weeks of the treatment with a static contact angle of 90.2°. (Table 2).

INSERT FIGURE 2

INSERT TABLE 2

3.2. Protective effectiveness

The protective effectiveness of the two anti-graffiti products applied on both granites was evaluated with different experimental techniques after the removal of blue and silver graffiti paints.

3.2.1. Stereomicroscopy

Stereomicroscopy allowed an initial evaluation of the graffiti cleaning effectiveness. A qualitative evaluation of the effectiveness of the cleaning of each graffiti from each coated surface was performed according to the classification numbers (CN) [38, 41] that define the degree of cleaning efficiency on the basis of the quantity of paint remaining on the surface and fissures of a substrate after cleaning of graffiti, from 0 (complete removal of colour) to 5 (no cleaning effect) [38]. The results of this evaluation can be found in Fig. 3. In general terms, less graffiti remains were detected on the surfaces of Rosa Porriño than on Albero surfaces; CN for Rosa Porriño are mostly 0 but in the case of Albero, 1 (Fig. 3). For Albero, residues of graffiti paints were mainly found in fissures regardless of the anti-graffiti product applied. On the silver graffiti cleaned samples, a bright and translucent film (paint remains) covering the brightest mineral grains (biotite and quartz) was observed (Fig. 3). This film, which appeared mainly on the surfaces coated with AGr1, could hinder the evaluation of the graffiti removal. On Albero, the mechanical procedure to extract graffiti from surfaces coated with AGr2 led to the opening of fissures or cracks (compare Fig. 2G-I with Fig 3, stereomicroscopy-micrographs of Albero coated with AGr2). Finally, by means of stereomicroscopy, no notable differences in the degree of graffiti removal were detected between the surfaces cleaned 3 and 30 days after the application of the graffiti (Fig. 3).

INSERT FIGURE 3

3.2.2. SEM-EDS

A more detailed analysis of the cleaned surfaces was performed via SEM-EDS by detecting paint residues on the surface and fissures of the granites. Elemental composition of both graffiti colours obtained by means of XRF and CHNS (Table 1) were used to track blue and silver paint remains. The former was detected through the voluminous bodies rich in C, Al, Mg, Ca and Ti (Fig. 4) whereas the silver one was observed as high contrast Al-rich particles of a few μm imbedded in a C-rich film (Fig. 5).

In general terms, and in concordance with stereomicroscopy examinations, the surfaces of Rosa Porriño exhibited lesser graffiti residues than the surfaces of Albero (blue graffiti cleaned surfaces: Fig. 4; silver graffiti cleaned surfaces: Fig. 5). On all the samples tested, except for the silver cleaned surfaces of Rosa Porriño with AGr2 (Fig. 5C and D) and silver cleaned surfaces of Albero with AGr1 (Fig. 5E and F), less graffiti remains were detected on the surfaces cleaned 30 days after graffiti application than on the surfaces cleaned 3 days after application. These differences in cleaning efficiency were not observed at the magnification of the stereomicroscope which showed the same residues of both spray paints at both removal times (Fig. 3). In the exceptions reported (silver graffiti cleanings in Rosa Porriño surface with AGr2: Fig. 5C and D; silver graffiti cleanings in Albero coated with AGr1: Fig. 5E and F), the surfaces cleaned 30 days after graffiti application showed similar cleaning levels or even worst results than those registered on the surfaces cleaned after 3 days.

Regarding graffiti composition, in agreement with [10], more remains were found on the surfaces cleaned of silver graffiti comparatively to blue graffiti due to the broader extent of the C-rich film with Al particles, mainly on the Rosa Porriño coated with AGr2 (Fig. 5D) and Albero surfaces coated with AGr1 (Fig. 5F). Despite in the current research, this film could be also assigned to remains of the sacrificial anti-graffiti coating that could not be completely extracted after the mechanical procedure (projection of water at 110°C and 90 bars), it was not considered because 1) this low contrast film rich in C also showed Al particles identified by SEM-EDS and their high contrast (Fig. 5G) and 2) on the surfaces of both granites with AGr2 cleaned of blue graffiti (Fig. 4D and H), no C-rich film due to sacrificial anti-graffiti remains was detected after cleaning.

INSERT FIGURE 4

INSERT FIGURE 5

3.2.3 FTIR

Fig. 6 depicts the most representative FTIR (absorbance) spectra for Rosa Porriño (A and B) and Albero (C and D) granites coated with AGr1 and AGr2 after cleaning of both graffiti colours (3 and

30 days after graffiti application), including the spectra for the uncoated and unpainted granite as a reference. Spectra were collected in apparently cleaned fissures identified by means of stereomicroscopy.

The spectra of granites exhibit the characteristic IR bands of silicates which appeared mainly in the 590–730 cm^{-1} , 1180–860 cm^{-1} and 1100–900 cm^{-1} regions [10, 42].

Absorptions IR bands of the blue paint were identified at around 3409 cm^{-1} (O-H stretching vibration of water); 2925 cm^{-1} and 2854 cm^{-1} (C-H asymmetric stretching vibrations of alkanes); 1729 cm^{-1} (stretching vibration C=O); between 1700 cm^{-1} and 1300 cm^{-1} (COC group vibration stretching) and at 740–700 cm^{-1} (primary alcohol group) [42]. For silver paint (only the spectra of the organic soluble was characterized via FTIR spectroscopy in [10] due to the high reflectance caused by this paint), most intense bands are those of C-H asymmetric stretching vibrations (2925 and 2854 cm^{-1}) whereas those of C=O and C-O functional groups are less visible. The absorptions bands are related with the binder composition of each graffiti paint; the blue graffiti has alkyd and polyester resins and silver graffiti has polyethylene-type polymers [10].

Regarding cleaning results and corroborating SEM observations, in general terms, the surfaces of Rosa Porriño exhibited lesser graffiti residues than the surfaces of Albero because less bands and/or less intense bands assigned to graffiti were identified in the FTIR spectra of cleaned Rosa Porriño surfaces. Speaking about Rosa Porriño covered with both anti-graffiti products, considering FTIR results (blue graffiti cleaned surfaces: Fig 6A; silver graffiti cleaned surfaces: Fig 6B), different behaviours were identified depending on the anti-graffiti nature: 1) in the surface coated with AGr1, bands assigned to graffiti (both colours) were identified in the FTIR spectra of the surfaces cleaned after both times (3 and 30 days after graffiti application) and 2) for samples coated with AGr2, FTIR spectra without any bands assigned to graffiti remains were obtained. In the case of surfaces coated with AGr1, SEM also allowed to find graffiti remains on the surfaces after the cleaning at both different times, but less graffiti remains 30 days after graffiti application comparatively to the surfaces cleaned 3 days after graffiti application. For surfaces coated with

AGr2, despite SEM allowed to find more blue graffiti remains on the surface cleaned 3 days after graffiti application and the same level of cleaning for silver graffiti after both times, by FTIR it was not possible to identify cleaned surfaces after the two times for both graffiti paints. This mismatching could be related with the measured area by the device, because the FTIR spectra tried to be taken in cleaned areas by means of stereomicroscopy.

In the case of Albero surfaces coated with AGr1 and AGr2 (blue graffiti cleaned surfaces: Fig. 6C; silver graffiti cleaned surfaces: Fig. 6D), blue and silver graffiti remains were still detected by their intense absorption bands in the FTIR spectra taken on the surfaces cleaned 3 days after graffiti application corroborating the results by SEM. It was observed that on Albero surfaces cleaned 30 days after graffiti application, in their FTIR spectra the bands assigned to graffiti were less intense or inexistent comparatively to these bands in the spectra registered on the surfaces cleaned 3 days after graffiti application.

Moreover, some surfaces of both granites coated with AGr1 and cleaned of both graffiti showed in their FTIR spectra an intense band at 3620 cm^{-1} , that was assigned to the vibration of O-H groups in coordination with metals of both paints.

