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# A Study on the Suitability of Mechanical Soft-Abrasive Blasting Methods to Extract Graffiti Paints on Ornamental Stones

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**Abstract:** Mechanical methods to extract undesired graffiti paints on ornamental stones are efficient cleaning methods from an economical point of view. However, effort on the optimization of mechanical cleaning procedures to avoid any damage to the substrate is required for large areas. In this study, two ornamental stones with different composition and texture, and which are commonly used in Spain and Portugal were selected: Granite Vilachán and Limestone *Lioz*. Moreover, the most common surface finishes were selected-disc-cutting and bush-hammering to simulate the stones found in buildings. Two graffiti spray paints were selected: Blue Ultramarine and Silver Chrome. As cleaning methods, three soft-abrasive blasting procedures: Hydrogommage (mixture of air–water–micro grained silicon abrasive), IBIX (mixture of air–micro grained silicon abrasive), and dry-ice procedure (carbon dioxide ice pellets), were tested at pressure below 0.4 MPa. The methodology for evaluating the effectiveness and harmfulness of each cleaning method was based on stereomicroscopy, scanning electron microscopy, color spectrophotometry, and confocal microscopy. As result, IBIX achieved the highest level of graffiti paint extraction although this method increased the surface roughness. Conversely, cleaning based on dry-ice projection did not achieve a satisfactory extraction of the graffiti, mainly of the blue paint. Dry-ice blasting can induce acid environments and IBIX causes dust emission during the projection. Hydrogommage was the most efficient cleaning method amongst the tested procedures, because it induced the lowest roughness change and although the graffiti extraction was not complete, it achieved the highest removal level. Therefore, the most satisfactory cleaning method was that achieving a satisfactory extraction level, minimal modifications of the surface roughness, an economic suitability, an environmental integration, and lower human health risks.

**Keywords:** graffiti; granite; limestone; finish; mechanical cleaning; ornamental stone

## 1. Introduction

Stone materials from buildings and monuments are commonly vandalized by uncontrolled graffiti application, leading to serious threats to the aesthetic of the building and to the conservation of historic and artistic pieces [1–3]. Therefore, graffiti cleaning is an important issue that requires funding by governments and municipalities. Additionally, an increase of knowledge about graffiti extraction and damages induced on the substrates is required. In most of the cases, graffiti are not shortly removed after their execution due to insufficient human and financial resources. Therefore, graffiti paints are usually cleaned after a long exposure allowing graffiti interaction with the environment and the stone

substrate. Indeed, Gomes et al. [4] analyzed the influence of SO<sub>2</sub> exposure of alkyd and polyethylene graffiti paints and verified the occurrence of physical and chemical alterations on the graffiti paints and the stone–paint coating interactions. Therefore, it is advisable to carry out conscientious cleaning operations soon after their execution, which is an economical way.

Traditionally, graffiti cleaning has been performed by professionals using chemical and mechanical procedures. Several scientific researches have published aiming at the evaluation of cleaning effectiveness achieved by different methods and the damage induced by the procedure on the stone [2,5–7], to establish the conditions that correspond to a satisfactory extraction level and the lowest damage to the substrate. Chemical cleaning is usually performed with solvents and paint strippers capable of dissolving and extracting the graffiti paints [7]. As a major disadvantage, they induce the penetration of the dissolved graffiti and the cleaner-liquid through fissures and/or cracks [8,9]. Mechanical cleaning methods do not have this disadvantage, since they are based on the removal of the paint through an abrasive process of the surfaces. However, due to their abrasive effect, damages on the stone surfaces can also occur. The first developments in mechanical cleaning methods come from the old procedures based on sand blasting, characterized by its high aggressiveness due to the high pressure (>50 MPa) and the high hardness of the abrasive. However, different mechanical alternatives have been used in recent years to reduce the damage induced on the stone, for example, evaluating different abrasives of variable grain sizes and/or reducing the pressure used [6,7,9–13]. Nevertheless, Careddu and Akkoyun [12] reported satisfactory cleaning results to extract red graffiti paint on non-polished Carrara marble using only a plain water-jet at high pressures (150–200 MPa). The authors pointed out the necessity to carry out these kinds of studies using other stones and different surface finishes, such as disc-cutting surfaces, characterized by their lower roughness compared to non-polished surfaces, such as bush-hammering and flaming. Moreover, Ortiz et al. [9] reported that low pressures of plain water-jet technology (<1 MPa) did not achieve satisfactory cleaning results to clean black, red, and green spray graffiti based on acrylic copolymers on marble, whilst specific chemical cleaners-Elephant Snot<sup>®</sup> with the subsequent application of Graffipaste<sup>®</sup> allowed them to reach a successful extraction [9].

Different abrasives working at low pressures have also been tested, such as sponge-like urethane polymer involving the abrasives calcium carbonate (Sponge-Jet<sup>TM</sup>), spherical calcium carbonate particles (Exastrip<sup>TM</sup>), pure silicon abrasives (Hydrogommage), etc. [11,12]. Moreover, dry-ice blasting cleaning has been applied [14], but extensive scientific results were not reported. Dry-ice cleaning is a blasting method based on the projection of CO<sub>2</sub> dry-ice pellets at pressures below 1 MPa, and at a temperature of −40 °C. This cleaning method involves thermal and mechanical removal mechanisms. Given the sublimation of CO<sub>2</sub>, no additional solid residues of the blasting medium remained except the removed contaminant (i.e., the graffiti paint).

Therefore, cleaning effectiveness achieved by the different chemical and/or mechanical methods depend on: (1) Graffiti paint composition, (2) the mineralogy and texture of the stone, and (3) the surface finish of the stone to be cleaned [11–13]. Firstly, acrylic and alkyd-based paints Montana Gold from Motip-Dupli<sup>®</sup> on limestone and sandstone were successfully removed with a mixture of ethanol, acetone, and xylene, whilst it was not successful to remove alkyd black paint Montana Black [15]. Moreover, in granite, the Silver Chrome from Hardcore Montana Mtn<sup>®</sup> required an addition application of a stripper, whilst for Ultramarine blue, Devil red, and Graphite black, the application of organic solvents and caustic removers was sufficient [13].

Secondly, mineralogical and physical properties of the stone were decisive parameters in choosing the type of cleaning procedure to be applied. Alkydic graffiti paints were successfully extracted with dry soft-abrasive blasting methods and an alkaline cleaner; however, the same methods did not achieve satisfactory results in removing the same graffiti paints on marble [11]. However, on granite, cleaning effectiveness using chemical products and the soft-abrasive blasting method Hydrogommage was similar in two texturally different granites from north-west (NW) Spain [13]. Despite the surface

cleaning being similar, the penetration of the graffiti paints through the fissures (influenced by the texture) hinders the evaluation of the cleaning.

Thirdly, considering the surface finish, rougher surfaces may be more complicated to clean since the graffiti penetrates the fissures and covers the valleys of the surface. Therefore, additional time is required to remove the graffiti compared to smoother surfaces.

Regarding the damage created by traditional cleaning procedures, Carvalhão and Dionisio [11] did not find contamination related to cleaning product remains and/or sub-products, but they reported grain extraction and dissolution of grain boundaries on carbonate stones. Pozo-Antonio et al. [13] reported a fine-grained powder rich in S and Fe, after the chemical cleaning of graffiti paints on granite; S is absent on graffiti and granite. The mechanical methods induced morphological changes, such as an increase in the average roughness ( $R_a$ ) around 10  $\mu\text{m}$  [11,13]. The plain water-jet system with high pressure technology induced modification of the topography, mainly on saw-surfaces [15,16]. Following these authors, it is necessary to optimize the cleaning conditions (i.e., pressure, jet inclination angle, stand-off distance, traverse speed, and distance between successive passes) to reduce the damage.

Mechanical methods show advantages over chemical procedures given: (1) the absence of chemical contamination due to the penetration of the liquid-cleaners and/or the dissolved paint, (2) they do not induce dissolution of the minerals grains, and (3) they can be applied faster [11]. Therefore, mechanical methods would be a suitable alternative for cleaning delicate stone surfaces in a rapid manner and safeguarding the substrate if lower pressures and softer abrasives are used.

The aim of this paper is to evaluate the cleaning effectiveness and harmfulness of three soft-blasting methods to remove two spray graffiti paints commonly used in vandalism, i.e., blue and silver paints. Two texturally and mineralogically different stones were selected: Spanish granite-*Vilachán* and Portuguese limestone-*Lioz*, because they are some of the most common ornamental stones in these countries. Two of the most commonly used stone finishes were used, i.e., disc-cutting and bush-hammering. The evaluation of the cleaning efficiency and harmfulness was performed by the detection of graffiti remains on the surface, the color change evaluation, and the average surface roughness changes. Moreover, from a practical point of view, additional estimation of costs, time, and risks, both for the environment and for human beings are discussed. The increased knowledge of graffiti cleaning procedures will provide valuable insight and greater understanding of graffiti paint cleaning methods on stone objects and is a tool for the decision-making community.

