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Evaluation of different gels and poultices to chemically remove graffiti from a *Lioz* limestone (Lisbon, Portugal)

Evaluación de diferentes geles y papetas para retirar químicamente graffiti de una caliza *Lioz* (Lisboa, Portugal)

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Abstract

In recent decades, graffiti paintings have become an artistic manifestation under the label of «Street Art». However, there are still many cases where its application is carried out with vandalic purposes. If we consider historical buildings, they cause an aesthetic alteration and jeopardise the long-term preservation of the stone used. This is why their removal is seen as necessary. In doing so, multiple factors must be considered, such as the stone substrate properties, the composition of the paint, and the cleaning method selected as all of them will determine the effectiveness of the graffiti removal.

For this purpose, a study was carried out based on the removal of graffiti paint from a *Lioz* limestone. This is a stone widely used in the architectural heritage of Lisbon (Portugal). In this article, the effectiveness on the removal of two kinds of spray paints (silver and black), commonly used in this type of vandalism, was evaluated. Different gels and poultices used in heritage conservation were compared as cleaning agents. The aim was to evaluate their effectiveness in terms of graffiti removal, leaving the minimum amount of residues on the surface of the stone. Regardless of the paint, the greatest cleaning level was achieved with gels, mainly with Nevek®.

However, further research must be conducted to avoid remains of the cleaning vehicles and chemical contamination.

Keywords: graffiti, cleaning, gels, poultices, *Lioz* limestone

Resumen

En las últimas décadas, las pinturas grafiti se han convertido en una verdadera manifestación artística bajo la etiqueta de «*Street Art*». Sin embargo, todavía hay muchos casos en los que su aplicación se lleva a cabo con fines vandálicos. Si consideramos los edificios históricos, estos actos provocan una alteración estética y ponen en riesgo la conservación a largo plazo de la piedra empleada en la construcción. Por lo tanto, se considera necesaria su eliminación. Para ello, hay que tener en cuenta múltiples factores como son las propiedades del propio sustrato pétreo, la composición de la pintura y el método de limpieza seleccionado, ya que todos ellos determinarán la eficacia en su eliminación.

Para ello, se ha realizado un estudio basado en la eliminación de pintura grafiti aplicada sobre una piedra caliza *Lioz*. Se trata de una piedra muy utilizada en el patrimonio arquitectónico de Lisboa (Portugal). En el presente artículo se evaluó la eficacia en la eliminación de dos tipos de pinturas tipo spray (plateada y negra), comúnmente utilizadas en este tipo de vandalismo. Se compararon diferentes geles y papetas comerciales empleados tradicionalmente en la conservación del patrimonio como agentes de limpieza. El objetivo final fue el de evaluar su eficacia en términos de eliminación de grafiti, dejando la mínima cantidad de residuos procedentes de los agentes limpiadores sobre la superficie de la piedra. Independientemente de la pintura, el mayor nivel de limpieza se consiguió con geles, principalmente con Nevek®. Sin embargo, es necesario seguir investigando para evitar restos de los vehículos de limpieza y contaminación química.

Palabras clave: grafiti, limpieza, geles, papetas, caliza *Lioz*

1. INTRODUCTION

The word graffiti originates from the Italian term *graffiare*, meaning ‘to scratch’. It can be described as the act of scribbling, scratching, drawing, or painting on various materials and surfaces (GARCÍA DE MIGUEL, 2011). Although it can be considered as an artistic manifestation i.e. ‘Street Art’, it is often a consequence of vandalism. In this context, the uncontrolled application of graffiti, either spray or brush-applied, pose a great risk to the preservation of historical buildings and cause an aesthetic alteration that distorts the understanding of the artwork. In addition to visual impact, one must anticipate significant maintenance expenses and other risks brought on by cleaning procedures. Still, their removal is essential to maintain the appearance of historical buildings, as well as ensuring their preservation. In this regard, the stone substrate beneath the graffiti must be considered since the stone properties (porosity, texture, cleavage, etc.) will highly influence the effectiveness of the removal procedures, as well as the preservation of the stone (GOMES *et al.,* 2017; RAMIL *et al.,* 2017). For instance, pore size will highly influence the penetration of the paint into the porous system (GARCÍA *et al.,* 2010); as well as the fissural system, which will determine higher or lower penetration of the paint (GIUSTI *et al*., 2020), thus influencing the cleaning effectiveness.

The composition of paint graffiti is also one of the most influential factors in obtaining satisfactory cleanings (WEAVER, 1995). They are generally composed of a pigment (organic or inorganic), binders (e.g. acrylic, alkyd, polyvinyl acetate, etc.), a solvent that allows the pigment/binder mixture to flow, fillers and additives (CHRISTIE, 2001; MARRION, 2004; SANMARTÍN *et al.,* 2014). Among the variety of pigments, carbon is generally reported as one of the main components in organic pigments (RIVAS *et al*., 2012; POZO-ANTONIO *et al.,* 2018). Inorganic ones are also widely used such as titanium dioxide, iron oxides or aluminium powder (SANMARTÍN *et al.,* 2014). The solvents used in the spray paint industry can be hydrocarbons (aliphatic, naphthenic and aromatic solvents), oxygenated (ketones, esters, glycol and alcohols) and water (SANMARTÍN et al., 2014). Regarding fillers, they are generally introduced to improve paint properties i.e. as opacifiers, to control flow or reduce gloss, such as rutile (TiO_2), calcite ($CaCO_3$), talc ($Mg_3Si_4O_{10}(OH)_2$) or barite ($BaSO_4$) (CHRISTIE, 2001; MARRION, 2004; SANMARTÍN *et al.,* 2014). Finally, additives with various functions are used: thickeners, biocides, pH buffers, coalescing agents, defoamers, etc. (CHRISTIE, 2001; MARRION, 2004). In all, the composition of graffiti paint is something that ought to be considered as it will influence the effectiveness of the cleaning procedure.