INSERT FIGURE 6

3.2.4. Water-repellency

The effect of the graffiti removing on the water-repellent properties of either permanent or sacrificial anti-graffiti coatings was also evaluated (Table 3). After the graffiti cleaning, the surfaces of Rosa Porriño coated with the AGr1 (the permanent water based fluoralkyl siloxane) were still water repellent because their static contact angles were higher than 90° [40]; the θ° were similar to the values showed by the coated granite before graffiti application (Table 2). Via SEM-EDS a few isolated graffiti remains were found on the Rosa Porriño surfaces coated with AGr1 (blue graffiti cleaned surfaces: Fig. 4A and B; silver graffiti cleaned surfaces: Fig. 5A and B) which were also detected by FTIR (Fig. 6A and B). For the Rosa Porriño surfaces coated with AGr2 (the sacrificial water based crystalline micro wax), considering the standard deviations, only the

surface cleaned of blue graffiti 30 days after graffiti application showed an increase of the θ° comparatively to the same surface before graffiti application, suggesting the presence of graffiti remains filling fissures. All the Rosa Porriño surfaces with the sacrificial anti-graffiti (AGr2), before graffiti application, did not exhibit water repellency, because their θ° were lower than 90° [40]. As was reported before, after the cleaning, SEM and FTIR allowed to find remains on all the Rosa Porriño surfaces coated with AGr2 and cleaned of both graffiti, mainly in fissures (blue graffiti cleaned surfaces: Fig. 4C and D; silver graffiti cleaned surfaces: Fig. 5C and D). These remains seem to increase the static contact angle. In the case of the coated Rosa Porriño surfaces, considering the standard deviations, different θ° were not detected between the surfaces cleaned 3 or 30 days after graffiti application.

In case of the coated Albero surfaces after the cleaning, those coated with the permanent anti-graffiti AGr1 showed θ° still higher than 90° showing their water repellency [40] and those coated with the sacrificial AGr2 exhibited θ° lower than 90° and even lower than those values registered for their counterparts before graffiti application.

Considering the number of days after graffiti application to perform the cleaning, for the surfaces of Albero coated with the permanent anti-graffiti AGr1, the surface cleaned of silver graffiti 3 days after graffiti application showed θ° higher than the value registered before the graffiti application (see Table 2 and 3). It should be mentioned that in this surface, by SEM, it was observed a wide C-rich film with Al-particles on the surface (Fig. 5E) and also FTIR allowed to find binder remains in the fissures (Fig. 6D). For the Albero coated with AGr2 (the sacrificial water based crystalline micro wax), slightly decreases of θ° after graffiti cleaning were detected, suggesting that this anti-graffiti product was partially removed during the cleaning. However, only the Albero coated with AGr2 cleaned of blue graffiti 30 days after the graffiti application showed a θ° of 0° which is the same measured on the uncoated reference surface (Table 2). This surface showed a complete extraction of graffiti via SEM-EDS (Fig. 4H), because graffiti remains were not identified neither on the surface nor on fractures and also, absorption bands assigned to graffiti remains in its FTIR

spectrum from the fissures were absent (Fig. 6C). Therefore, the fact that the rest of the cleaned Albero surfaces coated with AGr2 showed higher θ° than the reference surface suggests the presence of graffiti remains filling the fractures and fissures on the surfaces as was detected via SEM through voluminous C-rich volumes with Al, Mg, Ca and Ti for the blue graffiti and with Al-rich particle for the silver graffiti.

Curiously, θ° of the Albero surfaces coated with AGr1 after the cleaning were higher than those registered for the Rosa Porriño with AGr1 while before the graffiti application and also for the uncoated samples, Rosa Porriño showed higher θ° . As was identified by stereomicroscopy, SEM-EDS and FTIR, coated Albero surfaces showed greater graffiti remains after cleaning.

3.2.5. Colour and gloss

Regarding changes in colour and gloss measurements after graffiti removal, it is important to highlight that for samples treated with AGr2, the reference surfaces were the uncoated ones (since sacrificial coatings are made to be removed during the cleaning procedure) whereas for the granites treated with the permanent coating, AGr1, the reference surfaces were the anti-graffiti coated ones (Table 3).

Comparing both granites, except for the surfaces coated with AGr2 cleaned of blue graffiti 30 days after the graffiti application, ΔE^*_{ab} for the surfaces of Albero ($\Delta E^*_{ab} \leq 11.20$ CIELAB units) were higher than those registered on Rosa Porriño ($\Delta E^*_{ab} \leq 6.62$ CIELAB units). On both granites, the cleaning of silver paint caused higher ΔE^*_{ab} than the cleaning of blue graffiti paint. Despite only Albero with both anti-graffiti products cleaned of blue graffiti showed statically significant differences, global colour variations after the cleaning at 30 days after graffiti application were lower than the cleaning at 3 days after painting.

Gloss changes of the surfaces of Rosa Porriño coated with AGr1 and Albero with both anti-graffiti products after the cleaning of both graffiti paints were lesser than 2 units. Conversely, gloss changes of Rosa Porriño coated with AGr1 were higher than 20 units. It is important to highlight that the Rosa Porriño surface coated with AGr1 already showed a ΔG of 10 units in comparison

with the original gloss of the surface, while the Rosa Porriño with AGr2 and Albero with both anti-graffiti products exhibited a ΔG around 1 unit.

INSERT TABLE 3

4. Discussion

Despite the same number of applications were performed with both anti-graffiti products on both granites, the different consumption seems to be related with the porosity of the granite; the higher the porosity the higher the anti-graffiti product consumption, as was reported in consolidant and water repellent treatments [43]. Considering the anti-graffiti composition, the consumption for Rosa Porriño was similar for both anti-graffiti while for Albero more permanent anti-graffiti was deposited filling fissures. Therefore, the finer grain size of Albero could favour the accumulation of the permanent anti-graffiti product through the intergranular fissures, since the permanent product remains retained on the surface and in the fissures, while the sacrificial remained mainly on the surface of the forming minerals as was detected by SEM-EDS.

The application of anti-graffiti products on the granitic surfaces led changes in the water repellency level of the stone, as was detected by the results for the static contact angle. As was already published for the evaluation of water repellent and consolidant treatments, the composition of the additional product (anti-graffiti products in the current research) is a key parameter to understand the compatibility with the stone [43,44]. Regarding the hydrophobic character achieved by the anti-graffiti application, the surfaces of both granites coated with the permanent anti-graffiti were considered clearly hydrophobic, because their static contact angles were higher than 90° [40]. However, the surfaces coated with the sacrificial anti-graffiti (except Albero ten weeks after its application) were not hydrophobic because the measured contact angles were below 90° [40]. It is important to highlight that despite the static contact angles were slightly higher on the surfaces ten weeks after the application of the anti-graffiti products, only Albero surfaces with AGr1 showed significant differences between the values for the coated surface 2 weeks after product application and 10 weeks after. This fact shows that the permanent

water based fluoralkyl siloxane applied on the more porous granite could need more than seventy days to achieve the complete polymerization, which is also related with the amount of active residue of this anti-graffiti on this stone (the permanent anti-graffiti on Albero granite required the highest quantity of product showing the highest active residue).

The cracking observed in the permanent anti-graffiti retained in the fissures was similar to that detected on consolidant material, such as the commercial product *ESTEL 1000* [45]. The polymerizing process used by the permanent water based fluoralkyl siloxane (AGr1) seems to be similar to that showed by consolidant products composed of alkoxysilanes that polymerise inside the pore structure of the disintegrating stone, through a classic sol–gel process [44]. Therefore, the penetration of the permanent anti-graffiti in the fissures, as was reported for alkoxysilanes consolidants, seems to be dependent on the viscosity of the permanent anti-graffiti and it facilitated by its ability to form siloxane bonds [44]. Due to the filling of the fissures, the granites coated with the permanent granite showed higher values of static contact angle.