## 2. Materials and Methods

### 2.1. Stones and Graffiti Paints

Two stones with different mineralogy and texture were selected on the basis of their widespread use in Spain and Portugal as ornamental stones. As a granite, a commercially known as *Vilachán* from NW Spain was chosen. It is a fine-grained panalotriomorphic heterogranular granite [17], composed of quartz (47%), potassium feldspar (10%), plagioclase (15%), biotite (7%), muscovite (18%), and different mineral accessories (3%). The grain sizes of the different minerals range between 2 mm and 0.3 mm. Average open porosity (accessibility to water following Reference [18]) was 2.82%.

As a limestone, a Portuguese Cretacic limestone-commercially known as *Lioz* was chosen. It is a coarse-grained cream microcrystalline biogenic limestone [19,20]. It shows characteristic stylolites, which are highlighted when the rock is polished. This stone presents a very low value of open porosity (average water accessible porosity following Reference [18]) was 0.3%.

Regarding both stones, two of the most common finishes used in buildings were used in this study, being disc-cutting and bush-hammering. Two different spray graffiti paints were selected from Hardcore Montana Mtn<sup>®</sup> (Montana Colors, Barcelona, Spain), being Blue Ultramarine (RAL code: R-5002) and Silver Chrome (R-7001), which were previously characterized in Reference [21].

Concerning each stone and finish, three parallelepiped slabs of 0.5 m  $\times$  0.5 m  $\times$  0.02 m were obtained. First, keeping one slab of each stone and surface finish without painting, the remaining

slabs were painted with the corresponding graffiti (blue and silver). The paint was uniformly sprayed for 30 s at an average angle of 45° and from a distance of 20 cm from the slab, always at laboratory conditions (18 ± 5 °C and 75 ± 5% RH). After 24 h, a second application of graffiti spray was performed. Afterwards, the painted slabs were left to air-dry at laboratory conditions for one month. After this time, the painted and unpainted slabs were cut into four pieces of 0.1 m × 0.1 m × 0.02 m. Three pieces to test the three cleaning procedures and one test sample were left as references. Table 1 depicts the samples used and their nomenclature.

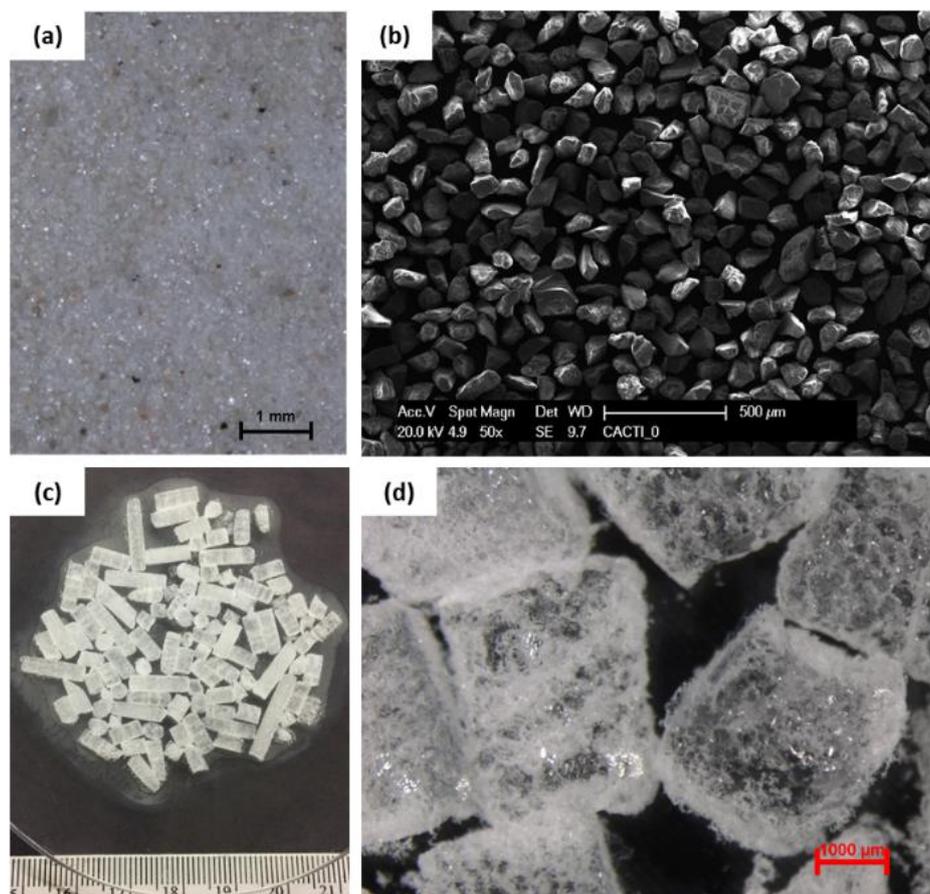
**Table 1.** Samples used in the experiment. Samples' nomenclature is shown. (n.a.: not applied.)

Stone	Finish	Graffiti	Cleaning Procedure	Samples' Nomenclature	
Vilachán granite (V)	Disc-cutting (D)	Without	n.a.	VD	
			Hydrogommage (H)	VDH	
			IBIX (I)	VDI	
	Disc-cutting (D)	Blue (B)	n.a.	VDB	
			Hydrogommage (H)	VDBH	
			IBIX (I)	VDBI	
	Disc-cutting (D)	Blue (B)	Dry-ice (D)	VDBD	
			Silver (S)	n.a.	VDS
				Hydrogommage (H)	VDSH
	IBIX (I)	VDSI			
	Disc-cutting (D)	Silver (S)	Dry-ice (D)	VSD	
			Without	n.a.	VU
Hydrogommage (H)				VUH	
IBIX (I)	VUI				
Disc-cutting (D)	Without	Dry-ice (D)	VUD		
		Blue (B)	n.a.	VUB	
			Hydrogommage (H)	VUBH	
Disc-cutting (D)	Blue (B)		IBIX (I)	VUBI	
		Blue (B)	Dry-ice (D)	VUBD	
			Silver (S)	n.a.	VUS
Hydrogommage (H)	VUSH				
IBIX (I)	VUSI				
Disc-cutting (D)	Silver (S)	Dry-ice (D)	VUSD		
		Without	n.a.	LD	
			Hydrogommage (H)	LDH	
Disc-cutting (D)	Without		IBIX (I)	LDI	
		Disc-cutting (D)	Blue (B)	Dry-ice (D)	LDD
				n.a.	LDB
Hydrogommage (H)	LDBH				
Disc-cutting (D)	Blue (B)	IBIX (I)	LDBI		
		Blue (B)	Dry-ice (D)	LDBD	
			Silver (S)	n.a.	LDS
Hydrogommage (H)	LDSH				
IBIX (I)	LDSI				
Disc-cutting (D)	Silver (S)	Dry-ice (D)	LDSD		
		Without	n.a.	LU	
			Hydrogommage (H)	LUH	
Disc-cutting (D)	Without		IBIX (I)	LUI	
		Disc-cutting (D)	Blue (B)	Dry-ice (D)	LUD
				n.a.	LUB
Hydrogommage (H)	LUBH				
Disc-cutting (D)	Blue (B)	IBIX (I)	LUBI		
		Blue (B)	Dry-ice (D)	LUBD	
			Silver (S)	n.a.	LUS
Hydrogommage (H)	LUSH				
IBIX (I)	LUSI				
Disc-cutting (D)	Silver (S)	Dry-ice (D)	LUSD		

## 2.2. Cleaning Methods

Three commercial mechanical soft-abrasive blasting media, specifically developed to clean sensitive and delicate surfaces, were used in this study. These were Hydrogommage<sup>®</sup> [22] (hereinafter designated Hydro), IBIX<sup>®</sup> [22] (hereinafter designated IBIX), and Dry Ice Blasting 7/40 Adv<sup>®</sup> from KÄRCHER S.A [23] (hereinafter designated DIB).

- Hydro is based on the circular projection of a mixture of air–water–micro grained silicon abrasive at low-pressure (0.2 MPa). The abrasive, as confirmed by stereomicroscopy (Nikon Eclipse 800, Tokyo, Japan) and Scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM-EDS, Philips XL30, Amsterdam, The Netherlands), has a grain size up to 200  $\mu\text{m}$  and the particles composed of silicon showed sharp edges (Figure 1a,b).
- IBIX is a dry-soft cleaning procedure using the circular projection of air and micro grained abrasive. The same abrasive used with Hydro was applied with this procedure (Figure 1a,b). A working pressure of 0.4 MPa was used.
- DIB used carbon dioxide ice pellets ( $-78\text{ }^{\circ}\text{C}$ ) projected with a pressure of 0.4 MPa. The dry-ice particles (Figure 1c,d), examined by means of stereomicroscopy (Nikon Eclipse 800), allowed to us verify that they were composed of slightly sharp-edged particles with a 2 mm-diameter up to 2 cm long.



**Figure 1.** Abrasives used in the Hydrogommage and IBIX (a,b) and dry-ice cleaning (c,d) systems.

## 2.3. Analytical Techniques to Evaluate the Global Cleaning

The evaluation of cleaning effectiveness of the different cleaning procedures was assessed in terms of graffiti extraction level and induced damages (either physical or chemical) to the stone.