The use of laser ablation in the removal of these vandalic expressions has been widely evaluated in the last decades (CHAPMAN, 2000; GÓMEZ et al., 2006; RIVAS et al., 2012; RAMIL et al., 2017; GOMES et al., 2018; POZO-ANTONIO et al., 2018; TSEREVELAKIS et al., 2019). And though they have proven to be useful, they are not always economically accessible. Hence, professionals often advocate for the use of traditional cleaning procedures for graffiti removal, whether it is through mechanical (using abrasives) or chemical cleaning techniques (WEAVER, 1995). From the point of view of roughness increase, chemical procedures are generally more respectful with the surface (VAZQUEZ-CALVO et al., 2012; CARVALHÃO and DIONÍSIO, 2015; POZO-ANTONIO *et al*., 2016; PEDERGNANA *et al.,* 2020). At the same time, they are more economical and easier to carry out. There are a grant variety of solvents for chemical cleaning capable of dissolving or breaking down spray paints (alkalis, acids, detergents, etc.). Depending on the intended outcomes, pure solvents, admixtures, and solutions can be used (SANSONETTI *et al.,* 2020). In addition, surfactants, chelating agents, or other compounds can also be added to accomplish an effective cleaning (SANSONETTI *et al.,* 2020). The selected cleaning solution can either be directly applied on the surface using a cotton swab or supported by an inert substance. The latter are absorbent materials or powders made of cellulose microfibers, clays, or micronized silica, known as poultices, which are then mixed with the cleaning solution (WEAVER, 1995; NORMANDIN and SLATON, 2006; SANSONETTI *et al.,* 2020). Moreover, over the past decades, the conservation community has become more interested in the use of gels. These consist of interconnected long polymer chains, which are dispersed into the solvent, forming a three-dimensional network (CREMONESI, 2000; WOLBERS, 2004; FRATINI and CARRETI, 2013). This is what is known as "solvent gels". This system allows a high degree of surface impregnation, regulating the fluid discharge to the substrate, acting at the same time as a molecular sponge, as it attracts the substances dissolved by the solvent into the gel, as well as preventing evident residual traces (CREMONESI, 2000; WOLBERS, 2004; SANSONETTI *et al.,* 2020). Something similar happens with some traditional poultices e.g. cellulose pulp or some clays, though the physical effect produced is different from that of gels and they generally leave residues on the surface.

In all, after all that has been exposed above, graffiti removal must be considered as a complicated task since stone substrate, paint composition, and cleaning procedures must be taken into consideration. Therefore, in this study, a *Lioz* limestone was selected to be vandalised with spray paints and test different cleaning procedures. The selection of this stone is based on the fact that it is widely found in historical buildings of the Portuguese city of Lisbon such as the Jerónimos Monastery and the Tower of Belém (SILVA, 2019; REDWEIK *et al.,* 2020). The widespread use of *Lioz* limestone is due to its good visual and mechanical properties, as well as the substantial reserves in the region (SILVA, 2019). During the eighteenth century, it earned the title of "Royal Stone" as it was selected to erect monumental buildings with the aim to demonstrate the grandiosity of the buoyant Portuguese kingdom (SILVA, 2019). Nevertheless, it has been used in practically all artistic periods (MILLER *et al.,* 2010), already exploited during the Roman Empire (SILVA, 2019). Two aerosol paint graffiti, silver and black, were applied onto *Lioz* limestone mock-ups. A mixture of n-butyl acetate and cyclohexane 80/20 (% v/v) was mixed with different kind of gels (Nevek®, Carbopol utrex 21® and carboxymethylcellulose) and poultices (cellulose pulp, betonite and sepiolite) separately. The cleaning effectiveness was evaluated by stereomicroscopy, colour spectrophotometry, polarized light microscopy and scanning electron microscopy with X-ray spectroscopy.

2. MATERIALS AND METHODS

2.1. Materials

The materials used for this study are presented in Table 1, showing suppliers specifications and/or results reported in previous research. The stone selected was a *Lioz* limestone. The stone has a microcrystalline grain-supported texture, beige in colour, mainly composed of calcite ($CaCO_3$), and with low porosity (open porosity of 0.3% and water absorption of 0.1%) (CASAL MOURA *et al.,* 2007). It is composed of 50% spiritic matrix with around 48% bioclasts species such corals and bivalves, classified as biosparite (LICCI *et al.,* 2022).

Table 1. Materials used in the study: stone substrate, graffiti paints and cleaning methods (gels-G- and poultices-P-).

Suppliers ID	**Authors ID**	**Composition**
Lioz limestone	LIOZ	CaO (55.54%), Al_2O_3 (0.41%), MgO (0.39%), SiO_2 (0.20%), K_2O (0.05%), Na_2O (0.04%) and Fe_2O_3 (0.02%) (CASAL MOURA et al., 2007).
Silver (#EX014H0101)	SG	Alkyd-based colour with polyethylene and an inorganic aluminium-rich pigment (RIVAS et al. 2012)
Black R-9011 (#EX014H9011)	BG	Alkyd-based colour (RIVAS et al. 2012)
Nevek®	G-N	Based on Agar-Agar, derived from red algae, particularly from species like *Gelidium* and *Gracilaria* (CTS web, accessed 3 December 2024)
Carbopol Ultrez® 21	G-C	Acrylic acid polymer that needs to be neutralised by polyethoxylated amine (commercialised as Ethomeen®) (CTS web, accessed 3 December 2024)
Carboxymethylcellulose®	G-CMC	Sodium carboxymethyl cellulose is a thickener derived from cellulose, i.e. a water-soluble sodium salt composed of 56% of carboxymethylcellulose, with an 8% of salt content and 38% of water (CTS web, accessed 3 December 2024)
Arbocel BC 1000®	P-CP	Mainly composed of pure cellulose fibres (99.5 %) with an average length of 700 µm and an average thickness of 20 µm (CTS web, accessed 3 December 2024)
Betonite®	P-BT	Absorbent aluminium phyllosilicate mainly composed of montmorillonite ($(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$). It is chemically composed of SiO_2 (53–60%), Al_2O_3 (16–20%), Fe_2O_3 (4–7%), MgO (3.5–4.5%), CaO (1.5–4%), K_2O (1–2.2%), Na_2O (0.3–1.8%), Ti_2O (0.3–0.4%), MnO_2 (0.14%) (CTS web, accessed 3 December 2024)
Sepiolite Pansil 100®	P-SP	Absorbent clay composed of a 60% of sepiolite ($Mg_4Si_6O_{15}(OH)_2{\cdot}6(H_2O)$) and other clays (40%). It is chemically composed of SiO_2 (59.5%), MgO (17.6%), Al_2O_3 (5.8%), CaO (2.8%), Fe_2O_3 (1.7%), K_2O (1.6%) and Na_2O (0.5%) (CTS web, accessed 3 December 2024)