Regarding the effect of the anti-graffiti products on the aesthetics, it was observed that only the application of AGr1 on Rosa Porriño caused a more intense pinkish colour of the K-feldspar grains, with an increase of the value of a^* coordinate (red hue). Also, the surfaces darkened (L^* decreased) and yellowed (b^* coordinate increased). These colour variations are enough to be perceived by a human eye, since ΔE^*_{ab} was higher than 3.5 CIELAB units [46], but are acceptable since $\Delta E^*_{ab} \leq 5$ CIELAB units, which is generally the threshold value in conservation interventions of built heritage [38, 47]. Only the gloss of Rosa Porriño changed after the application of AGr1 (decreasing by 10 CIELAB units) which, according [35], is a very small but perceptible change for a semi-matt surface like this Rosa Porriño's finish. AGr1 on Albero only changed its colour to an acceptable extent ($\Delta E^*_{ab} \leq 5$) but not its gloss. Conversely, the sacrificial anti-graffiti coating did not cause any change in colour and gloss visible to the naked eye on both granites since ΔE^*_{ab} and ΔG were lower than 3 and 2 units [38, 46] respectively.

Regarding the protection level provided by these two anti-graffiti products on both granites, the first approach performed by means of stereomicroscopy revealed a lesser amount of paint residues on the surface of Rosa Porriño than on Albero surfaces. In general terms, following the classification numbers (CN) defined in [38, 41] to evaluate the cleaning effectiveness of graffiti after visual inspection, the cleaning of Rosa Porriño and Albero with both anti-graffiti coatings could be described as satisfactory: for Rosa Porriño granite, essentially CN=0 (complete removal of the spray paints) and for Albero granite CN=1 (isolated residues in fissures and cracks). These differences in the cleaning effectiveness achieved in the surfaces protected with a permanent and a sacrificial anti-graffiti could be related to the different texture of the two granites: mineralogy, grain size and porosity. On Albero, the higher presence of fissures and fractures due to the smaller grain sizes favoured that the graffiti paints remained retained in those, particularly the blue paint. This difference in cleaning effectiveness between both graffiti paints was reported in [10] finding that laser cleaning of red, blue and black graffiti paints on granite was satisfactory whereas silver paint was not well extracted, remaining on the stones as a translucent film visible to the naked eye rich in C and Al. In the current research, this film rich in C was identified via SEM-EDS on the cleaned surfaces confirming the remains of the silver graffiti through the detection of Al rich particles with a dimension of a few μm imbibed in that layer. The presence of graffiti remains on the surfaces, mainly filling the fissures seems to lead an increase of the static contact angle comparatively to the value registered on the surface before anti-graffiti application. Rosa Porriño surface coated with the sacrificial anti-graffiti and cleaned of blue graffiti 30 days after graffiti application and Albero surface coated with the permanent anti-graffiti product and cleaned of silver graffiti 3 days after graffiti application showed higher static contact angles than those registered for the same surfaces before graffiti application. Graffiti remains were found on the surfaces and in the fissures by SEM-EDS and FTIR. Colour spectrophotometry results confirmed that after the cleanings, paint residues remained on Albero in a higher amount than on Rosa Porriño granite. In almost all the cases for Albero granite,

ΔE^*_{ab} after graffiti removal were higher than 3.5 CIELAB units, which is the threshold for the human eye perception [46], and also, higher than 5 CIELAB units which is the threshold for an acceptable intervention in Cultural Heritage [38, 47]. For the surfaces cleaned of Rosa Porriño, most of the ΔE^*_{ab} were lower than 5 and also 3.5 CIELAB units. The higher ΔE^*_{ab} for Albero granite are related with the higher presence of graffiti remains in fissures. The higher level of blue graffiti extraction on Albero coated with the sacrificial anti-graffiti 30 days after graffiti application was detected through an almost complete recovery of the colour surface, because $\Delta E^*_{ab} = 2.10$ CIELAB units and the static contact angle recovered the value of the uncoated Albero. On the matt surface of Albero, gloss differences were not perceived by naked eye after graffiti removal ($\Delta G < 2$ units; [38]). Conversely, on a semi-matt surface like Rosa Porriño, an increase of gloss was perceived only on the surfaces coated with AGr1 after removal of both graffiti paints with the chemical cleaner. These perceptible gloss changes are high if the reference gloss corresponds to the gloss of the coated granites ($\Delta G = 20-30$; Table 3), however when the reference sample is the original gloss of the uncoated material they can be considered as reduced. Only the gloss of Rosa Porriño cleaned of silver graffiti on surfaces coated with AGr2 decreased when the cleaning is performed 3 days after the graffiti application probably due to the presence of paints residues.

Despite by stereomicroscopy, no differences in the cleaning efficiency were found between the coated surfaces cleaned 3 and 30 days after the graffiti application, colour spectrophotometry, SEM-EDS and FTIR showed more graffiti residues on the samples cleaned 3 days after the graffiti application. These differences can be related to the degree of drying of the graffiti paints under laboratory conditions (18 ± 5 °C, $50 \pm 10\%$ RH). Therefore, at 3 days, the graffiti paints were possibly not totally dried, unlike at 30 days. This fact may suggest delaying the graffiti removal processes on anti-graffiti protected surfaces. Current guidelines of graffiti removal on historic building and monuments [48] recommend cleaning graffiti as quickly as possible not only to discourage future attacks but also to facilitate graffiti removal since fresh graffiti is considered easier to remove and

therefore its cleaning is less damaging to unprotected building materials. However, since this study has been carried out on particular anti-graffiti-coated surfaces under laboratory conditions (e.g. no pollution that can chemically combine with paints and renders cleaning more difficult) more research needs to be done to advice on best graffiti removal times.

5. Conclusions

This study evaluated the efficiency of two anti-graffiti coatings (permanent and sacrificial products) in facilitating graffiti removal on two different textural and mineralogical granites, Rosa Porriño (coarser grain size and lower porosity) and Albero (finer grain sizes and higher porosity). Results of the cleaning assessment with different experimental techniques, from stereomicroscopy and FTIR to SEM-EDS and spectrophotometry, revealed that texture is a key factor in successful graffiti extraction since ultimately it should govern the penetration of the paints through fissures and fractures. On Rosa Porriño, the less porous granite, higher cleaning effectiveness was achieved, while on Albero, its characteristic fissuration system and higher porosity would favour the penetration of the paints and hindered their removal.

Both sacrificial and permanent anti-graffiti coatings performed equally well on the two selected varieties of granite in spite of the different cleaning procedures used to remove paint from the protected surfaces: chemical for the surfaces coated with the permanent product and mechanical cleaning for the surfaces treated with the sacrificial coating. In contrast, blue spray paint, composed of alkyd and polyester resins, was more readily removed than silver paint, based on polyethylene-type polymers.

In general terms, more satisfactory cleaning results were obtained in the cleanings performed 30 days after graffiti application than those performed 3 days after graffiti application on both anti-graffiti-coated surfaces.

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References.