Firstly, the cleaned surfaces were observed with stereomicroscopy (Nikon Eclipse 800). A qualitative evaluation of the graffiti cleaning effectiveness was appraised, according to an evaluation scale based on the Classification Numbers (CN) adapted from Reference [24]. This scale considered the amount of paint remaining on the surface and in fissures of the substrate after cleaning. The scale ranges from CN 0 (complete removal of the paint) to CN 5 (no cleaning effect)

SEM-EDS (Philips XL30) in both secondary electrons (SE) and backscattered electrons (BSE) modes was applied to detect: (1) the location and morphology of the graffiti remains; and (2) the surfaces modifications, such as grain extraction and fissures generation. To detect the impact of cleaning methods on the substrata, SEM-EDS was applied to the stone surfaces without paint graffiti. Optimum conditions of observation were obtained at an accelerating potential of 15–20 kV, a working distance of 9–11 mm, and specimen current of ~60 mA.

The cleaning effectiveness was also evaluated using color measurements in CIELAB and CIELCH color spaces [25], with a Minolta CM-700d spectrophotometer (Osaka, Japan). The measurements were made in specular component included (SCI) mode, for a spot diameter of 8 mm, using illuminant D65 at an observer angle of 10°. Following Reference [26], twenty random measurements were taken per sample to statically define the color of polymineral surfaces such as granite.

The color coordinates measured were the three parameters:  $L^*$ , lightness, which varies from 0-absolute black- to 100-absolute white-;  $a^*$ , which is related to color changes in the red–green range ( $+a^*$ : red and  $-a^*$ : green); and  $b^*$ , which is associated with changes in the yellow–blue range ( $+b^*$ : yellow and  $-b^*$ : blue). Considering  $a^*$  and  $b^*$ , the chroma or intensity of the color ( $C_{ab}^*$ ) was computed:  $C_{ab}^* = (a^{*2} + b^{*2})^{1/2}$  and the hue ( $h_{ab}$ ) was calculated as follows:  $h_{ab} = \tan^{-1}(b^*/a^*)$ , as described in Reference [25].

$L^*$  and  $C_{ab}^*$  of the original surfaces and those after cleaning were represented to detect the recovery of the original color after cleaning. Moreover,  $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$ ,  $\Delta C_{ab}^*$ , and  $\Delta H^*$  were obtained as the differences of the final values after cleaning and the reference ones, i.e., the original color of the stones prior to the application of the spray paints [25]. The global color change  $\Delta E_{ab}^*$  was also calculated, following Reference [27] and considering the color of the unpainted surface as the reference:

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

Surface roughness of unpainted and painted samples before and after the cleanings were obtained by means of confocal microscopy (PLu 2300 Sensofar® optical imaging profiler, Co Meath, Ireland), to characterize the impact of the cleaning methods on the surfaces. Images of each surface were collected using an EPI 10X-N objective, a depth resolution of 2 µm, and a lateral resolution of 1 nm. Data were processed with Gwyddion 2.47 software to calculate the arithmetic average height  $R_a$  [28,29]. The average measurement of five measurements of 4 mm × 4 mm areas were performed per sample.

Following Reference [30] a damage threshold was established. It was calculated by adding to  $R_a$  values of the references, their respective standard deviations.  $R_a$  values of the cleaned surfaces were compared with this threshold.

Finally, to obtain additional information on environmental and human safety risk, the pH of the dry-ice pellets was determined. For this, 100 g of carbon dioxide ice pellets were mixed with 200 mL distilled, ultrapure, and tap water at 25 °C to measure their pH (Crison PH25, Barcelona, Spain).

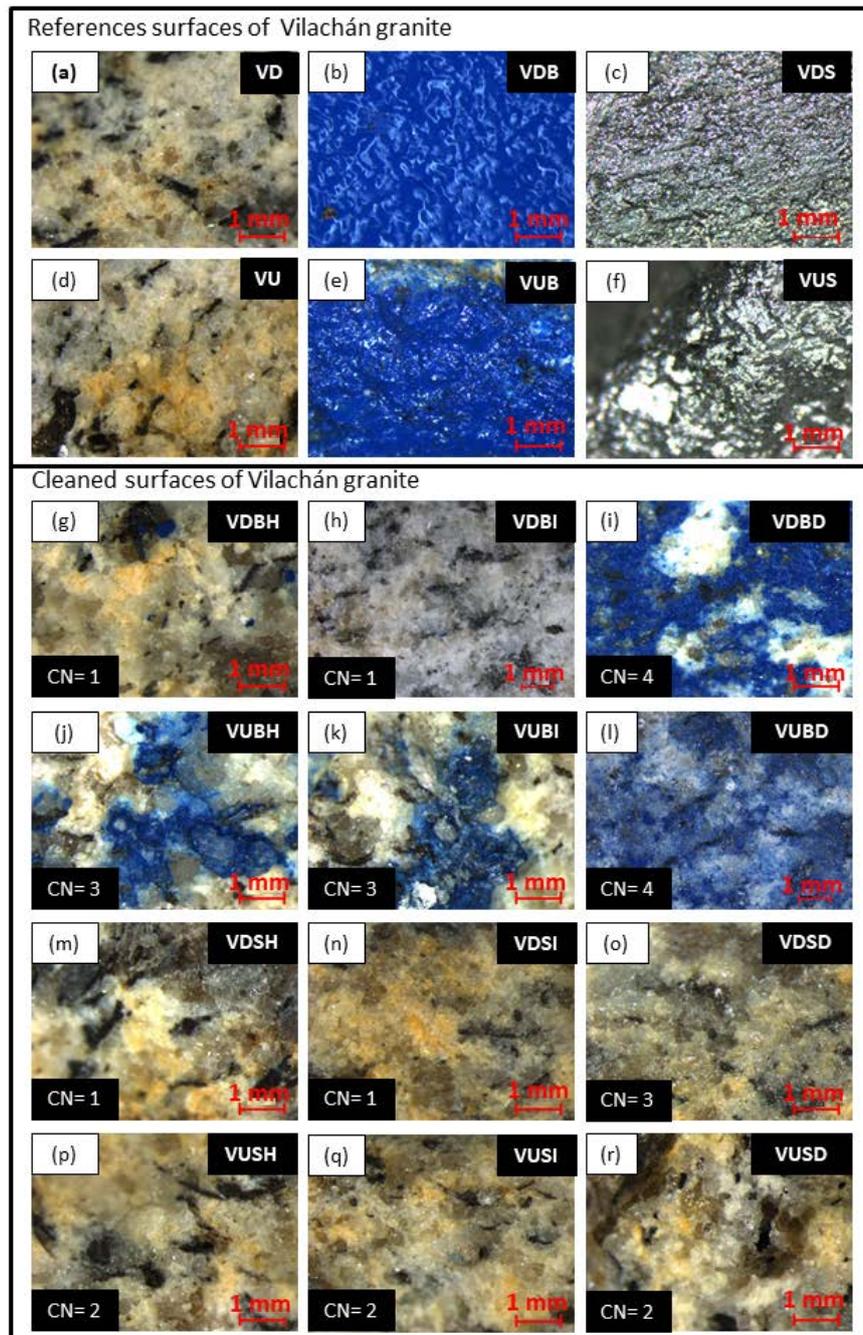
### 3. Results and Discussion

#### 3.1. Cleaning Efficiency

##### 3.1.1. Graffiti Extraction

Based on stereomicroscopy observations, a qualitative evaluation of the cleaning effectiveness of each cleaning procedure was performed according to the classification numbers (CN) [24]. These values are shown in Figures 2 and 3 and are associated with the representative micrographs by

