

Original article

Black manganese crusts on Galician Romanesque buildings: first analytical data on characterization and cleaning

T. Rivas^{a,*}, L. Espiño^a, S. Pozo-Antonio^a, C. López^b^a CINETEX, GESSMin group, Dpto. de Enxeñaría de Recursos Naturais e Medio Ambiente, Universidade de Vigo, 36310, Vigo, Spain^b Artegal restauraciones S.L. Silleda, 36540, Pontevedra, Spain

ARTICLE INFO

Article history:

Received 4 April 2025

Accepted 8 January 2026

Keywords:

Granite
Cultural heritage
Black crust
Manganese
Cleaning
Laser
Oxalic acid

ABSTRACT

This work presents the results of the characterization of Mn-rich black crusts developed on granite in a Galician Romanesque monastery and the initial experiments aimed at their removal. Once the crusts were characterized from a chemical, mineralogical and micromorphological point of view, several *in situ* cleaning methods were performed: microabrasion, a Nd:YAG laser and chemical cleaning processes (aqua regia, EDTA, oxalic acid, gallic acid and formic acid solutions). An *in situ* analytical methodology based on optical microscopy, colour spectrophotometry, LIBS and Raman spectroscopy was applied to characterize the cleaning effectiveness and the side effects exerted in the granite underneath. Among all the methods, saturated oxalic acid proved to be the most effective, although slight calcium contamination was detected. In contrast, less effective methods such as laser cleaning and microabrasion resulted in textural alterations in the granite.

© 2026 The Author(s). Published by Elsevier Masson SAS. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

1. Introduction

Manganese crusts are typical manifestations of rock weathering in natural environments. The crusts, characterized by a high Mn content, are dark black, sometimes bluish and slightly iridescent, and they occasionally have a metallic sheen. They occur in different types of environments (desert, continental, humid, etc.) and on different types of rock. Their formation is often associated with fungi and with heterotrophic bacteria involved in Fe and Mn geochemical cycles. The phenomenon has been examined in numerous scientific studies [1–5], because of the paleoclimatic implications, among other reasons. In these studies, the origin of the Mn is generally attributed to Mn-rich minerals present in the stone. The pH and Eh of the environment are essential factors involved in mineralization, either in the mobilization phase (dissolution or hydrolysis of the minerals, leading to release of Mn to the aqueous solution) and precipitation (which generates the dark black crusts).

Reports describing the presence of these crusts on stone monuments began to appear a few years ago. However, the phenomenon is not recent; the presence of these crusts has probably gone unremarked because they have been mistaken for biological coloniza-

tion or gypsum-rich black crusts, also common on stone-built heritage [6–10]. Thus, in contrast to the numerous studies involving manganese crusts in natural environments, studies of the presence of these crusts on stone monuments are scarce [11–15]. In these studies, the crusts are described as very thin, hard, rich in Mn and containing other elements such as P, Pb and Zn. In some cases [14], the crusts are described as being randomly distributed on the walls, without any apparent relationship with the monument structure, run-off of water or the intensity or direction of weathering agents (rain, sunlight radiation, wind, etc.); however, in most cases the distribution of the crusts is clearly influenced by the areas of the walls that are affected by the upward movement of water by rising damp. Only one of these studies [12] attributes the origin of the crusts to biogenic processes, and the other four studies attribute the origin to anthropogenic influences. Regarding the source of Mn, two different hypotheses have been proposed: one posits an anthropogenic source (fossil fuel burning, industrial emissions) [13,14] and another proposes the granite used in the buildings as the source [15].

In Galicia (NW Spain), where most of the architectural heritage is built in granite, manganese crusts have recently been detected in numerous religious buildings constructed between the 12th and 16th centuries and built exclusively with granite. In these buildings, the crusts affect ashlar walls independently of the geographical orientation and the structure (they are found on the central nave, lateral walls and/or apse, as well as on vertical walls

* Corresponding author.

E-mail addresses: trivas@uvigo.gal (T. Rivas), espinolopezlucia@gmail.com (L. Espiño), ipozo@uvigo.gal (S. Pozo-Antonio), artegalrestauraciones@gmail.com (C. López).

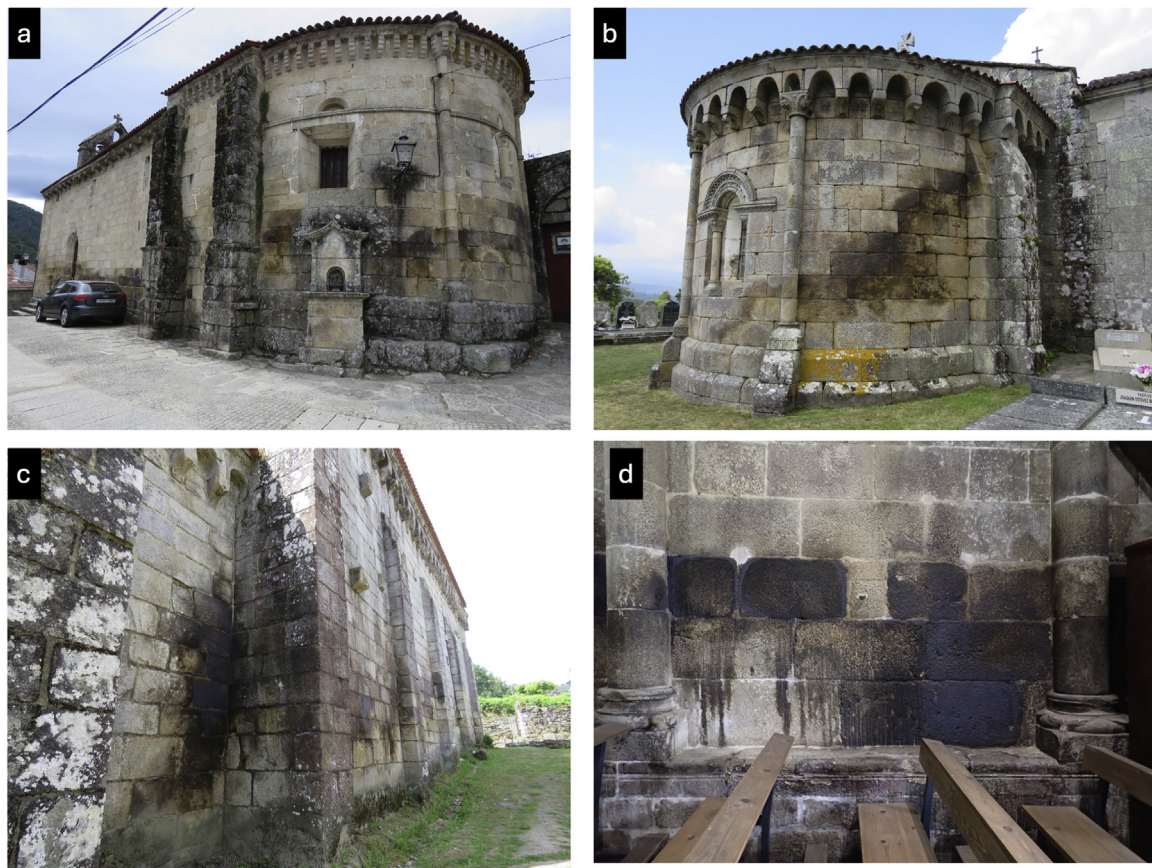


Fig. 1. Appearance of black manganese crusts affecting Romanesque religious buildings in the province of Ourense, Galicia (NW Spain): a) San Salvador de Pazos de Arenteiro; b) San Martiño de Cameixa; c); Santo Tomé de Serantes; d) San Julián de Astureses. Source: authors.

and vaulted ceilings, Fig. 1); they are also occasionally found on sculpted pieces adjacent to affected walls. A particular characteristic of these crusts is that they usually appear on both the interior and exterior parts of the wall; this is an unexpected finding as these buildings usually have double ashlar walls, consisting of two layers of masonry separated by a rubble-filled gap.