1. Sanmartín P., Cappitelli F., Mitchell R. (2014) Current methods of graffiti removal: A review, Construction and Building Materials 71: 363-374. doi.org/10.1016/j.conbuildmat.2014.08.093
2. Corby Borough Council, <http://www.corby.gov.uk/home/environmental-services/street-scene/enviro-crime/graffiti>
3. Bellmunt N., Paricio R., Vila A. (2002) Reconocimiento, diagnosis e intervención en fachadas, Instituto de Tecnología de la Construcción de Cataluña, Barcelona,
4. Doehne C.A., Price E. (2010) Stone Conservation: An Overview of Current Research (Second Edition), The Getty Conservation Institute, Los Ángeles, USA, <http://www.getty.edu/publications/virtuallibrary/9781606060469.html>
5. Pozo-Antonio J.S., Rivas T., Fiorucci MP., López AJ., Ramil A. (2016) Effectiveness and harmfulness evaluation of graffiti cleaning by mechanical, chemical and laser procedures on granite, Microchemical Journal. 125 1-9. doi.org/10.1016/j.microc.2015.10.040
6. Carmona-Quiroga P.M., Jacobs R.M.J, Martínez-Ramírez S., Viles H. A. (2017) Durability of anti-graffiti coatings on stone: Natural vs accelerated weathering, PLoS ONE 12(2) e0172347. doi.org/10.1371/journal.pone.0172347
7. Carmona-Quiroga P.M., Jacobs R.M.J., Viles H.A. (2017) Weathering of Two Anti-Graffiti Protective Coatings on Concrete Paving Slabs, Coatings 7(1) doi:10.3390/coatings7010001

8. The City of Edinburgh Council (2003) Treatment of Graffiti on Historic Buildings: Joint Protocol and Revised Policy Guidelines.
9. Chapman S. (2000) Laser technology for graffiti removal, *Journal of Cultural Heritage* 1: S75-S78.
10. Rivas T., Pozo S., Fiorucci M.P., López A.J., Ramil A. (2012) Nd:YVO₄ laser removal of graffiti from granite. Influence of paint and rock properties on cleaning efficacy, *Applied Surface Science* 263: 563-572. doi.org/10.1016/j.apsusc.2012.09.110
11. Fiorucci M.P., López A.J., Ramil A., Pozo S., Rivas T. (2013) Optimization of graffiti removal on natural stone by means of high repetition rate UV laser. *Applied Surface Science* 278: 268-272. doi.org/10.1016/j.apsusc.2012.10.092
12. Siano S., Agresti J., Cacciari I., Ciofini D., Mascalchi I., Osticioli I., Mencaglia A.A. (2012) Laser cleaning in conservation of stone, metal, and painted artifacts: State of the art and new insights on the use of the Nd:YAG lasers, *Applied Physics A: Materials Science and Processing* 106: 419-446. doi.org/10.1007/s00339-011-6690-8
13. Pouli P., Fotakis C., Hermosin B., Saiz-Jimenez C., Domingo C., Oujja M., Castillejo M. (2008) The laser-induced discoloration of stonework; a comparative study on its origins and remedies. *Spectrochim, Acta A Mol. Biomol. Spectrosc.* 71: 932–945. doi.org/10.1016/j.saa.2008.02.031
14. Urones-Garrote E., López A.J., Ramil A., Otero-Díaz L.C. (2011) Microstructural study of the origin of color in Rosa Porriño granite and laser cleaning effects, *Appl. Phys. A Mater. Sci. Process.* 104: 95–101. doi: 10.1007/s00339-011-6344-x

589

590 15. Pozo-Antonio J.S., Ramil A., Fiorucci M.P., López A.J., Rivas T. (2016) The use of
591 hyperspectral imaging technique to detect the most suitable graffiti-cleaning procedure, Colour
592 Research and Application, doi: 10.1002/col.22032

593

594 16. Sanjeevan P., Klemm A.J., Klemm P. (2007) Removal of graffiti from the mortar by using Q-
595 switched Nd:YAG laser, Applied Surface Science 253, 20: 8543-8553.
596 doi.org/10.1016/j.apsusc.2007.04.030

597

598 17. Carvalhão M., Dionísio A. (2015) Evaluation of mechanical soft-abrasive blasting and
599 chemical cleaning methods on alkyd-paint graffiti made on calcareous stones, Journal of
600 Cultural Heritage 16: 579–590. doi.org/10.1016/j.culher.2014.10.004

601

602 18. Samolik S., Walczak M., Plotek M., Sarzynski A., Pluska I., Marczak J. (2015) Investigation into
603 the removal of graffiti on mineral supports: Comparison of nanosecond Nd:YAG laser cleaning
604 with traditional mechanical and chemical methods, Studies in Conservation 60: S58-S64.

605

606 19. Careddu N. and Akkoyun O. (2016) An investigation on the efficiency of water-jet technology
607 for graffiti cleaning, Journal of Cultural Heritage 19: 426-434.
608 doi.org/10.1016/j.culher.2015.11.009

609

610 20. Pozo-Antonio J.S., Rivas T., Fiorucci M.P., Ramil A., López A.J. (2016) Effectiveness of granite
611 cleaning procedures in cultural heritage: a review, Science of the Total Environment 571: 1017–
612 1028. doi.org/10.1016/j.scitotenv.2016.07.090

613

21. García O., Rz-Maribona I., Gardei A., Riedl M., Vanhellemont Y., Santarelli M.L., Suput J.S. (2010) Comparative study of the variation of the hydric properties and aspect of natural stone and brick after the application of 4 types of anti-graffiti, *Materiales de Construcción* 60 (297): 69-82. doi: 10.3989/mc.2010.45507
22. Carmona-Quiroga P.M., Martínez-Ramírez S., Blanco-Varela M.T, Fort R. (2006) Valuation of the effectiveness of an anti-graffiti product applied to "Blanco Paloma" limestone. In *Proceedings of the International Conference on Heritage, Weathering and Conservation, HWC 2006* 2, 785-790.
23. Licchelli M., Malagodi M., Weththimuni M., Zanchi C. (2014) Anti-graffiti nanocomposite materials for surface protection of a very porous stone, *Applied Physics A: Materials Science and Processing* 116 (4): 1525-1539. doi 10.1007/s00339-014-8356-9
24. Lettieri M., Masieri M. (2014) Surface characterization and effectiveness evaluation of anti-graffiti coatings on highly porous stone materials. *Applied Surface Science* 288:466-477. doi.org/10.1016/j.apsusc.2013.10.056
25. Meng B., Mueller U., Garcia O., Malaga K. (2014) Performance of a new anti-graffiti agent used for immovable cultural heritage objects, *International Journal of Architectural Heritage* 8 (6): 820-834. doi.org/10.1080/15583058.2012.747116
26. Carmona-Quiroga P.M., Martínez-Ramírez S., Blanco-Varela M.T. (2008) Fluorinated anti-graffiti coating for natural stones, *Materiales de Construcción* 58 (289-290) : 233-246.

27. Carmona-Quiroga P.M., Martínez-Ramírez S., Sánchez-Cortés S., Oujja M., Castillejo M., Blanco-Varela M.T. (2010) Effectiveness of anti-graffiti treatments in connection with penetration depth determined by different techniques. *Journal of Cultural Heritage* 11 (3): 297-303. doi.org/10.1016/j.culher.2009.09.006
28. Mosquera M.J., Rivas T., Prieto B., Silva B. (2000) Capillary rise in granitic rocks: interpretation of kinetics on the basis of pore structure, *Journal of Colloid and Interface Science* 222:41–45. doi.org/10.1006/jcis.1999.6612
29. Rivas T., Prieto B., Silva B. (2000) Permeability to water vapour in granitic rocks. Application to the study of deleterious effects on conservation treatments, *Building and Environment* 36 239–246. doi.org/10.1016/S0360-1323(00)00003-2
30. IGME (1981) Mapa Geológico de España E 1:50000, Hoja 261 Tui, Segunda Edición, Servicio de Publicaciones, Ministerio de Industria y Energía, Madrid.
31. RILEM (Réunion Internationale des Laboratoires d’Essais et de Recherche sur les Matériaux et les Constructions). (1980). Commission 25 PEM. Protection et Erosion des Monuments. Recommandations provisoires. Essais recommandés pour mesurer l’altération des pierres et évaluer l’efficacité des méthodes de traitement. Test N°. II. 1: Open porosity and Test II. 2: Bulk and real densities.
32. Rojo A., Alonso F.J., Esbert R.M. (2003) Hydric properties of some Iberian ornamental granites with different superficial finished. A petrophysical interpretation. *Materiales de Construcción* 53, 269:61-72.