Two different coloured-graffiti, supplied by Montana Colors® (Barcelona, Spain), from the Hardcore series, were selected to vandalise the stone: a silver alkyd-based colour with polyethylene and an inorganic aluminium-rich pigment, and a black alkyd-based R-9011 colour, with an organic pigment (RIVAS et al. 2012). The cleaning media were supplied by CTS S.L. (Madrid, Spain). Nevek®, Carbopol ultrez 21® and carboxymethyl-cellulose were selected as gels (G). As poultices (P), cellulose pulp, bentonite and sepiolite were selected. Regarding the cleaning solution, a mixture of n-butyl acetate ($C_6H_{12}O_2$) and cyclohexane (C_6H_{12}), 80/20 (% v/v), was prepared and mixed with the gels and the poultices separately, following suppliers' specifications.

2.1.Samples preparation

In order to study the chemical composition of the graffiti paints selected, they were applied on aluminium supports. After air-drying at laboratory conditions (18 ±5 ºC and 65 ±5 RH) for seven days, paints were scraped from the surfaces and then analysed.

Fifteen mock-ups of Lioz were prepared by cutting 4 cm x 4 cm x 2 cm samples with disc-cut finish. The graffiti paints were applied using a standard universal aerosol cap (3 cm ø. / 1.18 in.). The samples were joined by colour, and the paint was applied at a distance of 15 cm, and at an angle of 45º. The painted samples were left to air-dry at laboratory conditions (18±5 ºC and 65±5 RH) for seven days.

2.2. Analytical techniques

In order to chemically characterize the graffiti paints, residue from both aerosols were scraped from the aluminium support and analysed by:

- X-ray fluorescence (XRF) using a SIEMENS SRS 3000 spectrometer to determine the elemental characterization of the graffiti paints.
- A Fisons EA-1108 elemental analyser to find the elemental composition (CHNS) of the paints.

Regarding the cleaning evaluation carried out by chemical procedures, references and treated surfaces were evaluated through the following protocol:

- The texture and appearance of the mock-ups were studied with a Nikon SMZ 1000 microscope. Cross-sections were studied under Polarized-Light Microscopy (PLM), in both plane-polarised (PPL) and cross-polarised (XPL) light modes.
- The colour of the mock-ups before and after cleaning were characterized using CIELAB and CIELCH colour spaces, measuring L* (lightness), a* and b* (colour coordinates) and C^*_{ab} (chroma) values using a Minolta CM-700d spectrophotometer. L* represents lightness, varying from 0 (black) to 100 (white). The other two parameters are chromaticity coordinates: a* goes from red to green (where +a* is red and -a* is green) and b* from yellow to blue (+b* is yellow and -b* is blue). C^*_{ab} is calculated according to the following formula: $C^*_{ab}=(a^{*2}+b^{*2})^{1/2}$. The measurements were made in specular component excluded

(SCE) mode, for a spot diameter of 8 mm, using illuminant D65 at observer angle 10º. A total of ten measurements were made for each mock-up and their average values and standard deviations (STD) were computed. ΔL^*, Δa^*, Δb^* and ΔC^*_{ab} and the colour difference (ΔE^*_{ab}) were calculated in order to evaluate the different cleaning methods.

- The micro-textural surface and cross-section was evaluated with a FEI QUANTA 200 Scanning Electron Microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS). For SEM visualization, the specimen was C- coated and observed using secondary (SE) and backscattered electron (BSE) detectors, applying 20 kV and a working distance of 10 mm.

3. RESULTS AND DISCUSSION

3.1. Characterization of the graffiti paints

The chemical characterization by the elemental analyser and x-ray fluorescence (XRF) of SG and BG graffiti paints is shown in Table 2, where it can be seen that they were mainly organic in composition (> 65% of organic carbon–C). SG was also characterised by the high presence aluminium (Al), keeping in line with the supplier specifications and RIVAS *et al.* (2012). The presence of Al in SG and silica (Si) in BG, was considered as markers to evaluate the removing level of each graffiti paint.

Table 2. Elemental characterization by x-ray fluorescence (XRF) of the graffiti materials. Results presented in percentage (%).

Silver graffiti (SG)		Black graffiti (BG)	
C	70.36	C	67.04
H	10.16	H	7.5
N	0.033	N	0.62
Al	19.43	Mg	2.6
Fe	0.0115	Si	8.32
Zn	0.00079	S	3.96
		Cl	0.79
		Ca	7.77
		Fe	0.11
		Co	0.702
		Cu	0.16
		Zn	0.059
		Zr	0.418

Figure 1 shows micrographs by stereomicroscopy and scanning electron microscopy (SEM) of the reference samples before cleaning. It was observed that SG-painted surfaces were rich in C and Al, whilst BG-painted surfaces were rich in C and Si. Additionally, fillers were sporadically identified by SEM-EDS in both spray paints, though in a very low percentage. This confirmed the mineralogical composition by XRD detected by RIVAS et al. (2012) in these graffiti paints. In SG, micrometric sized particles rich in barium (Ba) were identified, likely related to the presence of barite ($BaSO_4$). As for BG, Si and magnesium (Mg) rich particles were identified, probably in relation to talc ($Mg_3Si_4O_{10}(OH)_2$). Barite and talc are two of the most used fillers in modern paints (CHRISTIE, 2001; MARRION, 2004; SANMARTÍN *et al.,* 2014).