The origin of these black crusts on granite surfaces is not known, and studies aimed at clarifying the origin are required as the crusts strongly affect the state of conservation of the buildings owing to the negative visual impact of the dark black colouring of the stone (Fig. 1). Information about the chemical, mineralogical and micromorphological characteristics of the crusts is also limited. Existing studies have only been carried out for diagnostic purposes at the request of companies contracted by public authorities responsible for protecting the cultural heritage in Galicia (Xunta de Galicia). The diagnostic reports (unfortunately not openly available to the scientific community) merely confirm the Mn rich nature of the crusts and rule out the possibility that they are gypsum crusts, which are also common on granite monuments and buildings in the NW Iberian Peninsula; these gypsum crusts, unlike those of manganese, have been studied in detail [16–18] and the mechanism of formation has been established [19].

Establishing effective ways of removing this kind of crusts from cultural heritage buildings and monuments is another important challenge. Scientific knowledge about the effectiveness of different methods for cleaning granite rocks in cultural heritage has advanced greatly in the last decade and today it is known which methods (among those commonly used) are the most suitable (in terms of removal and impact on the stone) for removing biological patinas, remains of previous treatments (e.g. wax), gypsum crusts

and graffiti [20]. However, only one previous study has addressed the removal of manganese crusts [12], but it approaches it with a rock very different from granite (laterite), applying a method that is not very reproducible *in situ* (immersion) and without analysing the evaluation of the cleaning effectiveness. In the case of the affected Galician granite buildings, the lack of information about the nature of these crusts and the degree of interaction with the underlying stone prevents extrapolation of what is known about the efficacy of other cleaning methods to other types of crusts or patinas. There is therefore an urgent need to establish specific cleaning methods aimed at removing manganese crusts from granite.

2. Research aim

This study addresses the issue of Mn-rich black crusts on historical granite buildings in Galicia from two perspectives. First, a chemical, mineralogical, and micromorphological characterization was performed on crusts from the church of San Pedro de Vilanova de Dozón, a granite Romanesque monastery built in 1124 and representative of late 12th–13th century architecture in the region. This analysis provides the first scientific data on Mn crusts affecting Galician granite architectural heritage. The second part evaluates the effectiveness of selected methods for removed the Mn-rich crust and their impact on the underlying stone. The most used cleaning methods for granite conservation were tested: microabrasion, laser cleaning, and cellulose poultices with various chemical agents. Their performance and effects on the stone were *in situ* assessed.

3. Material and methods

3.1. Description of the building under study

The building selected for study is the San Pedro de Vilanova de Dozón Monastery, located in Dozón (province of Ourense, 42°35'43"N 8°02'48"O, elevation 740 m, straight line distance from the Atlantic ocean, 58 km) in Galicia (NW Spain). The building is located in a rural area, characterized by pasture for livestock mixed with deciduous trees (*Quercus robur*, *Castanea sativa* and *Betula celtibérica*) and shrubs characteristic of Atlantic European forests, as well as pine and eucalyptus crops. According to the FAO's agro-ecological zoning, the area where the church is located is characterized by a humid subtropical climate with rainy winters (1000–1200 mm annual accumulated precipitation) influenced by the entrance of low-pressure fronts from the Atlantic Ocean (from a S-SW direction) [21,22]. The mean annual temperature is 12–13 °C. Following the Köppen–Geiger climate classification system, the climate of the region corresponds to Csb warm temperate climate, with dry and cool summers [23]. The geological substrate in the area consists of two-mica adamellite granite formed by anatexis [24]. This rock is a light-coloured medium to coarse granite, with hypidiomorphic and equigranular texture, that outcrops as an elongated pluton in a north to south direction covering an area of 850 km². The pluton forms part of the group of granites defined by Capdevila et al. [25,26] as *granites with alkali affinity*, formed contemporarily with the last two phases (II and III) of Hercynian orogeny and that are predominant in the geological granite substrate in Galicia. Macroscopically, features associated with migmatization are distinguished in the rock, i.e. phylonian inclusions (aplites and pegmatites), centimetre accumulations of melanocratic minerals (sillimanite, tourmaline) and slight mineral orientation marked by micas. The stone also shows a variable colour, from light to yellowish-brown tones and present flow orientations; this textural feature is typical of Galician Hercynian granites [27] and it is associated with the release of Fe produced after the chloritization of the biotite which occurs under the slight metamorphism during the last phases of the orogeny [28]. The soils in the area are Umbrisols and Leptosols developed on the previously described granite.

Construction of the church began in the 12th century, and the original building consisted of a single nave, terminating in a semi-circular apse with large spans and adjoining columns (Fig. 2a). It is built from granite ashlar, either without mortar or joined with white mortar, although abundant additions of harder grey mortar (suggesting the use of Portland cement) are observed. Stylistically, it possesses a great richness of artistic carvings (corbels, cornices and oculi) typical of late Romanesque iconography and style. The building material is a medium grained equigranular two-mica granite, slightly oriented, with quartz and ferromagnesian veins and of variable colour (light to reddish brown), including the typical flow orientations. These macroscopic features coincide with those described for the granite of the geological substrate, strongly indicating that the construction material of the church is the same material. Moreover, most of the Galician architectural heritage is built with these alkaline affinity granites of Hercynian age [29] (such as those described in the geological substrate and in the monastery building): the conditions under which these granites outcropped led to rocks slightly more porous than commercial quality granite and therefore being much easier to carve by hand. Several emblematic examples of Romanesque buildings in Galicia are constructed with this type of granite, such as the emblematic cathedrals of Santiago de Compostela [30], Tui and Ourense [31].

The darkest black crusts were observed inside the church, affecting the walls of the apse (Fig. 2b, 2c) and reaching a height

of between 1,5 and 2,8 m. The black crusts covered the surface of some of the ashlar unevenly, with the darkest black areas found closest to the joints (Fig. 2d). Black crusts were also observed on the outer walls of the apse, reaching the same height as in the interior but less abundant, more disperse and not as dark-coloured.

3.2. Characterization of the building materials and crusts

As it was not possible to collect sufficient rock samples from the church masonry without causing damage, a survey was conducted in the surrounding area to identify granite outcrops with similar characteristics to that of the church. Two outcrops of a granite macroscopically similar to that of the church were found, which are currently being exploited to obtain commercial ornamental stone. The rock of these outcrops is included, following the cartography [24], in the two mica granite of alkaline affinity group; this fact, together with the macroscopic similarity with that of the church allows us to assume that the granite of the church corresponds to that of the geological substrate. Access was obtained to one of these quarries and two samples of the stone were obtained: a sample of light-coloured stone (GO1) and a sample of reddish-brown stone (GO2).