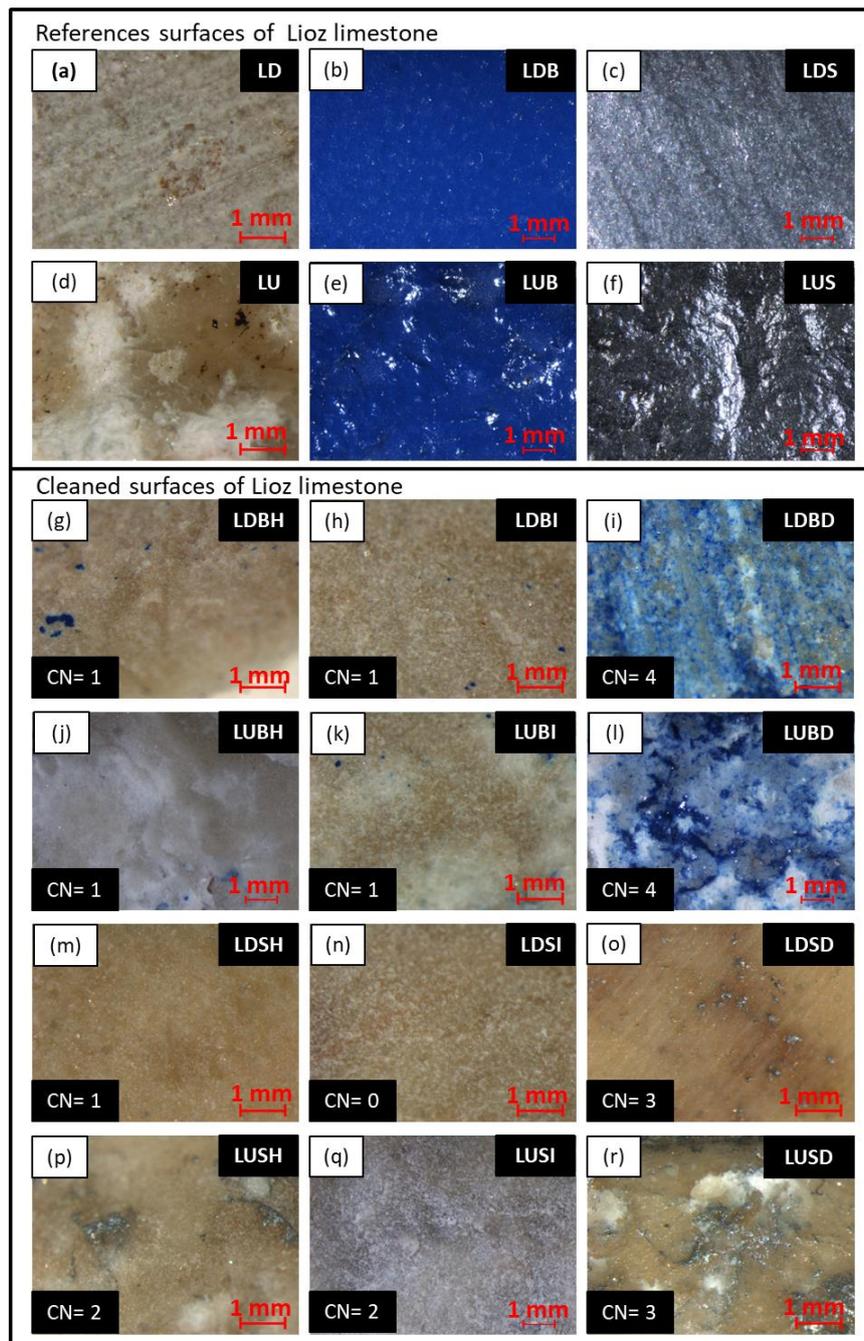
stereomicroscope of the cleaned surfaces. Macroscopically, it appeared that cleaning procedures applied on both stones showed similar CN, except for the cleaned surfaces of blue graffiti on bush hammering finish. Indeed, granite showed higher values than limestone, suggesting worse cleaning (Figures 2g–r and 3g–r). Regardless of the stone, both graffiti paints were better cleaned with Hydro and IBIX than with DIB on both the different surface finishes. On the former surfaces, small graffiti deposits were found on the surfaces, whilst on the DIB cleaned surfaces, mainly on the blue graffiti, extensive areas covered by graffiti were kept after the cleaning (CN = 4). With *DIB*, blue graffiti paint was more difficult to extract than the silver paint.



**Figure 2.** (a–f): References surfaces of Vilachán granite (disc-cutting and bush-hammering surfaces, unpainted and painted with blue and silver graffiti paints). (g–r): Granite surfaces cleaned of blue (g–l) and silver (m–r) graffiti paints with Hydrogommage, IBIX, and dry-ice blasting. See Table 1 for samples' nomenclature.

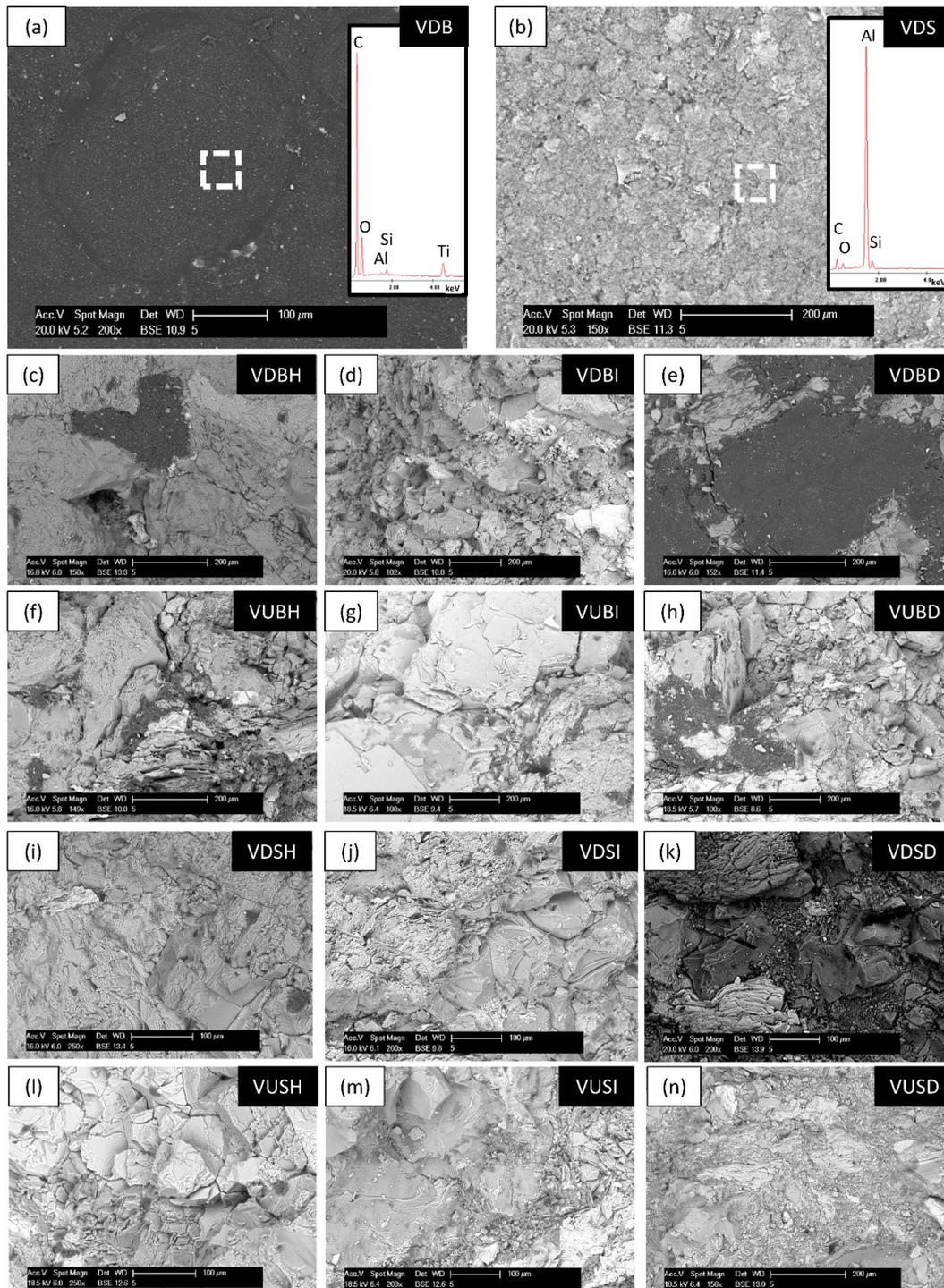
On the blue graffiti bush-hammering granite surfaces cleaned with Hydro and IBIX, paint remains were found within the fissures (Figure 2j,k). This probably corresponded to the ghosting reported in Reference [8] for porous stones, which hinders the evaluation of the cleaning as expressed by Rivas et al. [31] in their research based on the laser cleaning of graffiti paints on granites with different grain sizes.

It is important to highlight that only the cleaning of silver graffiti on limestone with IBIX allowed the complete removal of the graffiti paints (Figure 3n, CN = 0). After cleaning with the other methods, paint remains were still detected to some extent.



**Figure 3.** (a–f): References surfaces of *Lioz* limestone (disc-cutting and bush-hammering surfaces, unpainted and painted with blue and silver graffiti paints). (g–r): Limestone surfaces cleaned of blue (g–l) and silver (m–r) graffiti paints with Hydrogommage, IBIX, and dry-ice blasting. See Table 1 for samples' nomenclature.