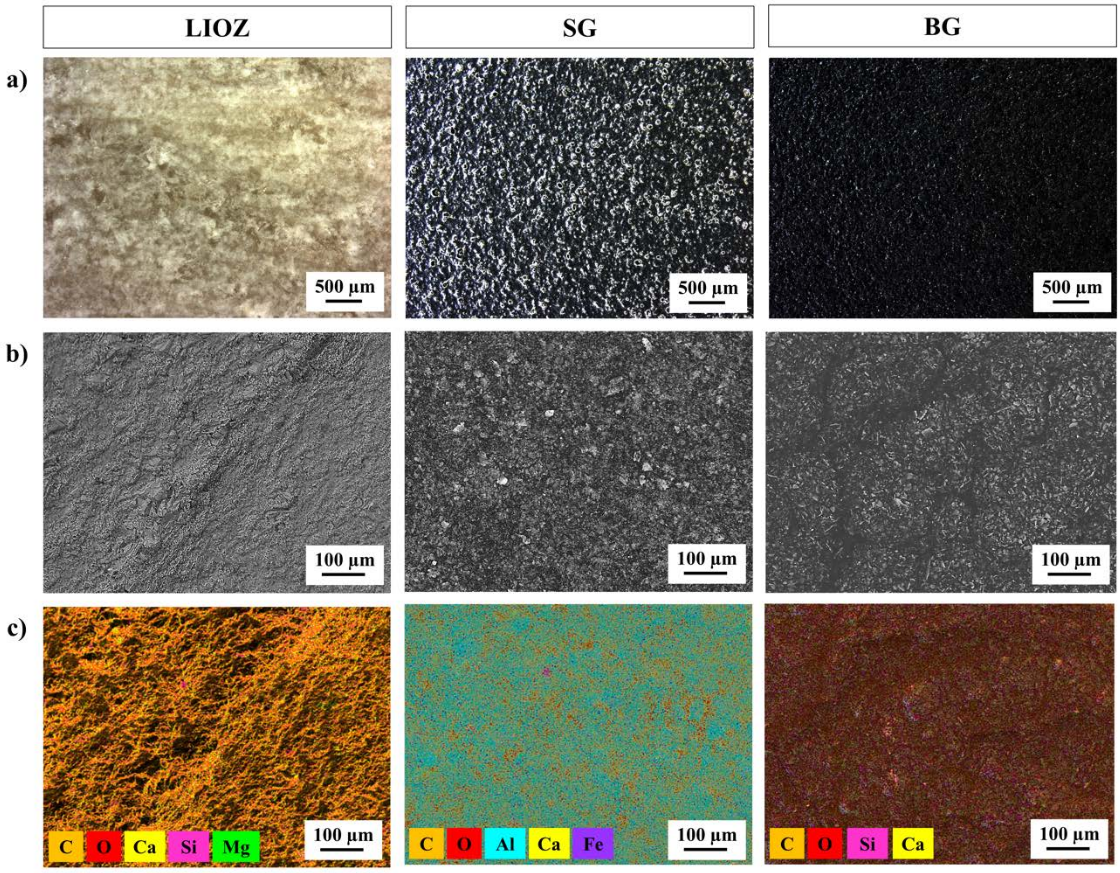

Figure 1. Reference micrographs of the stone substrate (LIOZ) without paint, with silver graffiti (SG) and with black graffiti (BG) by a) stereomicroscopy and b) SEM. c) Elemental compositional x-ray maps for each of the samples are included.

3.2. Cleaning evaluation

Evaluation by stereomicroscopy allowed to determine in general terms that SG was easier to remove than BG, as observed in Figure 2. Regarding the cleaning procedure, gels seemed to be more effective than poultices. All gels (N, C and CMC respectively) made possible the removal of SG. However, only with Nevek® (N) it was possible to remove BG, though not completely, as minor black traces were glimpsed on the surface of the *Lioz* limestone. As for poultices, only with bentonite (BT) it was possible to partially remove the paint graffiti, especially SG since evident black paint deposits were still present in BT-BG.