A sample of white mortar was also obtained from the exterior of the church, and which according to the restoration team, appeared to be original material; the sample was taken from an area not affected by back crust located between two pieces forming the fascia of the lateral door.

Finally, three representative samples of black crusts of approximately 3 × 3 × 1 mm in size were obtained by micro chisel (Fig. 2c):

- CN1: black crust on granite, from an ashlar at the back of the apse, at a height of 2 m, on the left of the main altarpiece. Dark black in colour, sometimes appears iridescent, depending on the lighting, variable degree of cover and strongly attached to the substrate.
- CN2: black crust on granite, from an ashlar adjacent to the one where the previous sample was obtained. Similar in appearance to the previous sample and of similar cohesion.
- CN3: black crust on granite, from the riser of the step separating the presbytery from the apse. Similar in appearance to the other two samples.

All of the samples were examined by stereomicroscopy (SMZ800 NIKON). Subsequently, a fraction was ground to a fine powder (less than 50 µm) and analysed by X-ray diffraction (XRD) (SIEMENS D5000 diffractometer) by the random powder method; the analysis was performed using Cu-K radiation with a Ni filter, voltage of 45 kV and intensity of 40 mA. The exploration range was 3° to 60° 2θ and the goniometer speed was 0.05° 2θ s⁻¹. The minerals were identified using the X'Pert Highscore software.

The granite samples from the outcrop were also chemically analysed by X-ray fluorescence (XRF, SIEMENS SRS 3000 spectrophotometer), preparing the samples in pellet form. Also, a thin section of each sample was prepared and studied with a petrographic microscope (PM) ZEISS Axioscope with an Axiocam 12 camera in order to petrographically characterize the stone.

The black crust and mortar samples were examined by optical microscopy (OM) (ZEISS Axioscope 5/7KMAT) and by scanning electron microscopy (SEM) (JEOL FEM 6010) with energy dispersive X-ray spectrometry (EDS), studying the surface of the samples and also cross sections; the cross sections were embedded in epoxy resin, cut and polished before analysis. For SEM study, samples were coated with carbon and secondary and backscattered electron detectors (SE and BSE respectively) were used.

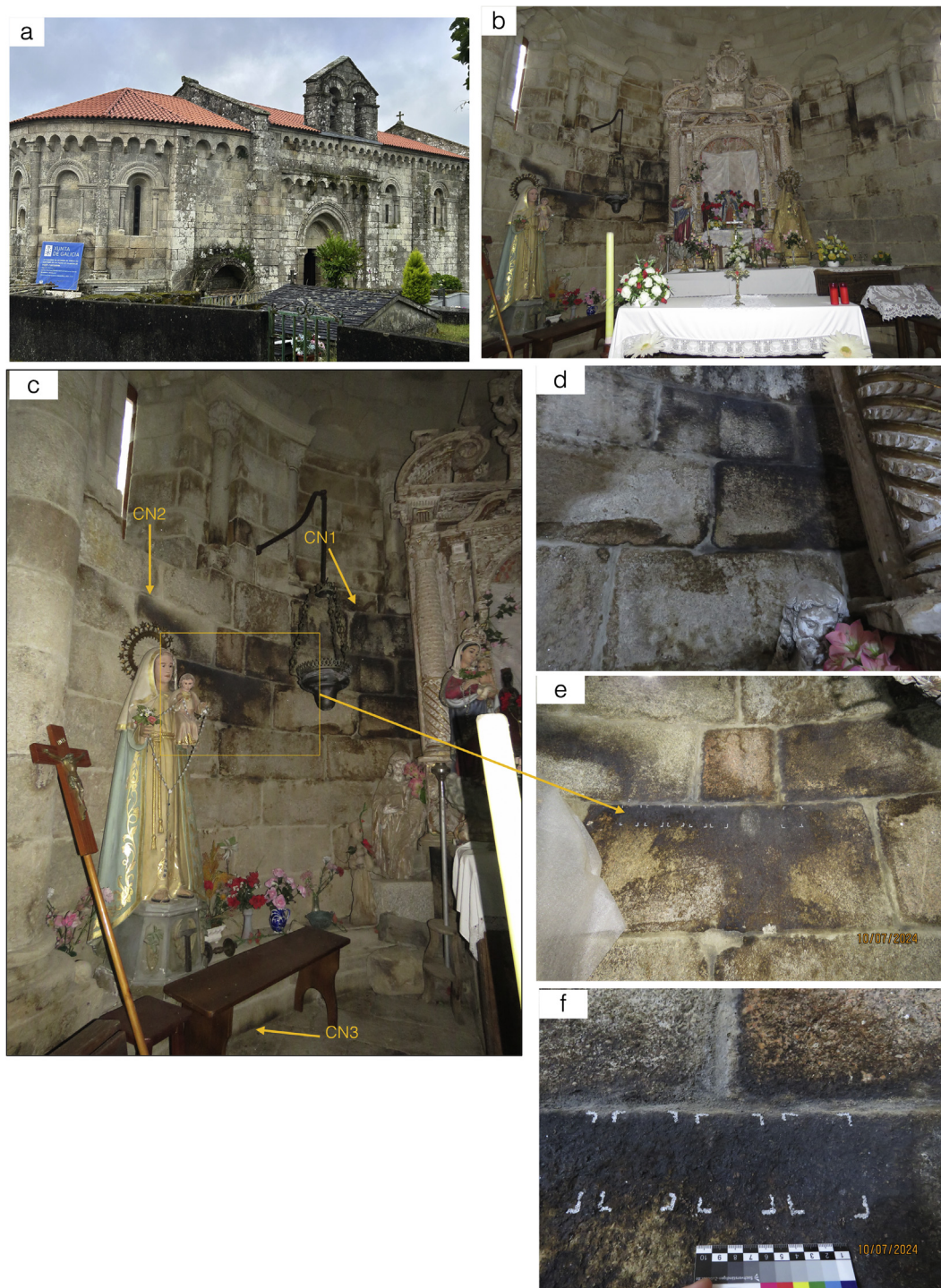


Fig. 2. A) The Church of San Pedro de Vilanova de Dozón, viewed from the apse. B) appearance of the inner wall of the apse, affected by black crusts. C) detailed view of the wall, indicating the points where samples of black crusts were collected and the location of the ashlar selected for testing the different cleaning treatments; D) detail of different ashlar affected by black crusts, which are particularly dense in areas close to the joints. E and F) detail of ashlar selected for cleaning treatments, with the test areas outlined in white.

The black crust samples were also analysed by Raman spectroscopy using a i-Raman Prime spectrometer (Metrohm) that employs a 1064 nm laser as the source of excitation energy and a high quantum efficiency CCD detector with deep cooling (-25°C) and a high dynamic range. Three spectra were obtained in each sample, by varying the laser power (between 10 and 30 % of the equipment's maximum power, which is 340 mW) and integration time (between 500 and 2000 ms). The Raman bands were identified on the basis of previous reports in the scientific literature.

3.3. Evaluation of the efficacy of the in situ cleaning treatments

This part of the study corresponds to scientific support provided to the restoration company responsible for cleaning the interior walls of the church affected by Mn-black crust. The company wanted to assess the effectiveness of a mechanical method (microabrasion), a physical method (laser), and different chemical formulations to remove black manganese crust. The scientific support consisted of 1) advice on the most appropriate characteristics

that the microabrasion and laser equipment should have, considering the composition and micro-morphology of the crust to be removed; the selection of these two devices was made by the company based to the scientific advice but the final selection criterion was largely determined by the availability of equipment on the market and the company's budget for the intervention; 2) the selection of five most suitable chemical cleaning formulations; and 3) the evaluation of a preliminary cleaning effectiveness in small, selected areas, with the aim of identifying the method that achieves the greatest crust removal and least damage to the granite substrate.