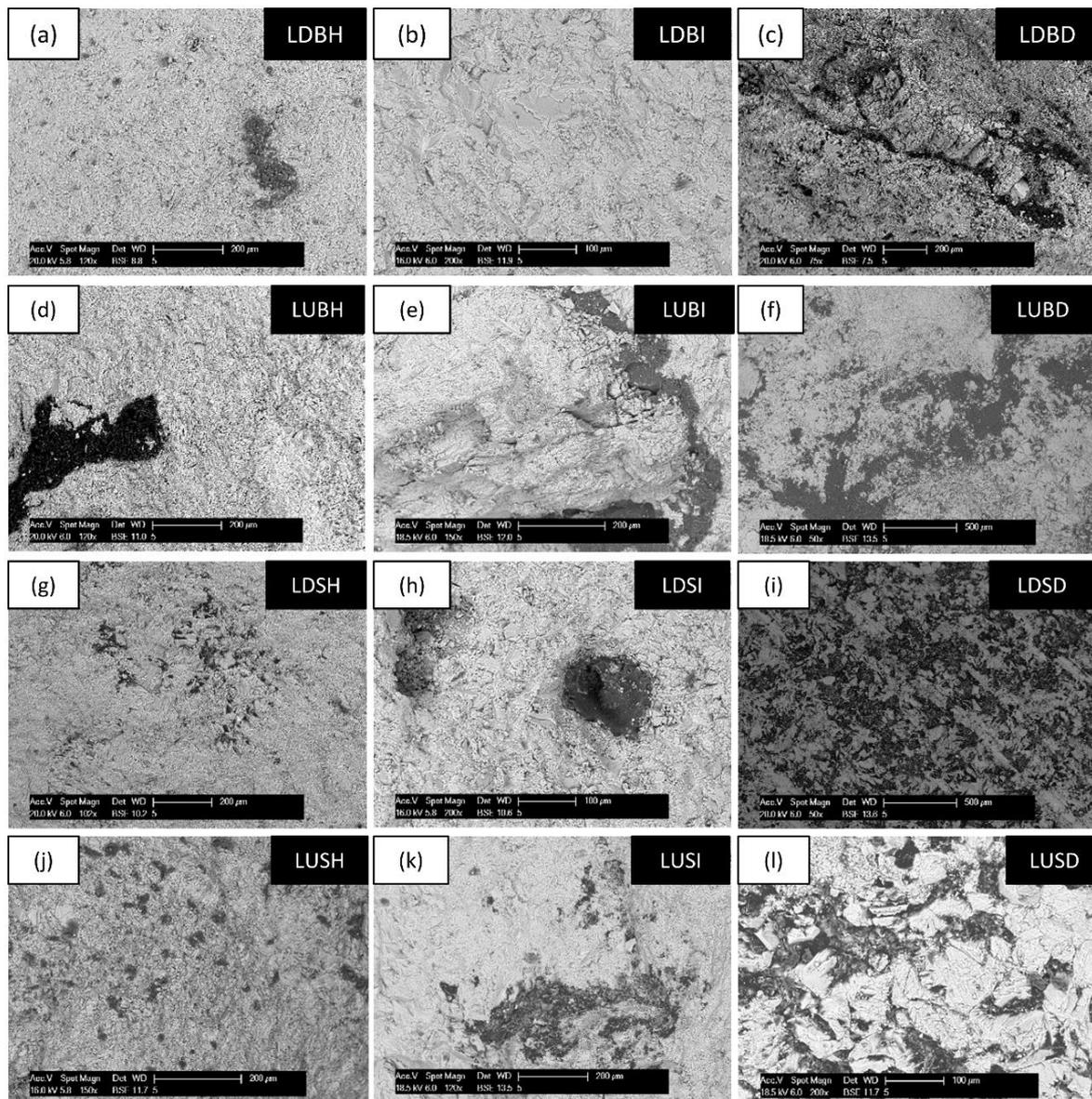
Under SEM, the appearance of each graffiti paint was different. Blue graffiti showed a cracked surface, whilst the silver graffiti surface was composed of an overlap of different size planar particles (Figure 4a,b). The composition of both paints was also different. The identification of blue graffiti paint remains was performed through the detection of low contrast C-rich deposits with Ti, Si, and Al (Figure 4a), and silver graffiti was identified through high contrast particles of Al embedded in C-deposits (Figure 4b). This composition was already identified in previous works [20,31,32].



**Figure 4.** SEM micrographs of the granite surfaces painted with blue and silver graffiti paints (a,b), and granite surfaces cleaned of blue and silver graffiti paints with Hydrogommage, IBIX, and dry-ice blasting. See Table 1 for samples' nomenclature.

Under SEM and with stereomicroscopy observations, a higher amount of graffiti remains were found on surfaces cleaned with DIB, mainly in the case of blue graffiti (Figure 4-granite and Figure 5-limestone).

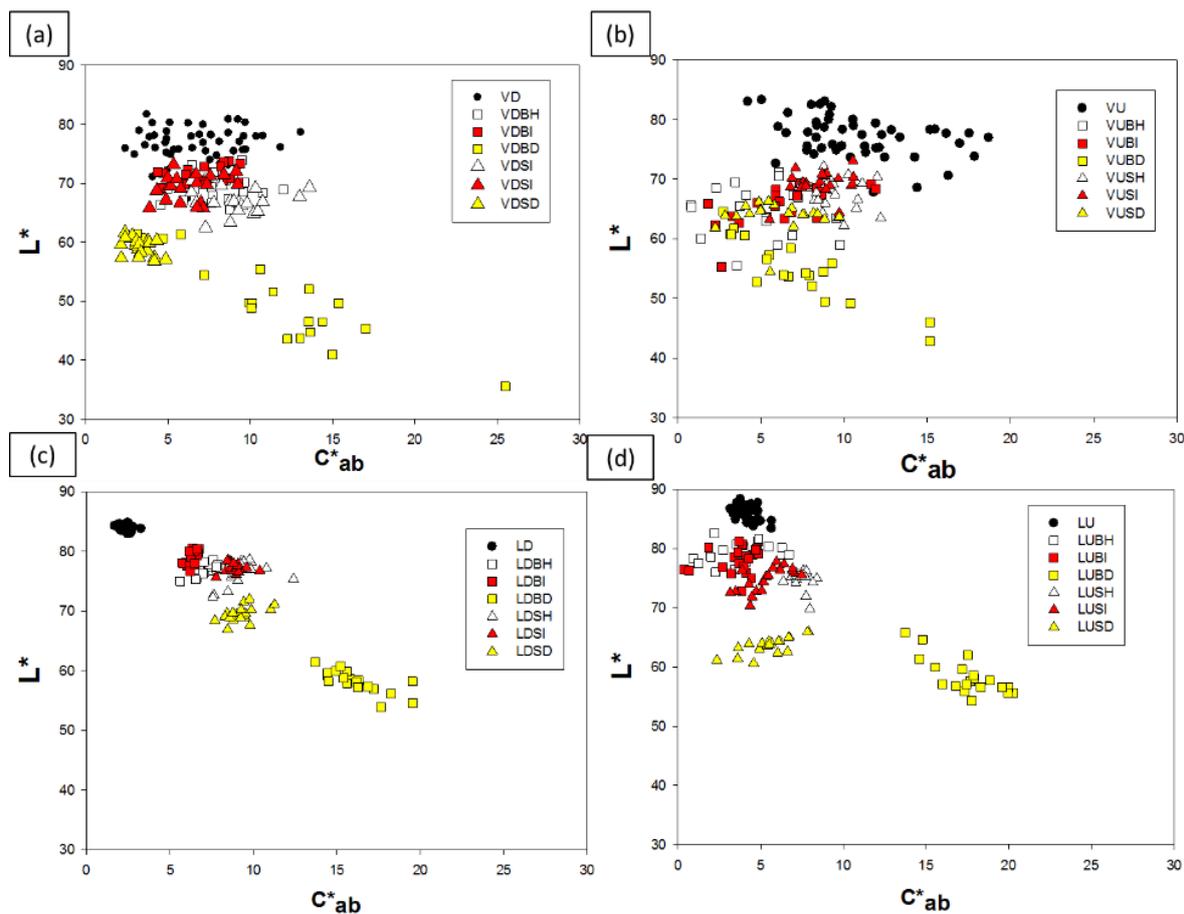
In the case of blue painted samples, the method that achieved the highest extraction in both stones was IBIX (Figures 4d,g and 5b,e). Note that, after this cleaning method, the disc-cutting granite surfaces (Figure 4d) became rougher, suggesting grains extraction. This result can be explained because IBIX does not use water and it is applied with a higher pressure than Hydro (Hydro: 0.2 MPa, IBIX: 0.4 MPa). On the granite, the remains of blue graffiti were found as spots on the surfaces (Figure 4c,e) or filling fissures (Figure 4f,h), whilst on the limestone, the remains were found as spots but also inside the stylolites (Figure 5d,e). This last situation was also reported by Carvalh o and Dionisio [11] after the application of soft-abrasive blasting methods (Sponge-Jet<sup>®</sup> and ExaStrip<sup>®</sup>), and a KOH chemical cleaning to extract blue, carmine red, and black-alkyd spray paints on *Lioz*.



**Figure 5.** SEM micrographs of the limestone surfaces cleaned of blue and silver graffiti paints with Hydrogommage, IBIX, and dry-ice blasting. See Table 1 for samples' nomenclature.

Regarding silver graffiti cleaning, Hydro and IBIX showed similar results though better than those obtained with DIB (Figures 4 and 5). On the limestone cleaned surfaces of silver graffiti, SEM allowed the identification of C-rich remains that were unnoticed with stereomicroscopy (Figure 5j,k). On the granite, silver remains rich in Al were detected in the filling fissures and cracks (Figure 4), whilst on the limestone, as similarly reported for the blue graffiti cleaning, the remains were found as deposits on the surfaces and within the stylolites.

Considering color spectrophotometry results,  $L^*$  and  $C^*_{ab}$  scatter plots (Figure 6) allowed us to determine that for both stones, the surfaces cleaned with DIB showed the most different color to the references, where the points of the point-clouds measured on the surfaces were further away from those corresponding to the original surface, especially after the cleaning of blue graffiti. Moreover, although the recovery of the original color after the cleaning was not obtained for any of the two stones, Hydro and IBIX seemed to better recover the original color of the surfaces (Figure 6). Conversely, in the macroscopically characterization performed using stereomicroscopy, color spectrophotometry ( $L^*$  and  $C^*_{ab}$  scatter plots in Figure 6) suggested that the cleaning obtained for the cleaning methods was different for both finishes depending on the stone. On the disc-cutting surfaces, Hydro and IBIX achieved surfaces with a color more similar to the original surfaces than that cleaned with DIB (Figure 6a), whilst on the bush-hammering surface, the color of the cleaned surfaces using the three methods was quite similar (Figure 6b), suggesting lower extraction levels by Hydro and IBIX on the bush-hammering granite. Conversely, on the limestone,  $L^*$  and  $C^*_{ab}$  scatter plots (Figure 6c,d) did not show a difference on the extraction obtained on both finishes.