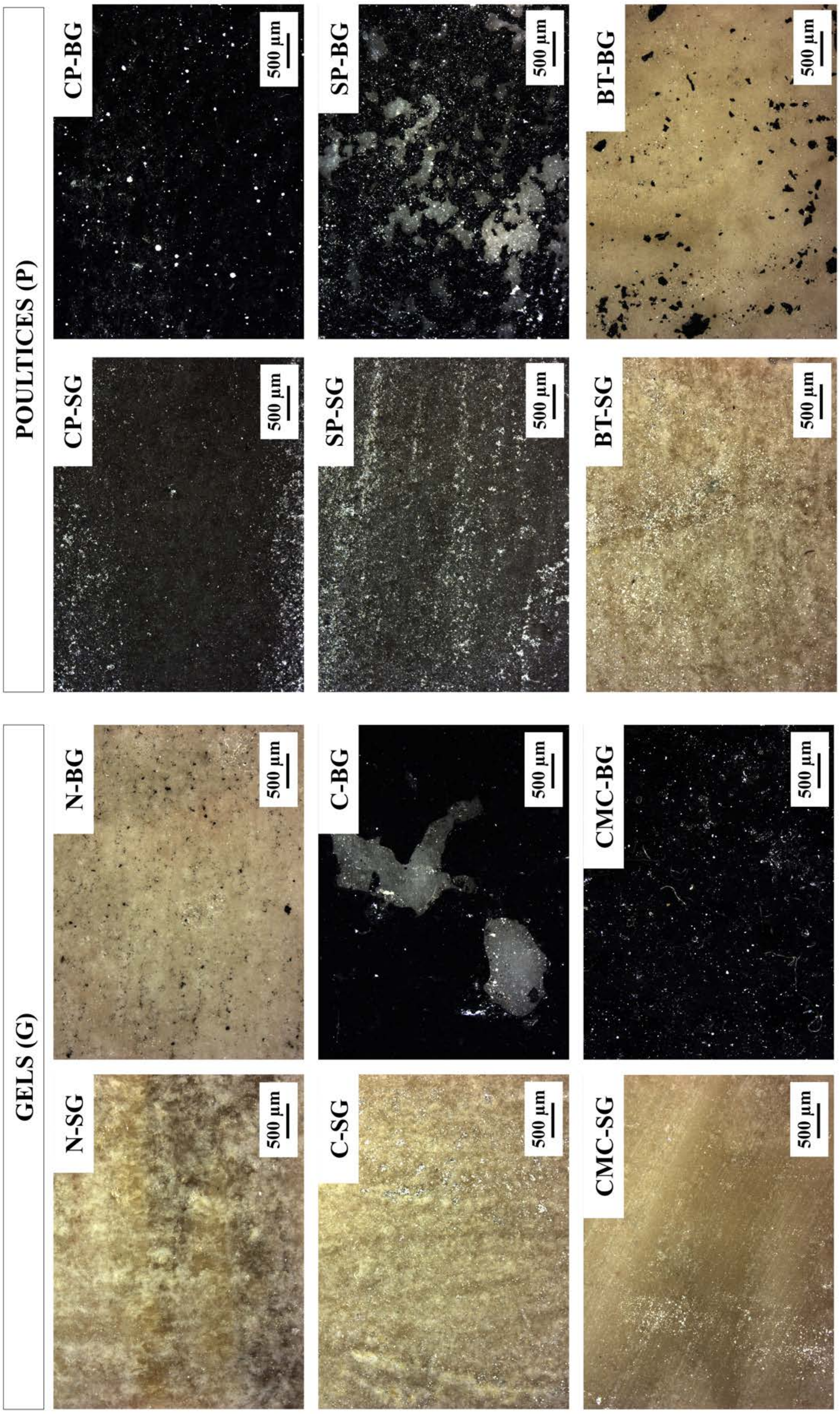

Figure 2. Stereomicrographs of the stone samples before and after cleaning with gels (G) and poultices (P). See Table 1 for explanation of the identification codes.

In Figure 3, the colour difference (ΔE_{ab}*) after the cleaning procedures is shown. Marked with a dashed line is 5 CIELAB units, value from which two different colours can be distinguishable (MOKRZYCKI and TATOL, 2011). It was noted that gels achieved greater successful removal of the paint graffiti compared to the poultices as values from the surfaces cleaned with the former were in general terms beneath 5 CIELAB units (except for C-BG and CMC-BG). However, in all the poultices-treated surfaces, their ΔE_{ab}* was higher than 5 CIELAB units, therefore removal was not effective. Nevertheless, considering the poultice-treated surfaces, BT, regardless of the paint, showed the lowest ΔE_{ab}*. Finally, it was also observed that BG was more difficult to remove as only N-BG showed values beneath 5 CIELAB units, followed by BT-BG.

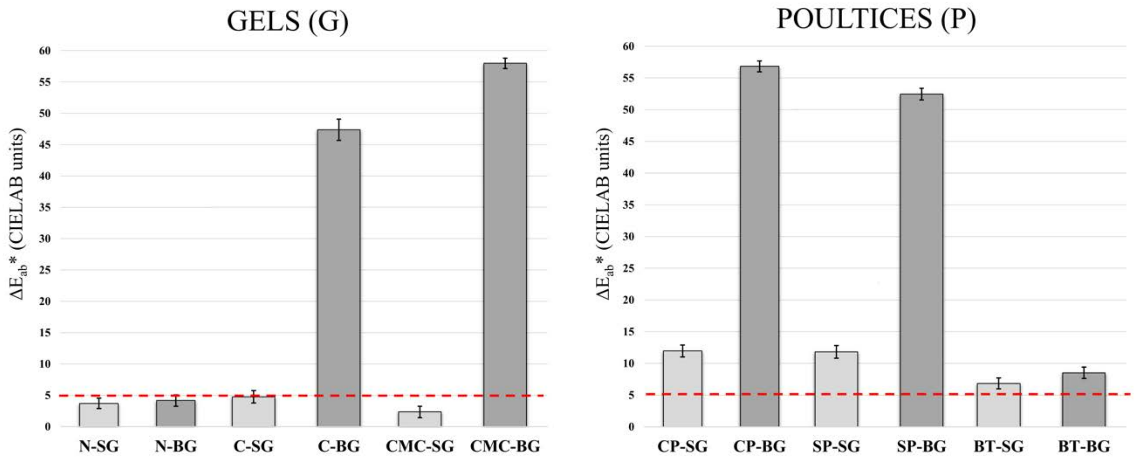

Figure 3. ΔE_{ab}* of the LIOZ surfaces after removing silver (SG) and black graffiti paints (BG) including standard deviations considering the original colour of the stone (before graffiti application) as reference. See Table 1 for explanation of the identification codes.

Based on stereomicroscopy observations and colour spectrophotometry results, the cleaning procedure that seemed more effective were the ones carried out with Nevek® (N) gel. However, the study by SEM-EDS of the surface of N-SG (Fig. 4a) allowed the punctual identification of Al-rich depositions in relation to SG (marked with a white square in the x-ray elemental maps). These were assigned to punctual traces of silver paint, with an extension bellow 5 µm, unnoticeable to the naked eye. The study of the cross-section of the N-SG sample also identified sporadic Al-rich particles on the surface (marked with a white rectangle in Fig. 4b), as well as Si-rich deposits (marked with a white arrow). On the N-BG surface, C- and Si-rich deposits were identified (marked with a white square in Fig. 4c), related to the graffiti remains. The study of the cross-sections also allowed the identification of these deposits, with a thickness of around 3-4 µm (as marked with a white arrow in Fig. 4d). C-rich residues were also observed (marked with white arrows in Fig. 4c) which could be related to the presence of gel residues.