The preliminary cleaning effectiveness evaluation was performed on an ashlar uniformly affected by black crust, located on the left-hand side of the apse, at a height of 164 cm from the level of the bench surrounding the apse, was selected for the tests. Seven test areas, each of 4 cm x 4 cm, were delimited on the ashlar (Fig. 2c, e and f).

The following cleaning methods were selected:

- M1: Cleaning with a portable laser (ArtLaser, <https://shop-espana.ctseurope.com/830-art-laser>), provided by CTS España (<https://shop-espana.ctseurope.com/>). According to the information provided by the company, it is a Q-Switch Nd:YAG laser, which emits at a wavelength of 1064 nm with a pulse duration of 10 ns. The spot size can be adjusted from 1 to 12 mm and the frequency and energy can be regulated at maximum levels of respectively 30 Hz and 350 mJ. The cleaning was carried out by applying a single sweep, setting the pulse energy to 250 mJ and the pulse frequency on 30 Hz, and working at a distance of 60 cm from the gun nozzle to the Stone surface. Under these conditions, the spot diameter corresponded to 5 mm and the working fluence to 1.27 J/cm². Q-switched laser equipment emitting at 1064 nm is a well-studied tool whose effectiveness in the cleaning of cultural heritage materials has been extensively demonstrated in the literature, especially since the 1064 nm wavelength is highly absorbed by various dark deposits like gypsum black crusts and biological patina growths (e.g. algae, fungi). Also, this type of lasers emits very short pulses (in nanosecond domain), which allows for precise ablation of unwanted surface layers without significantly heating or damaging the underlying stone [32,33].
- M2: Microabrasion. A mechanical method consisting of projecting compressed air with aluminium oxide particles as an abrasive. A microabrasivemeter device (model CTS-1) with a compressed air supply, a pressure gauge, a pressure regulator and a 0.7 mm diameter carbide nozzle were used. 180 mesh aluminium oxide microspheres were used as abrasive and the cleaning was carried out at a regulated pressure of 2 bar and under dry conditions, without applying moisture to the stone substrate.
- Five chemical methods, based on the use of wet carboxymethylcellulose poultices prepared with different chemical agents. The following chemical agents were tested:
 - M3a: Aqua regia (HCl and HNO₃ at a ratio of 3:1), 5 %, pH 1.3. Chosen as it is an acidic mixture commonly used to dissolve metals.
 - M3b: disodium EDTA, pH 4.5. Chosen as it is commonly used in the conservation-restoration field.
- For the three remaining methods, M3c, M3d and M3e, three weak acids with reducing capacity were chosen. These acids have been used in mining research for leaching manganese nodules [34] and in other applications requiring reducing agents [35]. The underlying hypothesis is that the Mn in the crusts will be present in the highest oxidation state, Mn IV, which is the most stable form in oxic environments. According to the Pourbois diagram for Mn, the stable form of Mn (IV) can

be converted to the unstable, soluble form in acidic, reducing environments. Thus, these three acidic agents (with low redox potential) should cause transformation of the Mn contained in the crust from the IV oxidation state (MnO₂) to the II oxidation state, thus favouring its mobilization and removal via carboxymethylcellulose. The following acids were used:

- M3c: Oxalic acid, evaluated in a previous study [12], used as a saturated solution (9.6 g/100 mL) and at 0.1 M.
- M3d: Gallic acid. A weak acid (pH 2.1) containing polyalcoholic radicals that confer reducing properties. It was applied at 2 %.
- M3e: Formic acid. This weak acid (pH 1.2) was applied at 6 %.

The five chemical products were each mixed with carboxymethylcellulose to produce a thick paste that could be applied to vertical walls without risk of runoff. After conducting preliminary (exploratory) tests on an adjacent ashlar, the poultices were left in place for 3 h preventing the material drying out. The poultices were then removed with the aid of a spatula and the area was neutralised by rinsing with distilled water.

Four non-destructive *in situ* evaluation methods were applied to the test areas before the cleaning and one week after the cleaning; also, they were applied in areas of granite affected by black crust and unaffected granite (considered reference areas). The methods are the following:

- (a) Portable microscopy. The surfaces were visualized using a portable DinoLite microscope to evaluate the presence of crust remains and their distribution among the rock minerals as well as textural changes caused by the methods.
- (b) Colour spectrophotometry. After removal of the black crust, the original colour of the stone should be restored, as far as possible. Thus, one way of evaluating the efficacy of cleaning methods is to determine the colour change on the cleaned surface. The colour change was evaluated by colour spectrophotometry (Minolta CM-700d spectrophotometer) in specular component excluded (SCE) mode. The measurements were made in spot diameter area of 3 mm, with illuminant D65 and observer angle of 10°. Eight colour measurements were made in each 4 cm x 4 cm test area, in an area of the ashlar not affected by the black crusts and also in an area affected by the crust; given that granite is a texturally heterogeneous rock, the number of eight measurements collected was established as proposed by [36], with the aim of ensuring reliable colour characterization. The colour was characterized according to [37] in the CIELab and CIELCh colour spaces, measuring the following coordinates: L*, which represents the lightness and varies between 0 (black) and 100 (white), a* (with positive values for red and negative values for green) and b* (with positive values for yellow and negative for blue). Also, C*_{ab}, or chroma, which expresses the purity or intensity of the colour, and h, the hue angle, which expresses the hue or shade of the colour, were calculated. The efficacy of the cleaning methods was determined by calculating the differences between the values of these parameters (ΔL^* , Δa^* , Δb^* , ΔC^*_{ab} and ΔH^*) before and after the cleaning, considering the reference colour 1) the data of the unaffected granite, which allows to evaluate the degree of recovery of the original colour of the rock, and 2) the data of the black crust, which allows to evaluate the degree of removal of the crust. The ΔE^*_{ab} parameter, or colour difference, was also calculated to indicate the overall colour change relative to the reference colour.
- (c) Laser Induced Breakdown Spectroscopy (LIBS) (SciAps HH-LIBS, model Z903) was used to analyse the chemical composition of the surfaces. The equipment consists of a high energy laser

emission source at 1064 nm, 3–6 mJ/pulse and 50 Hz repetition rate, effective measurement area of 0.1 to 2 mm and a analytical spectral wavelength range of 190 to 950 nm with a gas (argon) purging system. Three LIBS spectra were obtained for each surface considered (black crust, granite without crust and cleaning test areas) selecting 6 mJ/pulse and 1 mm effective measurement area. The equipment functions with basic internal calibration (GEOTECH) but was not calibrated using external standards, and the results obtained are therefore semi-quantitative. Thus, a cleaning method was considered effective if the Mn concentration on the surface of the cleaned stone was lower than the concentration in the black crust and similar to the concentration measured in the unaffected granite.