**Figure 6.**  $L^*$ – $C^*_{ab}$  graphs representing color data for the original surfaces and after cleaning of the blue and silver graffiti paints on Vilachán granite (a,b) and Lioz limestone (c,d). (a,c): Cleaned disc-cutting surfaces. (b,d): Cleaned bush-hammering surfaces. See Table 1 for samples’ nomenclature and for interpretation of the references to color in this figure legend.

Following Table 2,  $L^*$  was the colorimetric parameter more affected by the cleanings, as reported in previous researches [9,11]. Indeed, the decrease of their original values were detected, suggesting a darkening of the original color of the stone. Ortiz et al. [9] also detected decreases of  $L^*$  (higher  $\Delta L^*$  than in the current research) when pressurized water (<1 MPa) was applied on dolomitic white marble to extract black, red, and green acrylic paints. Conversely, Carvalho and Dionisio [11] reported  $L^*$  increases. In the current research,  $L^*$  decreases were higher on surfaces cleaned with DIB, with values higher than 13 CIELAB units. Stereomicroscopy and SEM allowed the identification of extensive graffiti remains, mainly of blue graffiti, on the surfaces cleaned with DIB.

**Table 2.** Colorimetric differences ( $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$ ,  $\Delta C^*_{ab}$  and  $\Delta H^*$ ) and global color change ( $\Delta E^*_{ab}$ ) of the surfaces cleaned with the different procedures. Differences were computed relative to the color of the reference stone; therefore, the lower the  $\Delta E^*_{ab}$ , the more similar to the reference surface the cleaned surface. See Table 1 for samples' nomenclature.

Vilachán Granite							
Conditions	Samples' Nomenclature	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta C^*_{ab}$	$\Delta H^*$	$\Delta E^*_{ab}$
Disc-cutting surface with blue graffiti							
Hydrogommage	VDBH	-7.35	1.05	1.16	0.70	0.66	7.52
IBIX	VDBI	-5.31	-0.45	0.33	0.30	0.42	5.34
Dry-ice	VDBD	-26.49	-4.14	-17.27	4.66	17.32	31.89
Bush hammering surface with blue graffiti							
Hydrogommage	VUBH	-12.39	-1.45	-5.65	-5.63	2.26	13.69
IBIX	VUBH	-11.48	-1.30	-4.31	-4.38	1.29	12.33
Dry-ice	VUBD	-22.13	-4.58	-16.59	-3.60	16.88	28.03
Disc-cutting surface with silver graffiti							
Hydrogommage	VDSH	-9.82	-0.07	2.33	2.32	0.17	10.09
IBIX	VDSI	-7.32	-0.27	-0.45	-0.47	0.18	7.34
Dry-ice	VSDS	-17.35	-0.67	-3.49	-3.52	0.49	17.71
Bush-hammering surface with silver graffiti							
Hydrogommage	VUSH	-9.73	-0.53	-1.03	-1.10	0.30	9.80
IBIX	VUSI	-7.82	-0.66	-2.13	-2.20	0.31	8.14
Dry-ice	VUSD	-13.27	-1.20	-4.71	-4.79	0.92	14.13
Lioz limestone							
Conditions	Samples' Nomenclature	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta C^*_{ab}$	$\Delta H^*$	$\Delta E^*_{ab}$
Disc-cutting surface with blue graffiti							
Hydrogommage	LDBH	-6.66	1.63	4.58	4.86	0.19	8.25
IBIX	LDBI	-4.73	1.04	3.85	3.96	0.35	6.19
Dry-ice	LDBD	-25.56	-7.11	-17.10	13.75	12.43	31.57
Bush hammering surface with blue graffiti							
Hydrogommage	LUBH	-6.52	0.08	-0.34	-0.29	0.02	6.53
IBIX	LUBH	-8.03	0.17	-0.69	-0.61	-0.11	8.06
Dry-ice	LUBD	-27.59	-5.70	-20.82	13.31	17.01	35.04
Disc-cutting surface with silver graffiti							
Hydrogommage	LDSH	-7.36	1.47	6.84	6.97	0.68	10.16
IBIX	LDSI	-6.44	1.15	6.42	6.47	0.78	9.17
Dry-ice	LSDS	-14.33	1.05	6.83	6.85	0.91	15.91
Bush-hammering surface with silver graffiti							
Hydrogommage	LUSH	-11.09	1.50	2.99	3.29	-0.71	11.58
IBIX	LUSI	-11.19	1.02	0.97	1.21	-0.81	11.28
Dry-ice	LUSD	-22.39	0.81	1.16	1.32	-0.52	22.44

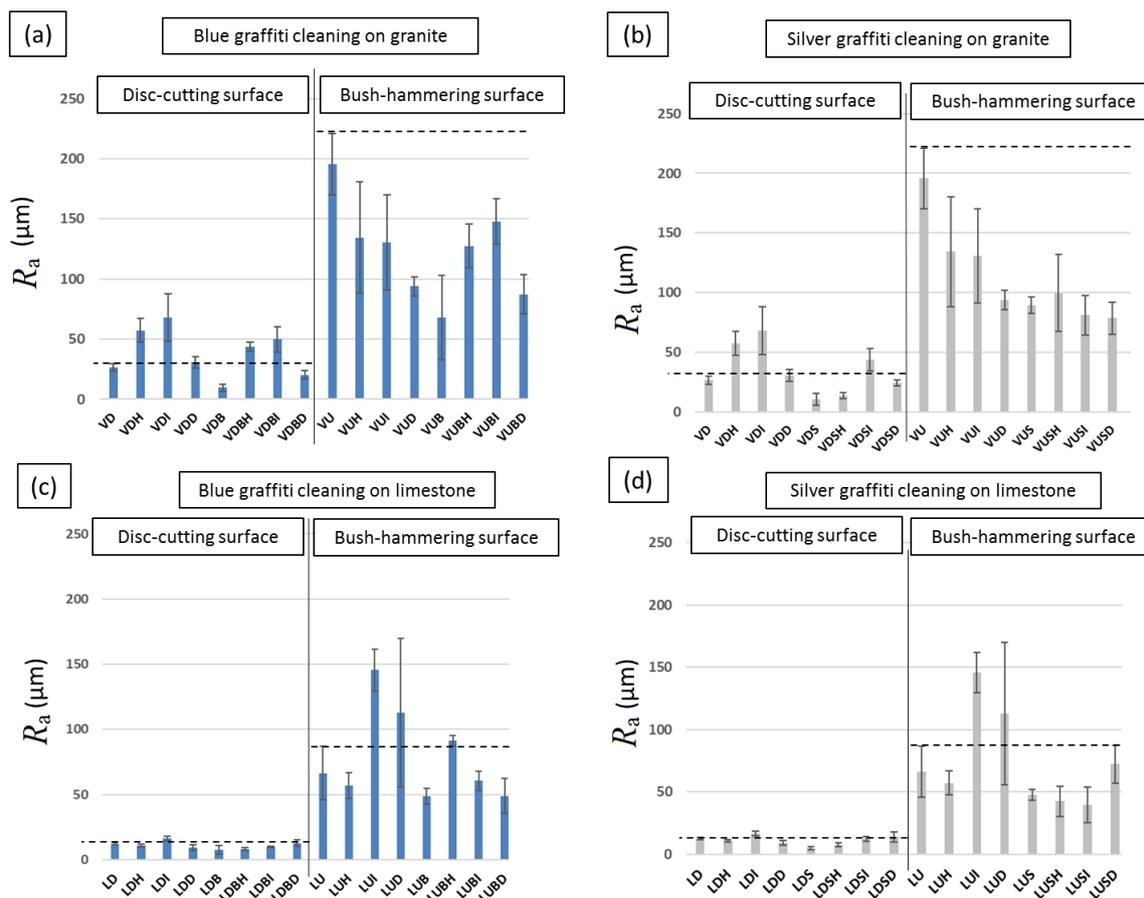
Moreover, the highest  $\Delta C^*_{ab}$  was also obtained on the surfaces cleaned with DIB, compared to those obtained by the other two cleaning methods (Table 2). This suggested the presence of more paint remains, except on the blue graffiti cleaned bush-hammering granitic surface (VUBD), silver paint cleaned disc-cutting limestone surface (LDS), and silver graffiti paint cleaned bush-hammering limestone surface (LUSD). In the granite,  $C^*_{ab}$  showed decreases with the exception of the disc-cutting surfaces with blue graffiti (VDBH, VDBI, VDBD) and the disc-cutting surface with silver graffiti cleaned by Hydro (VDSH), whilst in the limestone,  $C^*_{ab}$  showed increases except for the bush hammering surface with blue graffiti cleaned by Hydro (LUBH) and the bush hammering surface with blue graffiti cleaned by IBIX (LUBI). As this value was dependent on the  $a^*$  and  $b^*$  polar coordinates,  $a^*$  showed decreases for the granite and increases for the limestone. The surfaces were more green than red for the granite and more red than green for the limestone, suggesting a higher amount of graffiti remains on the former surfaces. The coordinate  $b^*$  which is the parameter related directly with the blue tone, showed that all the surfaces, except VDBH, VDBI, and VDSH, showed a more blueish color than the original surfaces because  $\Delta b^*$  showed negative values. For the limestone,  $b^*$  experienced increases due to the higher level of extraction, with the exception of the surfaces with both finishes cleaned of blue graffiti using DIB (LDBD and LUBD), which showed negative  $\Delta b^*$  (related to the visible blue graffiti remains on the surface). Moreover, the blue graffiti bush-hammering surfaces cleaned with Hydro (LUBH) and IBIX (LUBI) showed slight decreases of  $b^*$ .