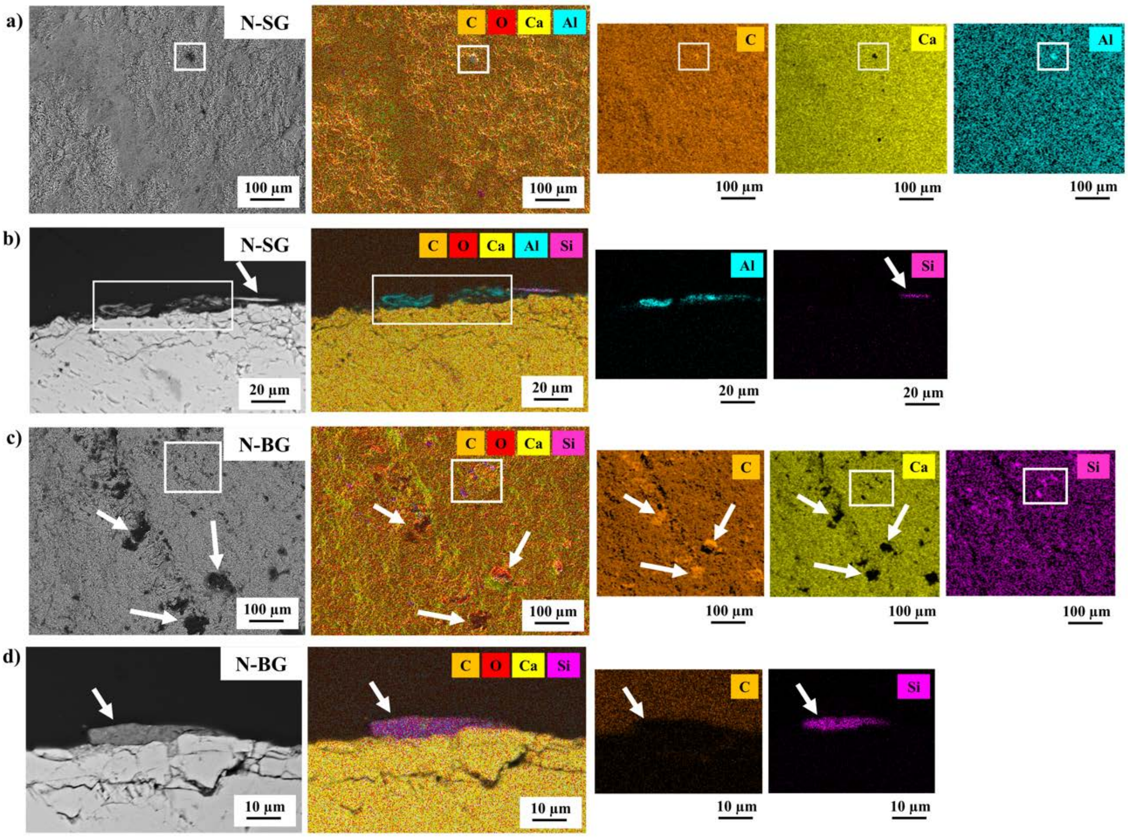

Figure 4. SEM micrographs and elemental compositional x-ray maps of the surface and cross-sections of samples a-b) N-SG sample and c-d) N-BG sample. See Table 1 for explanation of the identification codes.

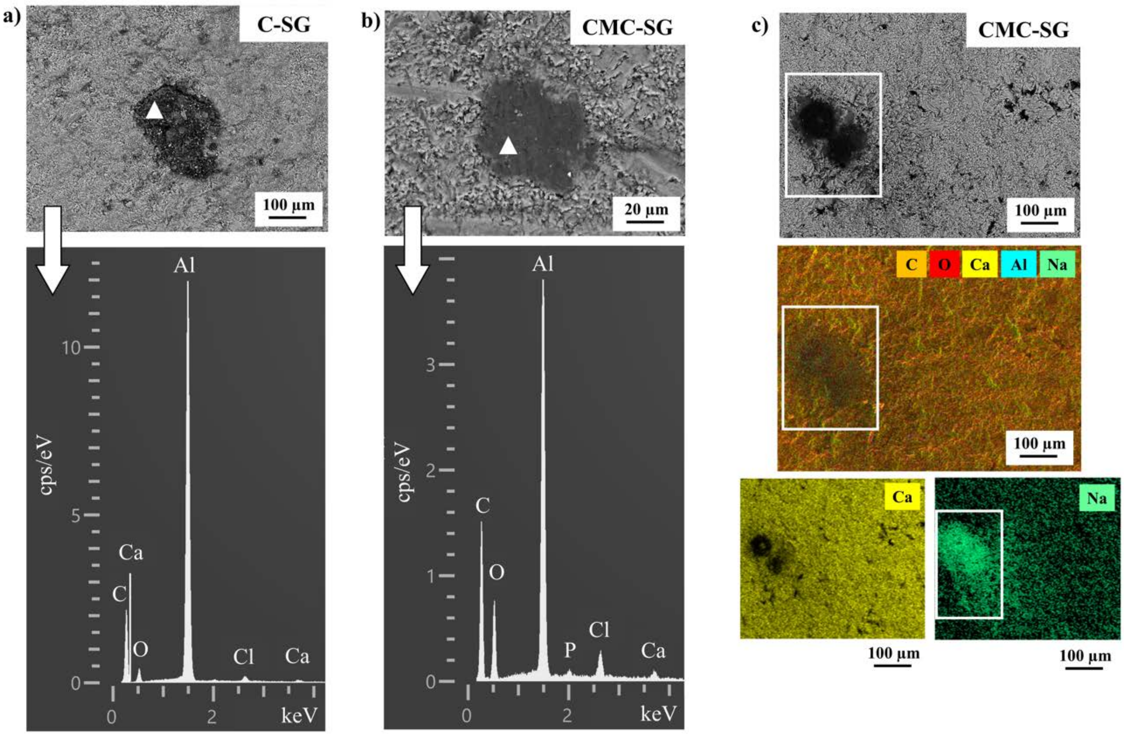

Figure 5. SEM micrographs and EDS analysis spectra of a) C-SG sample and b) CMC-SG sample. c) SEM micrograph and elemental compositional x-ray maps of CMC-SG. See Table 1 for explanation of the identification codes.

The other two gels that appeared to be effective on the removal of SG were Carbopol Ultrez 21® (C) and carboxymethylcellulose (CMC), as previously reported since ΔE_{ab}*< 5 CIELAB units. However, Al-rich deposits were identified on both samples. Even though they were generally small in size, deposits of around 100 µm were also observed (marked with a white triangle in Fig. 5a and b respectively). Between them, C-SG showed less Al-rich deposits compared to CMC-SG. Additionally, through an elemental compositional x-ray map of CMC-SG, sodium (Na)-rich residues were observed on the surface (Fig. 5c). These deposits were considerably extensive in size (around 100-150 µm), related to the CMC gel as it is a sodium-carboxymethylcellulose, as specified by the supplier.