Using data for the major chemical elements Al, Si, Ca, Mn, Fe, Na, Mg, and K, a one-way ANOVA was performed to detect statistically significant differences among areas cleaned with different methods, the area with crust and the unaffected granite. One-way ANOVA allows to determine whether the means of a numerical variable (in this case, each chemical element) differ significantly across several groups defined by a single categorical variable (the factor, in this case, each study area). It partitions total variability into between-group variance (explained by the factor) and within-group variance (random error) and compares them using Fisher's F-distribution. If the between-group variance is much greater than the within-group variance, it is concluded that the factor has a significant effect on the mean of the dependent variable, leading to rejection of the null hypothesis that all means are equal. When the ANOVA indicated significant differences, Tukey's HSD post hoc test was applied to control the experiment-wise Type I error rate and to identify which pairs of group means differed, using multiple comparisons based on the studentized range distribution. More information on these methods is available in basic academic literature [38].

- (d) Raman spectroscopy, using the equipment described above. At least three spectra were measured in each test area before and after cleaning, varying the laser power (between 10 and 30 % of the maximum power) and integration time (between 500 and 2000 ms). Likewise, spectra were also measured in the part of the ashlar not affected by black crust.

4. Results

4.1. Characterization of building materials and crusts

The results of the XRD analysis confirmed that the stone from the granite outcrop contains quartz, mica, sodium plagioclase (albite) and potassium feldspar as main minerals. Thin-section analysis further confirmed this composition, identifying quartz (26 %), potassium feldspar (microcline) (16 %), sodium plagioclase (albite) (30 %), muscovite (12 %) and biotite (5 %) as the main minerals, and apatite, zircon and opaque minerals (ilmenite) as accessory minerals. Examination of the samples in the petrographic microscope revealed that quartz appeared allotriomorphic crystals of 3–0.6 mm in size, with pressure shadows and undulatory extinction, and also as recrystallised quartz in intergrain positions. The plagioclase (albite) was observed in idio-subidiomorphic phenocrysts (< 3 mm in size) with polysynthetic twinning and scarce alteration processes to sericite. The potassium feldspar is microcline and is observed as subidiomorphic crystals with cross-hatched twinning and Carlsbad twinning; myrmekites and perthites are common textural features in this rock. The micaceous minerals (muscovite and biotite) appeared in large crystals (up to 2.25 mm) and also as microinclusions (0.13 mm) in the feldspars. The biotite is observed as lamellar crystals with typical reddish-brown pleochroism and in aggregates subordinate to the muscovite crystals. Locally, chlorite alterations

Table 1

Chemical elemental composition (expressed in % of element oxide) of the two samples from the granite outcrop obtained by XRF.

Element	GO 1	GO2	Element	GO 1	GO2
SiO ₂	66.14	69.94	Rb ₂ O	0.042	0.037
Al ₂ O ₃	18.7	16.8	ZrO ₂	0.018	0.022
K ₂ O	6.99	5.98	MnO	0.018	0.015
Na ₂ O	3.8	3.77	SrO	0.016	0.014
Fe ₂ O ₃	1.58	1.29	ZnO	0.011	0.0010
CaO	0.959	0.821	Cl	0.01	0.015
P ₂ O ₅	0.76	0.64	SO ₃	0.0041	0.0064
MgO	0.52	0.35	Ga ₂ O ₃	0.0033	0.0032
TiO ₂	0.344	0.251	NiO	0.0027	0.0022
BaO	0.065	0.048	CuO	0.0017	0.0021

are identified but without formation of independent sections. As accessory minerals, apatite (< 0.15 mm) is found associated with muscovite, zircon (< 0.06 mm) is observed as inclusions in biotite (showing marked pleochroic halos) and ilmenite occasionally appears dispersed, filling some fissures.

The chemical composition of the stone samples from the outcrop, obtained by XRF, is shown in Table 1. The main elements are Si, Al, K and Na, consistent with the modal composition; Na is present in greater amounts than Ca, confirming the albite character of the plagioclases. The Fe content differed only slightly between samples, so the reddish-brown coloration may therefore be associated with a higher degree of dehydration and oxidation of the Fe (which usually confers reddish coloration) rather than with a higher Fe content. The P, present in proportions less than 1 %, indicates the presence of apatite. Note the very low content of Mn (0.015–0.018 %).

Regarding joint mortar sample, X-ray diffraction identifies as main components calcite, quartz, feldspars and micas. Observation by stereomicroscopy revealed that the aggregate phase is composed of heterometric (1800 µm–30 µm) silicate grains with angular edges, indicating that they come from a crushing aggregate. The cement matrix is cream-coloured and shows good adhesion to the aggregate. The nature of the aggregate and its texture were confirmed by SEM analysis: grains of quartz, potassium feldspar, sodium plagioclase, biotite and muscovite were identified. SEM also revealed the existence of a microporosity, unnoticed under stereomicroscopy, which is formed by pores of irregular shapes, isolated and smaller than 50 µm. The cementing phase is mainly composed of Ca, C and O, showing an atomic % ratio similar to that of calcium carbonate, with smaller quantities of Si and Al; no Mn was detected. The SEM analysis confirms the presence of Portland cement phases: some are rich in Si and Al corresponding to the hydrated phases; others are rich in Al and Ca and corresponds to the non-hydrated calcium aluminate phases of clinker.

In black crust samples (CN1, CN2 and CN3), quartz, potassium feldspar, sodium plagioclase and micas are detected by X-ray diffraction; no Mn-rich mineral phases were detected; therefore, if present they will be below the limit of detection of this technique or correspond to low crystallinity phases. Analysis by Raman spectroscopy confirmed the presence of Mn in the crust by means a series of peaks at 591, 631, 644, 740 and 770 cm⁻¹ (Fig. 3a), which are typical of pyrolusite- and hausmannite-type Mn (IV)-O [39,40].

Stereomicroscopy observation of the surface of samples CN1, CN2 and CN3 confirmed the existence of a very fine deposit, of brownish black colour, on the granite. Under SEM, this thin layer is seen to be unevenly distributed (Fig. 4b); thus, in some areas the deposit is smooth, softened and continuous, while in others it has a granular texture. The EDS analysis showed that the deposit is rich in Al and Si (main elements) with notable quantities of Ca, Mn and Cl; eventually, crystals rich in S and Ca were detected in