Under stereomicroscopy it was observed that the disc-cutting limestone surfaces cleaned of silver paint with Hydro and IBIX showed satisfactory results (Figure 3m,n). However, SEM allowed us to detect C-rich deposits unnoticed by means of stereomicroscopy (Figure 5j,k), which can modify the color of the surface, increasing the variation of the color parameters.

$L^*$  and  $C^*_{ab}$  scatter plots agreed with  $\Delta E^*_{ab}$  values (Table 2); Hydro and IBIX achieved the highest graffiti extraction because the cleaned surfaces with these procedures showed the lowest  $\Delta E^*_{ab}$ . Conversely, surfaces cleaned with DIB showed the highest  $\Delta E^*_{ab}$  for all the samples. All the cleaned surfaces showed  $\Delta E^*_{ab}$  higher than 5 CIELAB units, which is the maximum value recommended for a conservation intervention in a porous stone [24]. This is expected noting that as found by stereomicroscopy, none of the cleaning methods allowed the total extraction of the paint. Then,  $\Delta E^*_{ab}$  were also higher than 3 CIELAB units (threshold for the human eye perception of a visible change [33]). In general, IBIX cleaned surfaces showed the lowest  $\Delta E^*_{ab}$  with the exception on the blue graffiti bush-hammering limestone, where Hydro induced the lowest  $\Delta E^*_{ab}$ . However,  $\Delta E^*_{ab}$  on the surfaces cleaned with both methods was similar; difference between  $\Delta E^*_{ab}$  (Hydrogommage) and  $\Delta E^*_{ab}$  (IBIX) was lower than 3 CIELAB units. Hence, cleaning level differences obtained between Hydro and IBIX would not be noticed by an unexperienced observer [33].

### 3.1.2. Damages Exerted to the Stones

Regarding the evaluation of the harmful effects due to the application of mechanical procedures, the average roughness ( $R_a$ ) is a useful parameter to determine the method that induced (or not) mineral grains extraction. Figure 7 (see Table S1 in Supplementary data) shows the average and standard deviation values of  $R_a$  obtained for different situations, i.e., (1) reference stones without paint application; (2) painted surfaces; (3) unpainted surfaces subjected to the cleaning procedures; and (4) surfaces cleaned of graffiti with the three soft-blasting mechanical methods.  $R_a$  difference between both finishes was higher in the granite than in the limestone. In fact,  $R_a$  of  $26.5 \pm 3.18 \mu\text{m}$  and  $195.6 \pm 25.66 \mu\text{m}$ , were obtained for disc-cutting and bush-hammering granite, respectively. For limestone,  $R_a$  values of  $12.20 \pm 0.90 \mu\text{m}$  and  $66.34 \pm 20.51 \mu\text{m}$  were obtained for disc-cutting and bush-hammering finishes, respectively. These roughness differences are also qualitatively observed in Figure 8a,d,g,j.



**Figure 7.**  $R_a$  (arithmetic average of the roughness,  $\mu\text{m}$ ) of the cleaned surfaces of blue and silver graffiti with Hydrogommage, IBIX, and dry-ice blasting. The roughness of the reference surface, the painted surface, and the surface after the application of the mechanical methods on unpainted surfaces are also provided. (a): Granite with blue graffiti. (b): Granite with silver graffiti. (c): Limestone with blue graffiti. (d): Limestone with silver graffiti. Standard deviation values are also shown. See Table 1 for samples' nomenclature.

Adapting the methodology proposed in Reference [30],  $R_a$  thresholds were computed for the references samples and are shown as dotted lines in Figure 7 where: (1) disc-cutting granite (VD): 29.68  $\mu\text{m}$ ; (2) bush-hammering granite (VU): 221.26  $\mu\text{m}$ ; (3) disc-cutting limestone (LD): 13.01  $\mu\text{m}$ ; and (4) bush-hammering limestone (LU): 86.85  $\mu\text{m}$ .

After graffiti paint application,  $R_a$  values were remarkably lower than those registered on the reference stones, i.e., the paint created a film that filled the valleys of the stone, smoothing the surfaces. Nevertheless,  $R_a$  reduction was higher on the granite than on limestone, specifically: (i) In the case of the disc-cutting surfaces, for the granite, there was a ~64% and ~60% reduction of  $R_a$  after blue and silver graffiti, respectively, and for the limestone, a ~37% and ~60% reduction of  $R_a$  after blue and silver graffiti, respectively; and (ii) in the case of bush-hammering surfaces, for the granite, a ~67% and ~54% reduction of  $R_a$  after blue and silver graffiti, respectively, and for the limestone a 26% and ~28% reduction of  $R_a$  after blue and silver graffiti, respectively.

After the application of different tested mechanical procedures on unpainted surfaces, different tendencies regarding the stone were found, compared to the original surfaces (Figure 7):

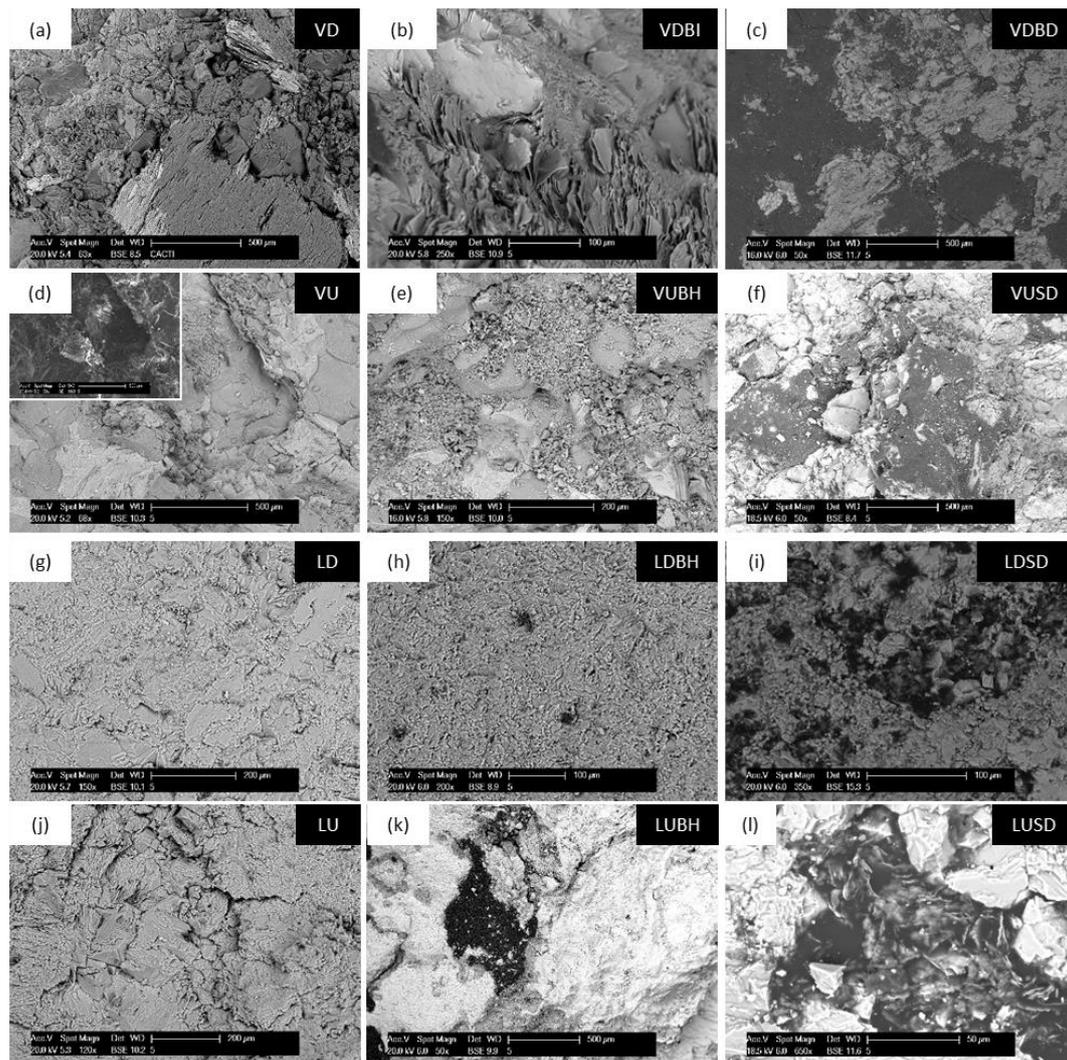
- In case of the disc-cutting granite (Figure 7a,b),  $R_a$  increased after Hydro and IBIX, whilst  $R_a$  remained after DIB. In the bush-hammering granite, the three methods provoked a reduction in  $R_a$ . However,  $R_a$  differences before and after cleaning were statistically different only after IBIX and DIB.