33. Vázquez P., Alonso F.J., Esbert R.M., Ordaz J. (2010) Ornamental granites: Relationships between p-waves velocity, water capillary absorption and the crack network. *Construction and Building Materials* 24: 2536–2541
34. ICR-CNR-Instituto Centrale do Restauro-Commisione Normal. Doc. NORMAL 11/85 (1985). Assorbimento d'acqua per capillarità. Coefficiente di assorbimento capillare.
35. Feijó J., Ramón Nóvoa X., Rivas T., Mosquera M.J., Taboada J., Montojo C., Carrera F., Granite desalination using electromigration. Influence of type of granite and saline contaminant, *J. Cult. Herit.* 14 (2013) 365–376.
36. Prieto B, Sanmartín P., Silva B., Martinez-Verdú F. (2010) Measuring the color of granite rocks. A proposed procedure. *Color Res Appl.* 35(5), 368-375.
37. Commission Internationale de l'Eclairage (CIE), Colorimetry, Bureau central de la CIE, Paris, 1976.
38. García O., Malaga K. (2012) Definition of the procedure to determine the suitability and durability of an anti-graffiti product for application on cultural heritage porous materials, *Journal of Cultural Heritage* 13: 77-82. doi.org/10.1016/j.culher.2011.07.004
39. García Mercero O. (2008) Design and study of the behaviour of a new antigraffiti concept specific for its application in Cultural Heritage. Doctoral Thesis, Universidad del País Vasco, Spain.

689 40. Tsakalof A., Manoudis P., Karapanagiotis I., Chrysoulakis I., Panayiotou, C. (2007)
690 Assessment of synthetic polymeric coatings for the protection and preservation of stone
691 monuments, *Journal of Cultural Heritage* 8: 69–72. doi.org/10.1016/j.culher.2006.06.007
692

693 41. Federal Highway Research Institute (2006) Technische Prüfvorschriften für Anti-Graffiti-
694 Systeme, TP AGS, Federal Highway Research Institute.
695

696 42. Socrates G. (2001) *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*,
697 third edition, John Wiley and Sons.
698

699 43. Mosquera M.J., Pozo J., Esquivias L., Rivas T., Silva B. (2002) Application of mercury
700 porosimetry to the study of xerogels used as stone consolidants, *Journal of Non-Crystalline Solids*
701 311: 185-194. doi.org/10.1016/S0022-3093(02)01370-4
702

703 44. Wheeler G. (2005) Alkoxysilanes and the consolidation of stone, The Getty Conservation
704 Institute. Los Angeles (USA).
705

706 45. de Rosario I., Elhaddad F., Pan A., Benavides R., Rivas T., Mosquera M.J. (2015) Effectiveness
707 of a novel consolidant on granite: Laboratory and “in situ” results, *Construction and Building*
708 *Materials* 76: 140–149. doi.org/10.1016/j.conbuildmat.2014.11.055
709

710 46. Mokrzycki W.S., Tatol M. (2011) Colour difference ΔE - A survey, *Machine Graphics and*
711 *Vision* 20 (4): 383-411.
712

713 47. Berns R.S. (2000) *Billmeyer and Saltzman’s Principles of Color Technology*, Wiley- Interscience,
714 New York (USA).

715

716 48. Historic England (1999) Graffiti on historic buildings and monuments - Methods of removal
717 and prevention (Technical Advice Note).

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FIGURE CAPTIONS

Fig. 1. Flow chart of evaluation procedure.

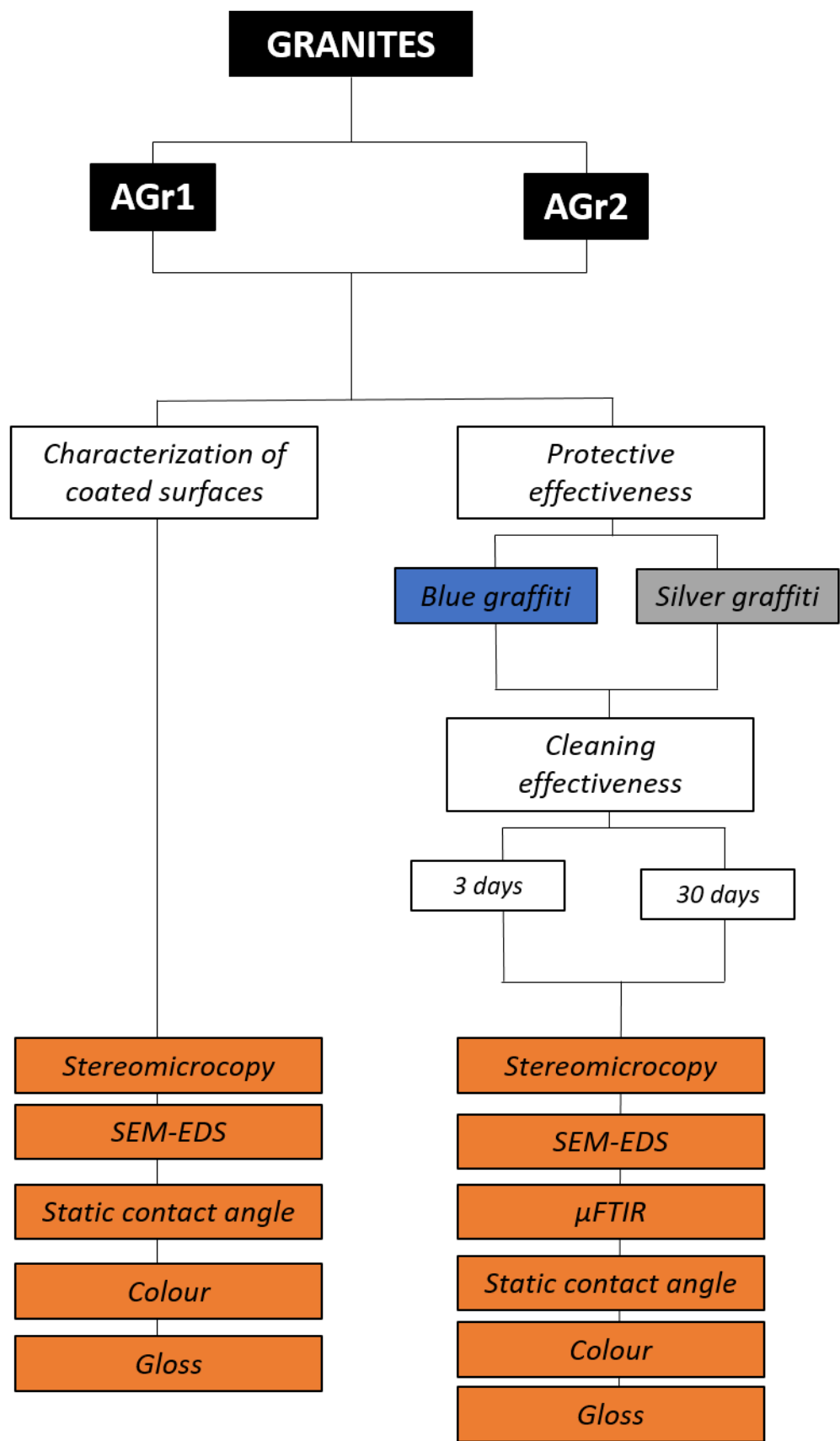
Fig. 2: Stereomicroscope and SEM-micrographs of the uncoated surfaces of both granites (Rosa Porriño: A and D; Albero: G and J) and the anti-graffiti coated surfaces with AGr1 (Rosa Porriño: B and E; Albero: H and K) and AGr2 (Rosa Porriño: C and F; Albero: I and L). EDS spectra for the AGr1 and AGr2 on both granites are also shown.