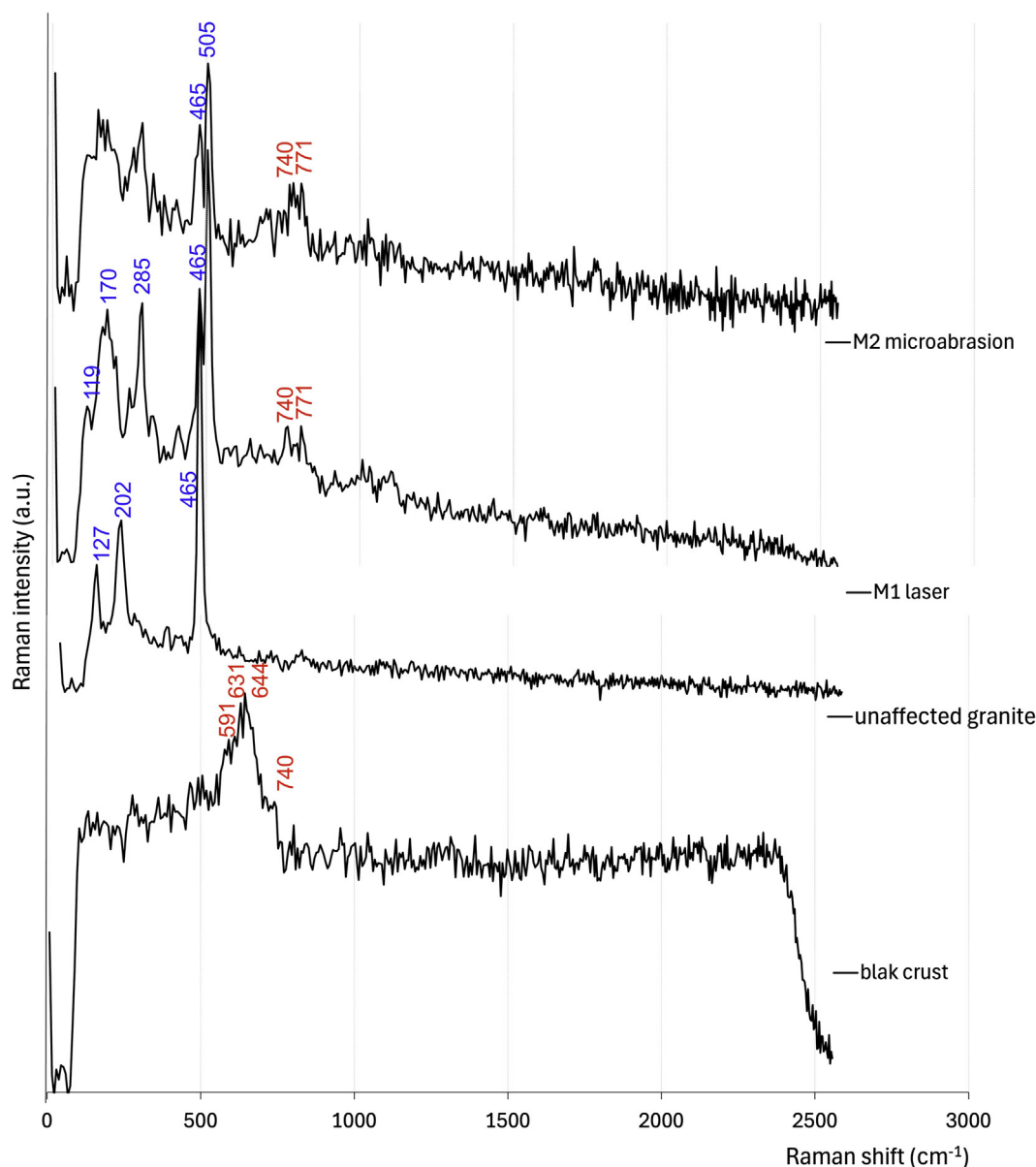


Fig. 3a. Raman spectra of the black crust, the unaffected granite (ref) and of the areas cleaned by laser and microabrasion. The peaks typical of silicates (blue) and Mn(IV)-O (red) are shown.

sample CN3 (from the stairway in the apse). Examination of the cross section by SEM (Fig. 4c and d) confirmed 1) the scarce thickness of the crust (5–10 μm), 2) the presence of Al and Si, as major elements, with smaller amounts of Na, K and Mn; 3) the existence of S and Ba rich grains, probably forming barium sulphate and 4) the net limit between the crust and the stone beneath, suggesting more likely that the crust was produced by precipitation on the surface and not by weathering of the surface layer of the rock.

4.2. Evaluation of the efficacy of the in situ cleaning treatments

The micrographs of the black crusts before and after cleaning by the different methods are shown in Fig. 5, which also includes micrographs of the surface of the reference granite, not affected by black crust. These micrographs firstly confirmed the contrast between the dark black appearance of the crust and the unaffected granite.

Regarding the cleaned areas, it is observed that M1-laser method was quite effective; however, it did not achieve complete

removal of the crust (remains are visible) and also caused a noticeable increase in microroughness, which suggests that the laser has caused the breakage and detachment of mineral grains. Method M2-microabrasion also did not completely remove the crust, although it appeared to be more effective than the laser-based method M1; M2 also caused a slight increase in the microroughness of the stone surface.

The following results were obtained for the chemical methods: 1) the complete ineffectiveness of method M3a-aqua regia: there was no evident difference in the appearance of the crust before and after application of this product; 2) methods M3b (EDTA), M3d (gallic acid) and M3e (formic acid) did not completely remove the crust. Of the three agents, gallic acid was slightly more effective, as some clean mineral grains were observed after application, with some remains of the crust observed in holes on the stone surface; 3) method M3c (oxalic acid) was very effective. The application of a saturated solution of oxalic acid enabled complete removal of the crust without any apparent changes in the texture or colour of the stone. Treatment with 0.1 M oxalic acid was less effective,