The only poultice-based procedure that was relatively effective, regardless of the paint, was the one carried out with bentonite (BT), as seen in Figure 2 and Figure 3. Nevertheless, many small Al-rich particles were identified in BT-SG sample (Fig. 6a) related to SG. In addition, the study of the cross-sections by optical microscopy allowed the identification of an extensive layer of SG on the surface (Fig. 6b). When carrying out elemental compositional x-ray maps of BT-SG it was possible to identify deposits rich in Al and Si within the stone fissures, marked with a white square in Figure 6c. This is surely related to montmorillonite $((Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$ or other clay residues that constitute the BT-poultice. Lastly, a similar situation was observed in BT-BG, though deposits were larger in size (~100 µm) (Fig. 6d), as well as in extension, as observed by optical microscopy (marked with a white rectangle in Fig. 6e).

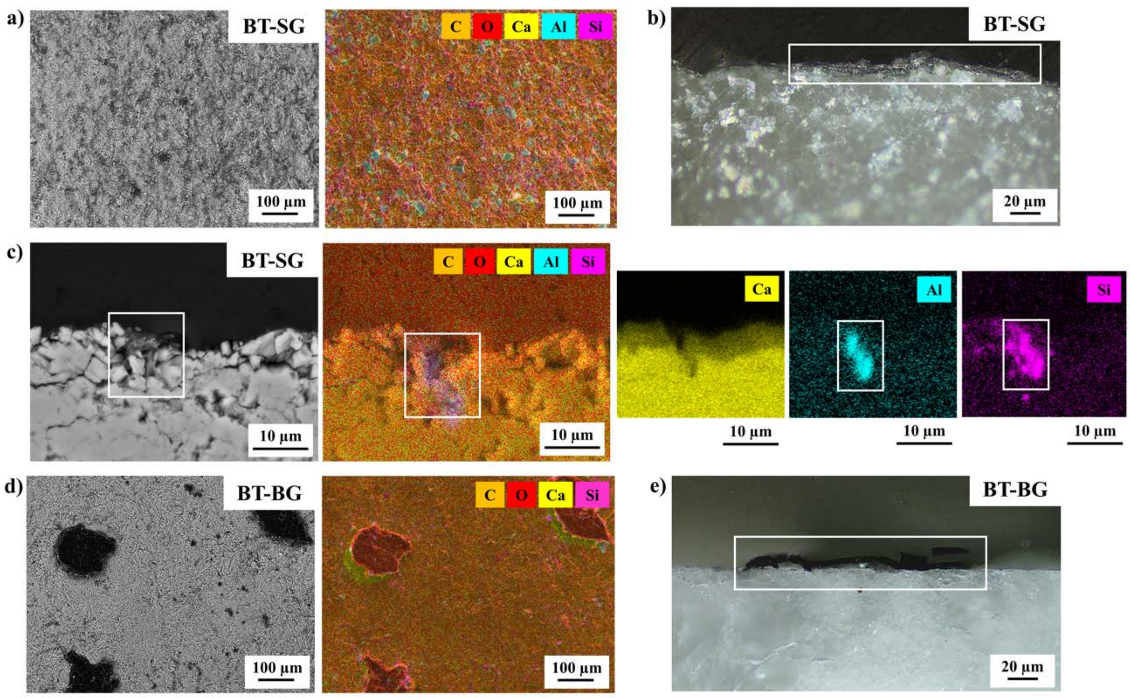

Figure 6. SEM micrographs and elemental compositional x-ray maps of a) BT-SG sample; b) micrograph by optical microscopy of BT-SG sample; c) SEM micrograph and elemental compositional x-ray maps of BT-SG cross-section; d) SEM micrographs and elemental compositional x-ray maps of BT-BG sample; and e) micrograph by optical microscopy of BT-BG sample. See Table 1 for explanation of the identification codes.

As is well known, one of the most reported harmful effects on stones treated by chemical methods is the chemical contamination (POZO-ANTONIO *et al.,* 2016; GOMES *et al.,* 2017; JELAVIC *et al.,* 2018). In this regard, Na- and chloride(Cl)-rich particles (marked with a white square in Fig. 7a and b) were encountered, regardless of the cleaning procedure used (gels or poultices).