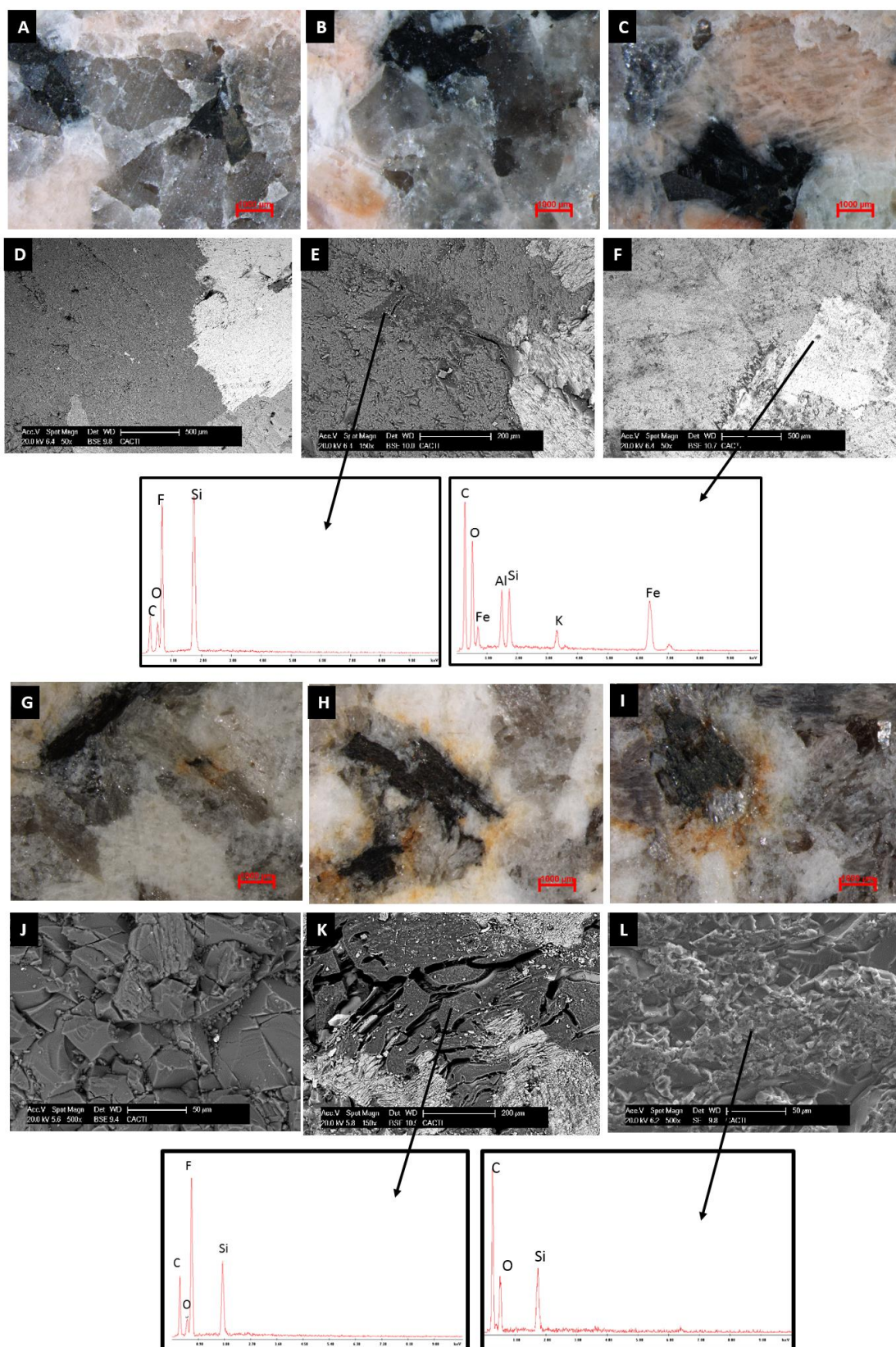
Fig. 3. Evaluation of blue and silver graffiti cleanings on anti-graffiti coated Rosa Porriño and Albero granites. CN (Classification Number) defined in [38,41]; CN=0, complete removal of the sprays. CN=1, isolated residues in fissures and cracks.

Fig. 4: SEM micrographs, EDS spectrum and compositional maps (C, Al and Ti) of the surfaces of Rosa Porriño and Albero granites with anti-graffiti products AGr1 and AGr2 after the extraction of blue graffiti.

Fig. 5: SEM micrographs and EDS spectra of the surfaces of Rosa Porriño and Albero granites with anti-graffiti products AGr1 and AGr2 after the extraction of silver graffiti.

Fig. 6. Fourier transform infrared (FTIR) spectra (absorbance) obtained for the evaluation of the cleaning effectiveness of blue (A and C) and silver graffiti (B and D) on uncoated samples of Rosa Porriño (A and B) and Albero (C and D) and coated with AGr1 and AGr2 anti-graffitis. Spectra obtained at 3 days and at 30 days after the graffiti application are depicted.





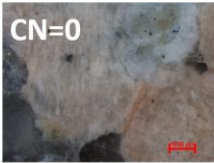
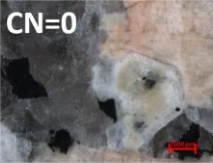
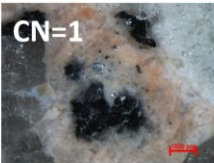

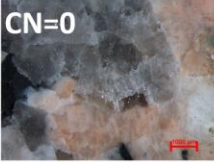
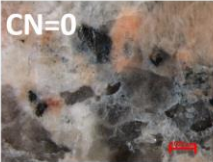

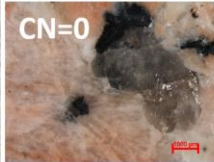
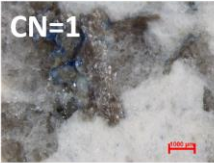
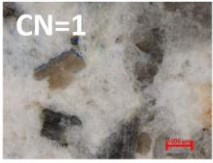
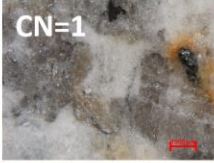
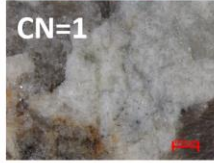
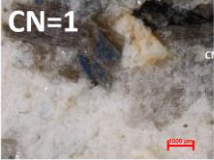
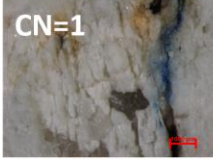
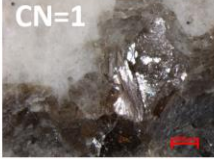

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		Blue graffiti cleanings		Silver graffiti cleanings	
		3 days	30 days	3 days	30 days
Rosa Porriño	AGr1				
	AGr2				
Albero	AGr1				
	AGr2				