- In the limestone (Figure 7c,d), original  $R_a$  data were already much lower than in the granite. In the disc-cutting samples, none of the three methods modified the original  $R_a$ . Conversely, on bush hammering samples, DIB and Hydro provoked  $R_a$  variations but these were not statistically significant. Finally, IBIX exerted a high roughness increase; in this case it was statistically different to the original  $R_a$ .

After the cleaning of painted samples, different tendencies were found depending on the stone and the surface finish:

- For the disc-cutting granite (Figure 7a,b), regardless of the graffiti applied, IBIX induced a  $R_a$  increase assigned to the grain extraction and the aperture of the exfoliation planes of biotite and K-feldspar grains (Figure 8b in comparison with Figure 8a). DIB induced a  $R_a$  reduction compared to the original unpainted surfaces, due to the extensive remains of paints found on the surface originally painted with blue graffiti (Figure 8c), and cracks filled with silver graffiti (Figure 4k). Careddu and Akkoyun [12] reported that roughness of the cleaned surfaces can be close to that of the reference surface due to the filling of original pores with paint which made it smooth, because painted surfaces have small roughness. Although Hydro applied to extract blue graffiti promoted an  $R_a$  increase,  $R_a$  was reduced when Hydro was applied to remove silver graffiti. Despite a few graffiti remains on both surfaces found by stereomicroscopy and SEM (CN = 1 for both paints-Figure 2g,m), the different trend can be due to the fact that blue graffiti is more noticeable under the naked eye than silver paint, leading to an overcleaning of the blue painted surfaces, increasing the surface roughness.
- For the bush-hammering granite (Figure 7a,b), regardless of the graffiti applied, the three cleaning methods induced  $R_a$  decreases that were statistically different to the original  $R_a$ . These  $R_a$  decreases may be due to (i) the abrading effect of the methods, as was reported for the application of the methods on the unpainted surfaces; and (ii) the existence of graffiti remains filling cracks and fissures (Figures 5d–f and 8f).
- For the disc-cutting limestone (Figure 7c,d),  $R_a$  variations after the cleanings were less intense than on granite.  $R_a$  of the surfaces cleaned with Hydro and IBIX showed low decreases of  $R_a$  (up to 1  $\mu\text{m}$ ), compared to the original surface (Table S1 in Supplementary data). DIB induced a similar  $R_a$  to the original surface, but higher standard deviation values than the original surface (LD:  $12.20 \pm 0.90 \mu\text{m}$ , LDBD:  $12.66 \pm 2.56 \mu\text{m}$ ; LDSD:  $13.80 \pm 4.06 \mu\text{m}$ ), suggesting a more inhomogeneous cleaning.
- For the bush-hammering limestone (Figure 7c,d), regardless of the graffiti, the three methods induced surfaces with lower  $R_a$  that was statistically similar to that of the reference, except for the cleaning of blue graffiti with Hydro (LUBH-Figure 7c), which showed a significant increase in roughness. In the former cases (LUBI, LUBD, LUSH, LUSI, and LUBD), since some graffiti remains were found on the surfaces,  $R_a$  decreases can be related to these filled fissures (Figure 8l). In case of the surface cleaned of blue graffiti with Hydro, despite graffiti remains being found on the surface as deposits (Figure 8k),  $R_a$  increase was due to the grains extraction because of overcleaning.

Therefore, considering all the results reported above, the method that achieved the highest extraction of graffiti paints was IBIX; however, the roughness increases due to the absence of water did not allow us to recommend this method on valuable surfaces. Then, as DIB did not show satisfactory results on graffiti extraction, Hydro was the method that may obtain a satisfactory extraction of both graffiti paints with minimal damages to both stones.



**Figure 8.** SEM micrographs of some cleaned surfaces of granite and limestone. See Table 1 for samples' nomenclature.

### 3.2. Operation Time, Costs Estimation, Environmental Impact, and Health Risks

From a practical point a view, it is necessary to know not only the method that achieves the highest efficiency, but also the required time, intervention costs, and the health risks for the environment and for human beings. Table 3 shows an estimation of the time and costs of the different methods tested. Regarding, the operation time required, IBIX requires more time because the flat jet nozzle is narrower than those used in Hydro and DIB. For this reason, IBIX price per square meter is much higher than that for Hydro. DIB is faster than IBIX, but the higher price of the dry-ice pellets compared to the silicon abrasive increases the total cost of the method; the price per square meter of DIB was similar to IBIX.

Regarding environmental risks, the three methods required the collection of the abrasives used. In case of DIB, it has to be applied outdoors because the sublimation of the CO<sub>2</sub> pellets may produce an oxygen deficiency. Moreover, in outdoor conditions, this method should be applied in dry conditions, because when dry-ice pellets are dissolved in water (pH of distilled water:  $6.49 \pm 0.07$ ; pH of ultrapure water:  $6.40 \pm 0.06$ ; pH of tap water:  $6.93 \pm 0.08$ ), it was observed there was a decrease of pH values of approx. 2 units:

- pH (carbon dioxide ice pellets in distilled water):  $4.31 \pm 0.05$
- pH (carbon dioxide ice pellets in ultrapure water):  $4.36 \pm 0.11$
- pH (carbon dioxide ice pellets in tap water):  $4.87 \pm 0.03$

The presence of water can induce acid solutions that would damage the integrity of the rock, mainly carbonate stones. During DIB application, the pH decrease can also be dangerous to workers. Therefore, personal protective equipment (PPE) must be used. Considering the health risks, IBIX needs special attention regarding the dust emission during the projection because converse to Hydro, IBIX is a dry method. Therefore, it is necessary to ensure the protection of the operators against inhaling dust particles. Furthermore, eyes and ears must be protected with goggles or face screens and earplugs or earmuffs, respectively.

**Table 3.** Estimation of average costs for the different soft-blasting methods to clean graffiti paints on a wall (10 m<sup>2</sup>).

Parameters	Hydrogommage	IBIX	Dry-Ice Blasting
Working time	4 h	10 h	6 h
Equipment and products	560 €	480 €	800 €
Abrasives	0.16 €/kg	0.16 €/kg	7 €/kg
Labor force	100 €/h	100 €/h	100 €/h
Total costs	960 €	1480 €	1400 €
Costs/m <sup>2</sup>	96 €/m <sup>2</sup>	148 €/m <sup>2</sup>	140 €/m <sup>2</sup>

#### 4. Final Remarks

The behavior of three commercial mechanical soft-abrasive blasting technologies to extract two graffiti paints with different compositions, from calcareous (*Lioz* limestone) and silicate (*Vilachán* granite) stones, was analyzed and discussed. Moreover, we analyzed the influence of the stone surface finish (i.e., disc-cutting and bush-hammering) on the cleaning efficiency.

Cleaning efficiency was assessed in terms of extraction level and damages induced on the surfaces, such as grain extraction and aperture of exfoliation planes. The complete extraction of the paints without damaging the surfaces was not obtained by any of the three methods evaluated. Moreover, required time, intervention costs, and the health risks both for the environment and for the human beings, were also considered in the evaluation of the global effectiveness.

The multi-analytical approach used in the current research allowed us to identify that the extraction level achieved by these three procedures was dependent on the graffiti composition (pigment and binder), the stone, and the surface finish (roughness). Blue graffiti with an alkyd binder was harder to remove than the polyethylene-based silver graffiti, using the three commercial mechanical soft-abrasive blasting technologies tested in this study. The best visual identification of blue graffiti remains compared to silver graffiti, results in application of the procedure for a longer time, causing in some cases damage to the stone. The physical properties of the stone, specifically the fissure system, will influence the penetration of the paint and cleaning effectiveness. The typical fissure system of granite with the three types of fissures will contribute to a greater permanence of the paint after cleaning. The rougher finish induced a higher penetration of the paint through the fissures formed. Dry ice blasting was not a successful method to extract graffiti paints on ornamental stones. Although paint extraction was not complete, Hydrogommage and IBIX achieved similar extraction levels for both graffiti. However, IBIX, as a dry procedure, induced roughness increases because grain extraction was found in both stones and in the granite, and aperture of exfoliation planes was detected.

Considering the environmental impacts and the health risks, dry-ice blasting can induce acid environments and IBIX can cause dust emission during the projection.

Therefore, considering the compromise between the graffiti extraction, the topography modification, the time required, the costs, the environmental impact, and the human health risks, Hydrogommage was the most efficient cleaning method, because it had similar extraction levels to IBIX and lower modifications of surface roughness were detected.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2079-6412/8/10/335/s1>, Table S1:  $R_a \pm DS$  ( $\mu\text{m}$ ) of the cleaned surfaces.

**Author Contributions:** All the co-authors conceived and designed the experiments; J.S.P.-A. and L.L. performed the experiments; J.S.P.-A., L.L., and T.R. analyzed the data; J.S.P.-A., L.L., A.D. and T.R. wrote the paper.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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