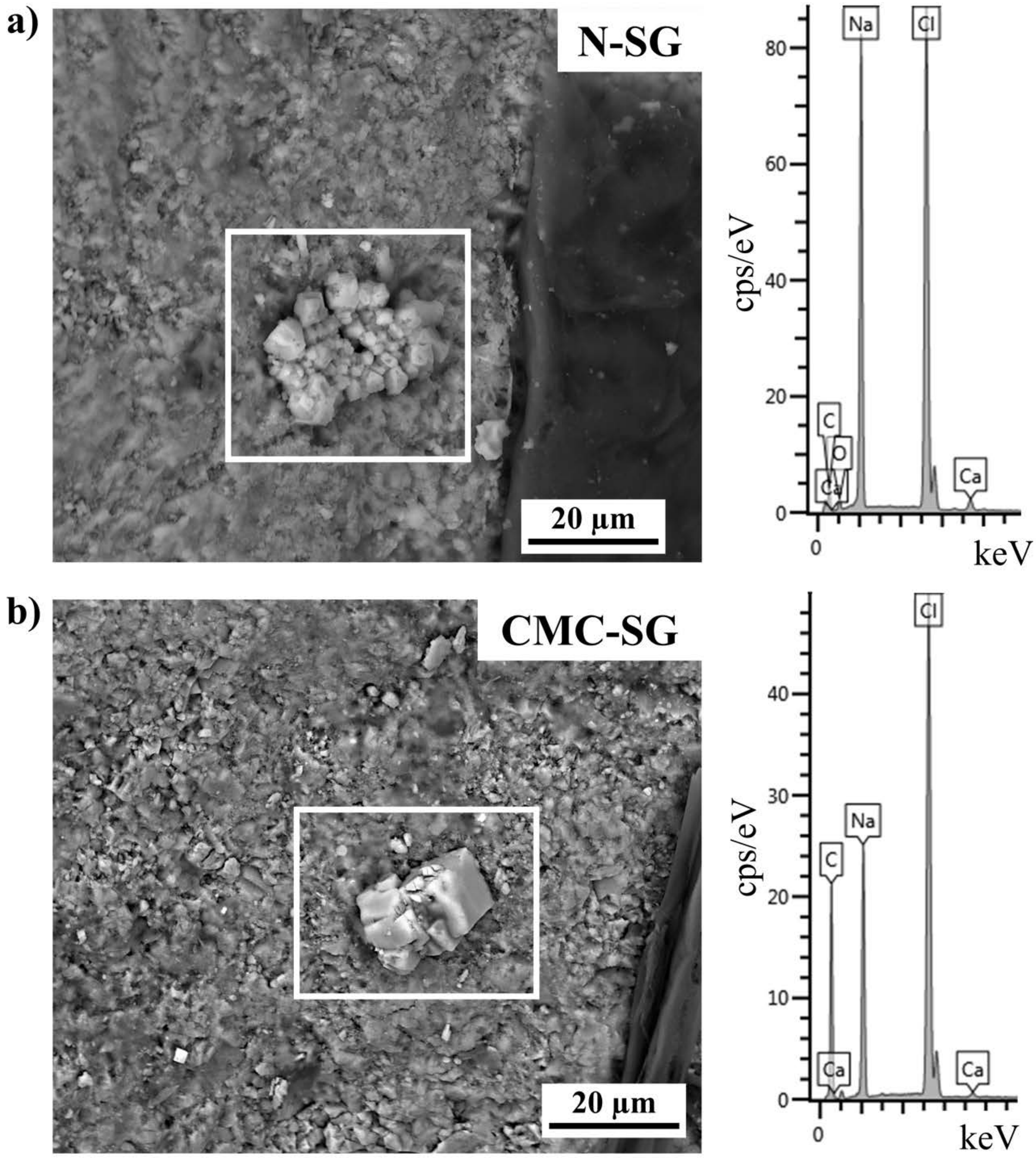

Figure 7. SEM micrograph of samples a) N-SG sample and b) CMC-SG sample. See Table 1 for explanation of the identification codes.

Overall, it was observed that the substrate, the paint chemical composition, and the different cleaning vehicle (gel or poultice) influenced the effectiveness in the removal of the graffiti paints.

- Firstly, it was clear that the *Lioz* limestone properties, specifically the fissural system, influenced the depth to which the solvent gels and poultices acted in dissolving the graffiti. Residue traces of either Si or C were identified on the surface when using gels (N, C and CMC), and clay-based residues composed of Si and Al when using BT within fissures of the limestone. In the latter, paint remains cannot be ruled out either as SG is also composed of Al. The interposition of Japanese paper between the cleaning vehicle (gel or poultice) and the stone surface could avoid residues.

- Secondly, the different chemical nature of the paints was also a determining factor since BG was not as easy to remove as SG. The unsuccessful removal of BG has been previously reported (SAMOLIK *et al*., 2015), though this study showed that with Nevek® it was possible to remove most of the black paint. As gels act like a sponge, extracting the paint by soaking up the solubilized material, longer application times were probably necessary to ensure a better removal of BG.
- Thirdly, the different cleaning procedures tested was also determining. Even though paint-related residues, regardless of size and extension over the surface, were present in all samples, Nevek® was the most effective gelling agent amongst them. When mixed with the cleaning solution, this solvent gel removed the vast majority of silver and black graffiti paint (residues below 5 µm). Carbopol ultrez 21® and carboxymethylcellulose followed, where SG residues were larger in size (around 100 µm) and more widespread. However, C and CMC were not able to remove the BG.
- Lastly, regarding the solvent solution used (n-butyl acetate and cyclohexane, 80/20 % v/v), it appeared to be rather effective, as it worked by weakening the adhesion between the paint and the limestone. These organic solvents act by breaking down the alkyd-based paints by a saponification process (UQUHART, 1999). Still, based on the Threshold Limit Value-Time-Weighted Average (TLV-TWA), these solvents were highly toxic as they showed 50 and 100 ppm respectively. The TLV-TWA represents the maximum amount of solvent (in ppm) that a worker can safely be exposed to on a daily basis (8h/day, 40h/week) without suffering adverse effects. Thus, the search for lower toxicity and environmentally friendly solvents should be future researched.

4. CONCLUSIONS

In this research, the effectiveness of different cleaning vehicles (gels: Nevek®, Carbopol ultrez 21® and carboxymethylcellulose; and poultices: cellulose pulp, bentonite and sepiolite) has been evaluated, using as cleaning agent a mixture of n-butyl acetate and cyclohexane (80/20 %, v/v) to extract two graffiti of different composition (a silver alkyd-based colour with polyethylene and an inorganic aluminium-rich pigment, and a black alkyd-based paint with an organic pigment). The use of gels in the removal of silver and black graffiti were confirmed as the most effective by means of stereomicroscopy and colour spectrophotometry. However, only Nevek® accomplished a relatively satisfactory removal of the black graffiti paint as the other gels (Carbopol ultrez 21® and carboxymethylcellulose) only partially removed it, leaving considerable large deposits on the surface. Among poultices, only bentonite allowed to achieve a slightly effective removal, whilst cellulose pulp and sepiolite were not at all effective. Overall, it must be taken into consideration that no procedure was 100% effective, as larger or smaller deposits were always encountered on the surface, though some unnoticeable to the naked eye as they were below 5 µm in Nevek®-cleaned samples.

Regarding side effects, Na- and Cl-rich particles were found on the cleaned surface and, regardless of the cleaning vehicle used (gels or poultices), all procedures left residues on the surface, mainly in those where bentonite was used as vehicle. In all, i) further research must be conducted focusing on the possible effect that residues coming from the cleaning vehicles may have on the durability of the stone, ii) as well as in searching for more environmentally friendly solvents (i.e. green solvents) which prevent chemical contamination and are less harmful to conservators.

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