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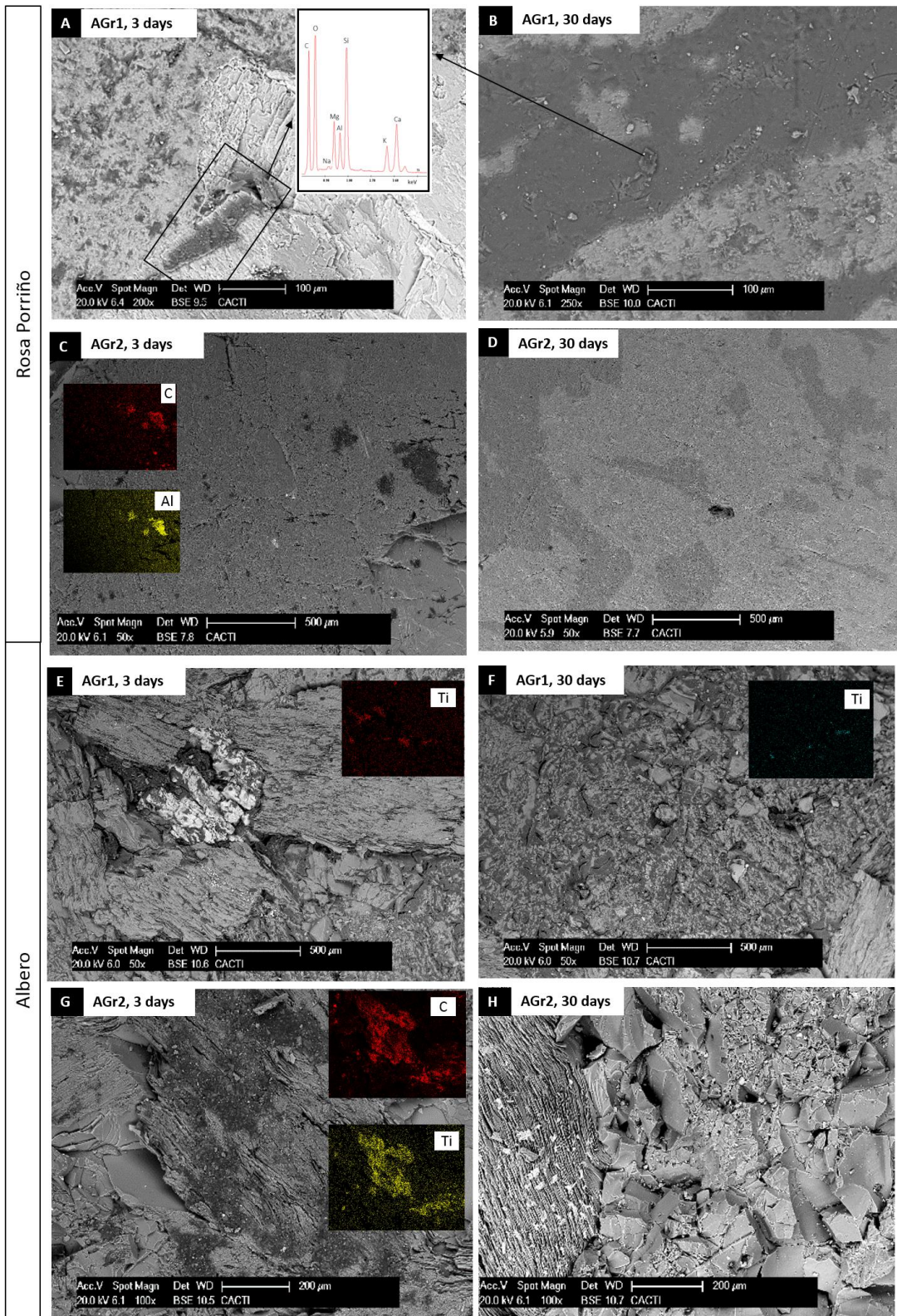
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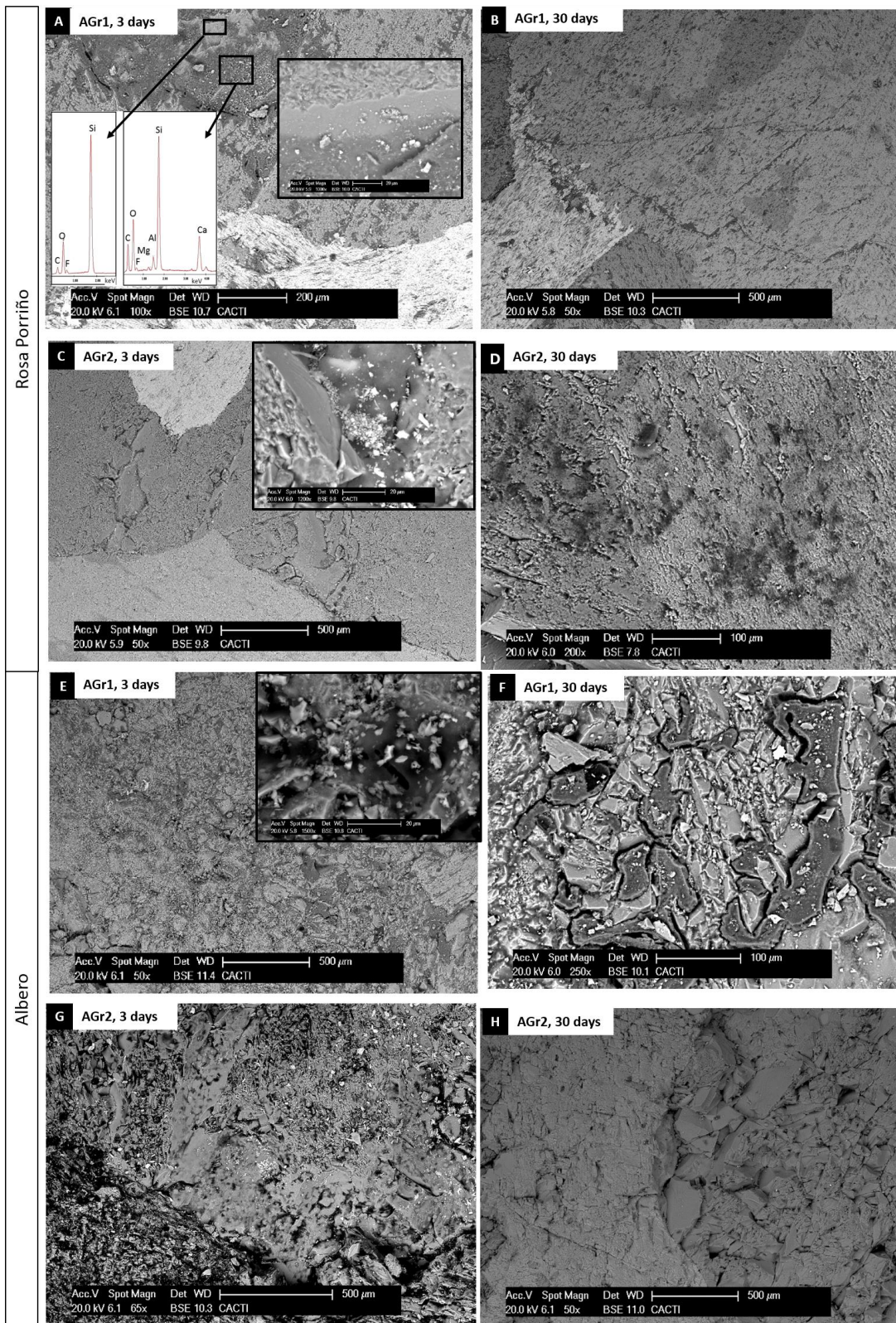
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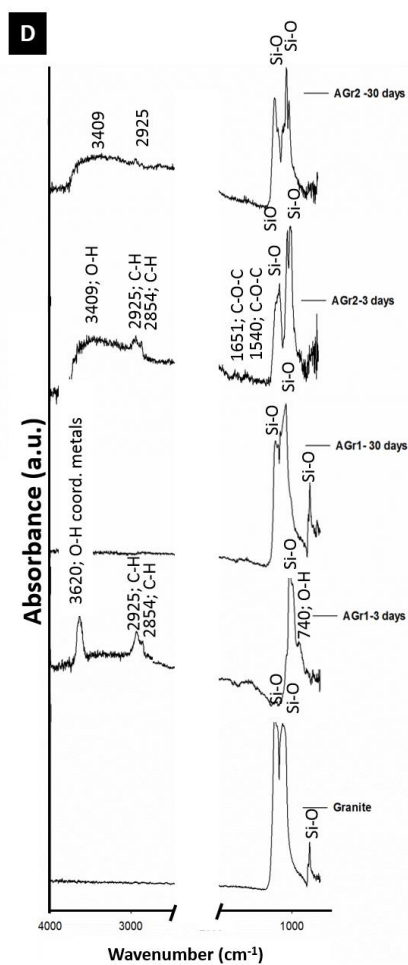
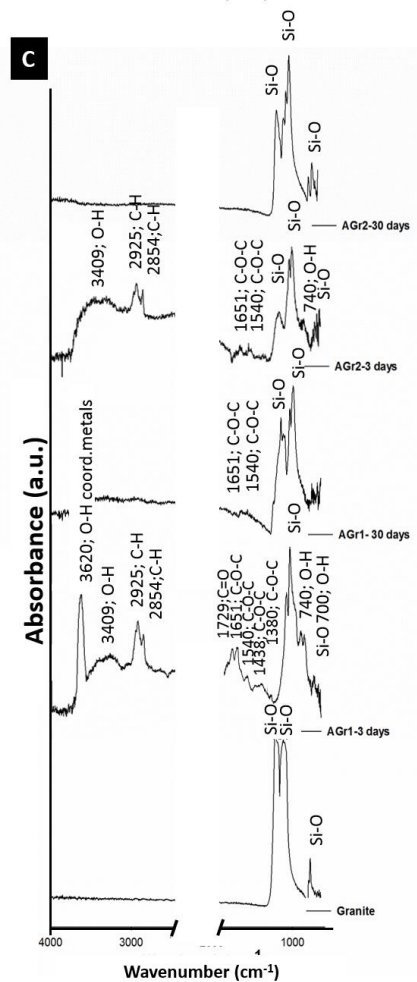
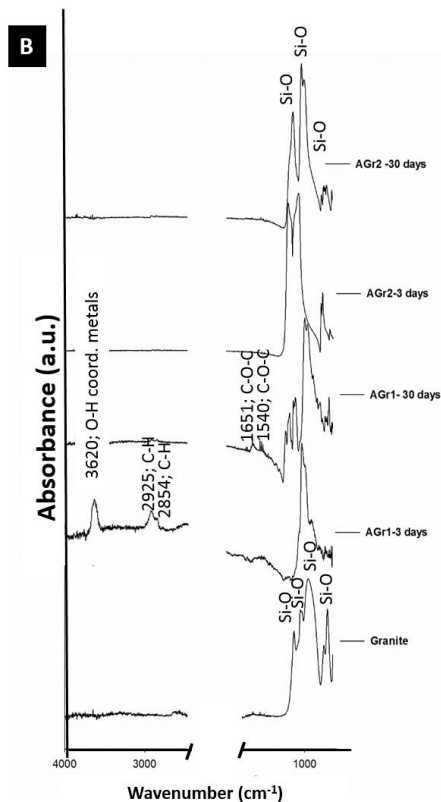
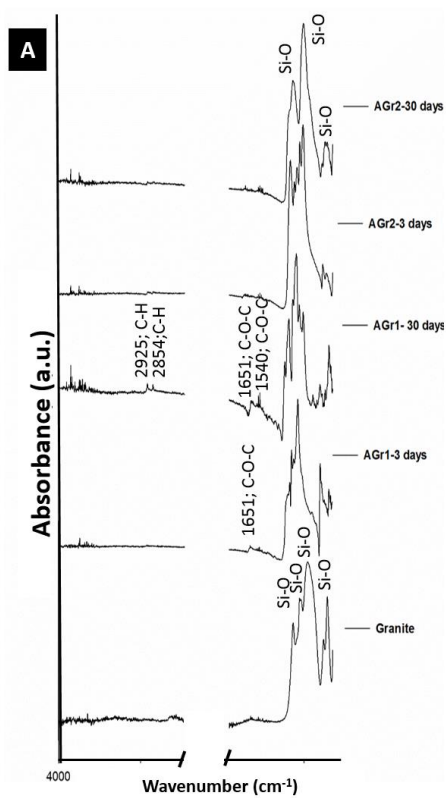
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779 Table 1: Chemical composition (%) of Blue Ultramarine and Silver Chrome graffiti paints by XRF
780 and CHNS.