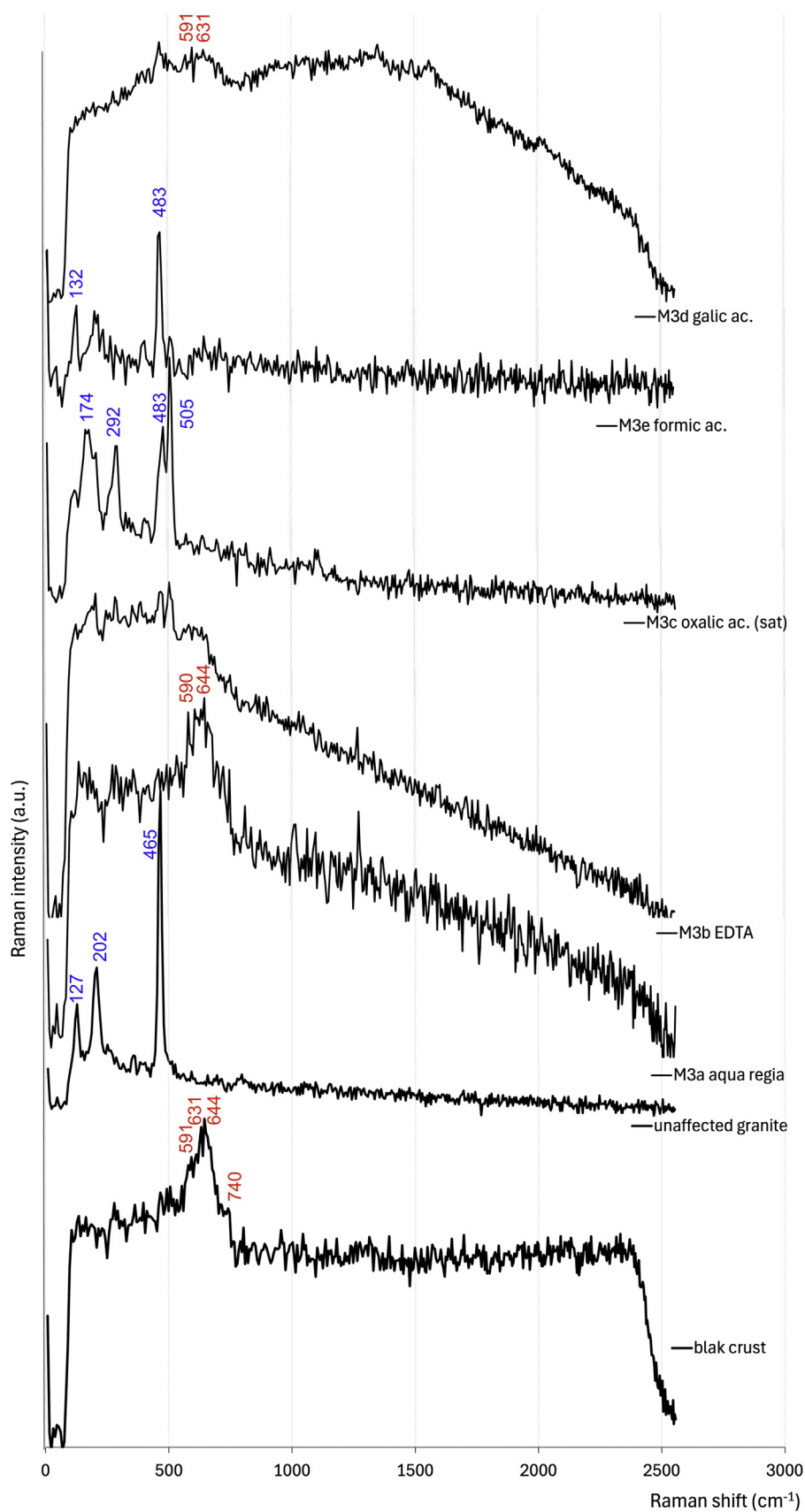


Fig. 3b. Raman spectra of the black crust, the unaffected granite (ref) and of the areas cleaned with the chemical formulations. The peaks typical of silicates (blue) and Mn(IV)-O (red) are shown.

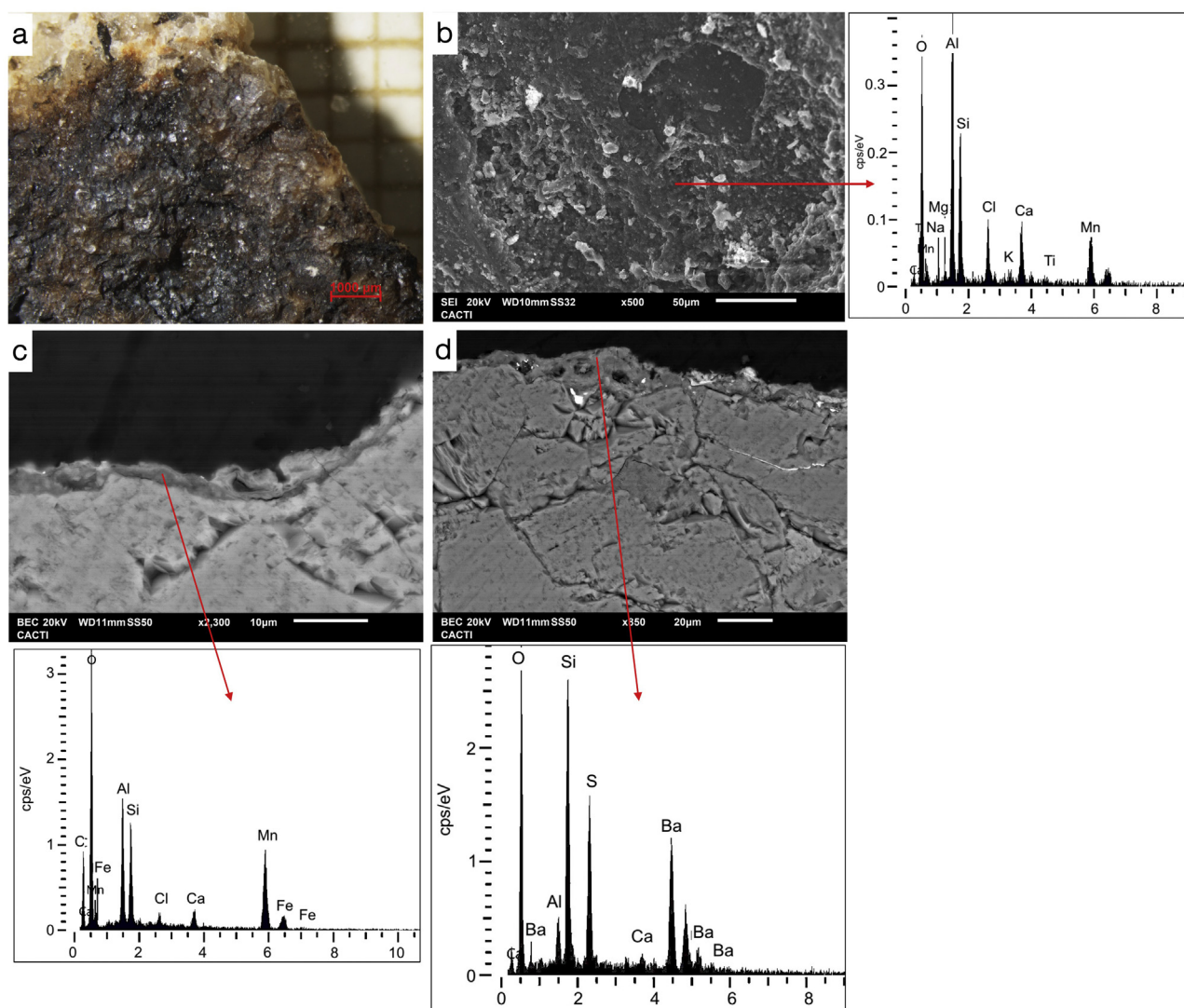


Fig. 4. a) appearance of the CN1 sample under stereomicroscopy; b) SEM micrograph of the surface of CN1 sample, with EDS spectrum in which Si, Al and Mn were identified; c and d) cross sections of CN1 and CN3 samples, showing the scarce thickness of the crust, the presence of Mn and also the presence of S and Ba in CN3.

as very small remains of crust were observed across the stone surface. Nonetheless, the dilute solution of this acid was more effective than the gallic acid.

In summary, evaluation of the different cleaning methods based on the microscopic appearance of the stone surface ranked the efficacy in the following order: saturated solution of oxalic acid > 0.1 M oxalic acid > laser > microabrasion > gallic acid > formic acid > EDTA > aqua regia.

The results of the evaluation of the efficacy of the cleaning treatments based on the colour differences expressed in the CIELab and CIELCh colour spaces are shown in Table 2. The ΔL^* , Δa^* , Δb^* , ΔC^*_{ab} , ΔH^* and ΔE^*_{ab} were calculated relative to two different reference colours: 1) the colour of the black crust, with higher values indicating greater levels of removal of the crust; 2) the colour of the unaffected granite, which enabled evaluation of the similarity between the colour of the clean surfaces and the original colour of the granite, with smaller values indicating greater similarity and thus higher efficacy of the treatment.

Considering the colour of the black crust as the reference colour, the efficacy of the cleaning methods was ranked in decreasing order, as follows: saturated oxalic acid > 0.1 M oxalic acid > microabrasion > laser > gallic acid > formic acid = EDTA > aqua regia. Treatment with aqua regia scarcely generated any

colour change, indicating the inability of this solution to remove the black crust. By contrast, the most effective methods (saturated oxalic acid and microabrasion) generated the highest ΔE^*_{ab} . The colorimetric parameter that underwent the greatest change after the cleaning treatments was L^* , indicating disappearance of the black crust.

Considering the colour of the unaffected granite as the reference colour, the efficacy of the cleaning methods was ranked decreasing order, as follows: saturated solution of oxalic acid > 0.1 M oxalic acid > microabrasion > laser > formic acid > gallic acid > EDTA > aqua regia.