Blue Ultramarine		Silver Chrome	
C	62.91	C	70.36
H	7.25	H	10.16
N	1.27	N	0.03
MgO	1.30	Al ₂ O ₃	19.43
Al ₂ O ₃	1.10	Fe ₂ O ₃	0.01
SiO ₂	5.03	ZnO	0.001
SO ₃	1.07		
Cl	0.75		
K ₂ O	0.05		
CaO	1.55		
TiO ₂	14.20		
Fe ₂ O ₃	0.09		
CoO	0.20		
CuO	1.05		
Br	0.03		
ZrO ₂	0.13		

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Table 2. Active residue (g.m^{-2}), colorimetric parameters, gloss measurement and water-rock static contact angle ($^\circ$) of Rosa Porriño and Albero uncoated (UC) and coated with the permanent (AGr1) and the sacrificial anti-graffiti (AGr2). n/a: not applicable

	Rosa Porriño			Albero		
	UC	AGr1	AGr2	UC	AGr1	AGr2
ACTIVE RESIDUE						
Active residue	n/a	9.4±1.4	11.7±2.7	n/a	21.1±2.8	15.0±2.2
COLOUR MEASUREMENTS IN CIELAB SPACE						
L*	65.57±6.52	63.70±6.57	63.54±7.03	79.27±4.33	76.31±5.59	78.82±4.55
a*	4.08±2.16	5.08±2.42	4.02±2.35	0.38±0.50	0.43±0.69	0.36±0.63
b*	7.16±2.65	10.60±2.94	7.68±2.82	4.01±1.43	6.25±1.66	5.17±1.72
ΔE^*_{ab}	n/a	5.17±1.70	2.35±1.35	n/a	4.25±1.85	1.87±1.19
GLOSS MEASUREMENTS						
Gloss (85°)	30.3±3.7	21.0±3.5	30.4±3.0	2.2±0.6	3.0±0.8	3.4±0.6
ΔG (85°)	n/a	-10.0±4.4	-0.6±2.4	n/a	1.0±0.3	1.2±0.4
STATIC CONTACT ANGLE (θ°)						
2 weeks after coating application	42.09 ± 5.84	114.2±2.4	83.8±4.6	0.0	116.2±2.3	82.9±6.9
10 weeks after coating application		118.6±1.2	87.5±4.4		126.6±0.7	90.2±1.7

Table 3. Static contact angle (θ°), global colour change (ΔE^*_{ab}) and gloss variation (ΔG) of the anti-graffiti coated Rosa Porriño and Albero granites after the cleaning of blue and silver paints. For samples coated with AGr1, colour and gloss reference values were those of the anti-graffiti coated surfaces; for the samples coated with AGr2 colour and gloss reference values were those of the uncoated granites.

Granite	AGr	Graffiti	Days after graffiti application	θ°	ΔE^*_{ab}	ΔG
Rosa Porriño	AGr1	Blue	3 days	116.87±4.65	3.04±1.97	26.8
			30 days	115.26±2.47	2.99±1.86	30.9
		Silver	3 days	115.66±3.66	6.62±3.99	24.1
			30 days	117.27±6.84	5.33±4.68	19.6
	AGr2	Blue	3 days	95.86±6.2	2.47±0.35	-0.1
			30 days	102.03±3.16	2.58±1.47	2.4
		Silver	3 days	96.2±15.49	4.30±1.58	-1.3
			30 days	92.05±3.57	3.44±0.57	-0.8
Albero	AGr1	Blue	3 days	123.03±4.6	7.57±0.74	0.2
			30 days	131.7±7.06	4.42±1.48	-0.3
		Silver	3 days	133.28±2.79	8.85±0.63	0.4
			30 days	127.73±7.37	9.99±2.02	0.2
	AGr2	Blue	3 days	77.44±11.15	9.06±1.32	-0.6
			30 days	0	2.10±0.94	-1.4
		Silver	3 days	72.23±22.7	11.20±3.88	-1.0
			30 days	83.34±5.94	8.65±1.79	-1.3