Thus, it can be seen that the order of efficacy of the cleaning methods determined using the different criteria was similar, at least for the first four most effective methods.

The L^* and C^*_{ab} scatter plot of all the areas considered is shown in Fig. 6. The colour of the black crust was categorised as very dark black, whereas the colour of the granite was very light, with much higher L^* and C^*_{ab} values. The effectiveness of the cleaning method will be greater the further the colour measurement is from the colour of the crust and the closer it is to the colour of the reference granite. For the areas cleaned by the methods using saturated oxalic acid and microabrasion (the two most effective methods according to the results reported above) the values of L^*

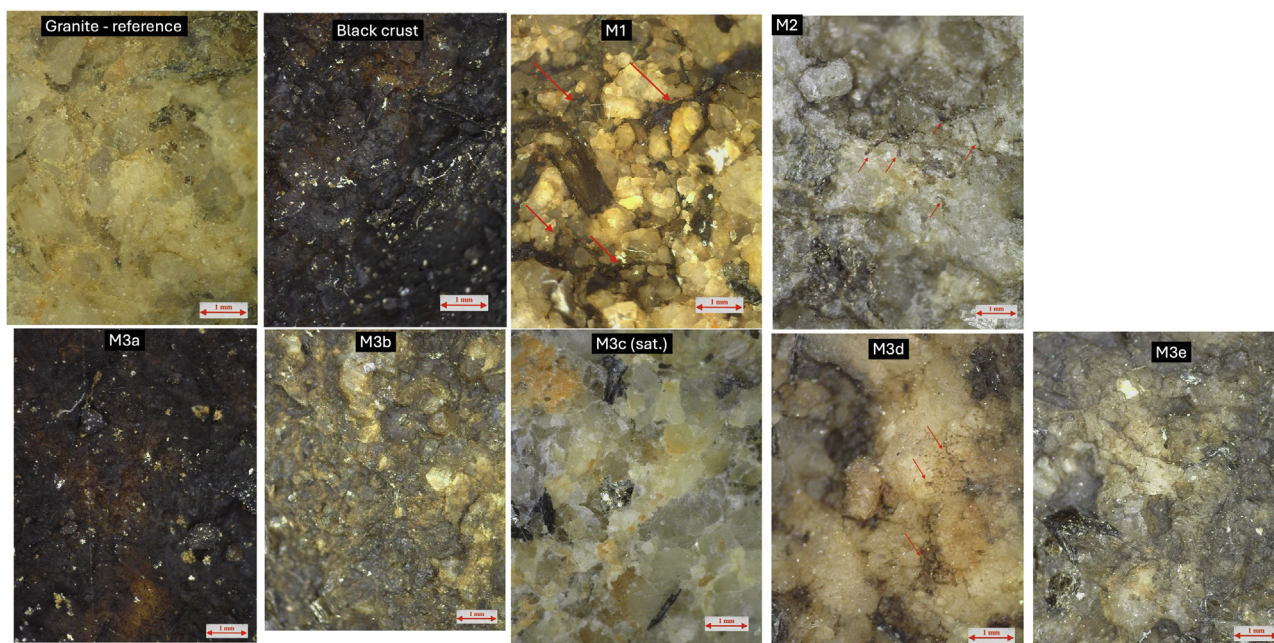


Fig. 5. Photomicrographs of the surface of the unaffected granite (reference granite), of the black crust and of the areas treated with the different cleaning methods: M1: laser; M2: microabrasion; M3a: aqua regia; M3b: sodium EDTA; M3c: oxalic acid (saturated solution); M3d: gallic acid and M3e: formic acid.

Table 2

ΔL^* , Δa^* , Δb^* , ΔC^*_{ab} , ΔH^* and ΔE^*_{ab} calculated relative to the colour of the black crust and that of the unaffected granite.

	ΔL^*	Δa^*	Δb^*	ΔC^*_{ab}	ΔH^*	ΔE^*_{ab}
Differences relative to black crust						
M1-Laser	9.0	2.8	14.5	13.5	−6.8	17.3
M2-Microabrasion	20.8	1.4	6.4	6.2	2.6	21.8
M3a-Aqua regia	0.8	1.2	2.8	2.2	−4.0	3.2
M3b-EDTA	4.1	2.7	12.7	12.0	−4.9	13.5
M3c-Oxalic acid (saturated solution)	26.3	2.8	10.1	9.5	−7.4	28.4
M3c-Oxalic acid (0.1 M solution)	20.8	1.8	9.6	8.7	−5.3	23.0
M3d-Gallic acid	10.2	2.5	9.3	9.0	−6.3	14.0
M3e-Formic acid	10.3	2.3	8.4	8.1	−0.1	13.5
Differences relative to the unaffected granite						
M1-Laser	−12.9	−0.6	−2.2	−2.3	−0.1	13.1
M2-Microabrasion	−0.3	−0.9	−7.4	−7.3	−1.5	7.5
M3a-Aqua regia	21.1	2.3	13.9	13.6	4.3	25.3
M3b-EDTA	−20.0	−0.4	−3.0	−3.0	−0.5	20.2
M3c-Oxalic acid (saturated solution)	0.9	−0.4	−6.0	−5.8	−1.5	6.1
M3c-Oxalic acid (0.1 M solution)	−3.2	−1.3	−6.3	−6.4	−0.7	7.2
M3d-Gallic acid	−16.1	−0.7	−6.2	−6.1	−1.1	17.3
M3e-Formic acid	−15.5	−0.7	−7.2	−7.0	−1.8	17.1

were highest and furthest from those of the black crust, indicating greater removal of the crust. Regarding the C^*_{ab} values, both methods yielded values within those obtained for the reference granite, which are very variable as granite is a polymineral stone.

Scatter plots of the a^* and b^* values for all the areas considered are also shown in Fig. 6. This graph includes two parameters: the hue (in this case the balance between red and yellow) and the chroma (purity or saturation of the colour, with higher values indicating higher purity). The values obtained for the crust are located on the extreme lower left, with the lowest values of each coordinate. The colour of the reference granite is located at the other extreme, with high a^* and b^* values and the hue corresponding to yellowish brown. In this graph, it can be seen that the values for the most effective cleaning methods (oxalic acid and microabrasion) fall within the area defined by the values of the original colour of the granite; the values for the other methods, except those with aqua regia and formic acid, are close to those of the reference granite, indicating that minimal removal of crust is

sufficient for the stone to acquire higher chroma and move away from the neutral colour of the crust.

The scatter plots indicate that the colour of the black crust is homogeneous (very little variation between the values), whereas the colour of the surface after the cleaning treatments is much more variable. The high dispersion of values can be attributed to 1) the polymineral nature of the stone, which contains light (quartz, feldspars) and dark (biotite) grains and also whiter or even transparent (quartz) and brown (feldspar) grains and 2) remains of the black crust adhering to the surface after cleaning. Thus, the high dispersion of the $L^* - C^*_{ab}$ values observed after cleaning with oxalic acid and microabrasion reflects the greater efficacy of these methods in removing the crust.

The percentage of the main chemical elements obtained with LIBS (relative values of the elemental composition) in the black crust, the unaffected granite and the cleaned areas are shown in Table 3. Also, this table presents the Tukey's post-hoc test results (see Material and methods section), which are expressed using let-

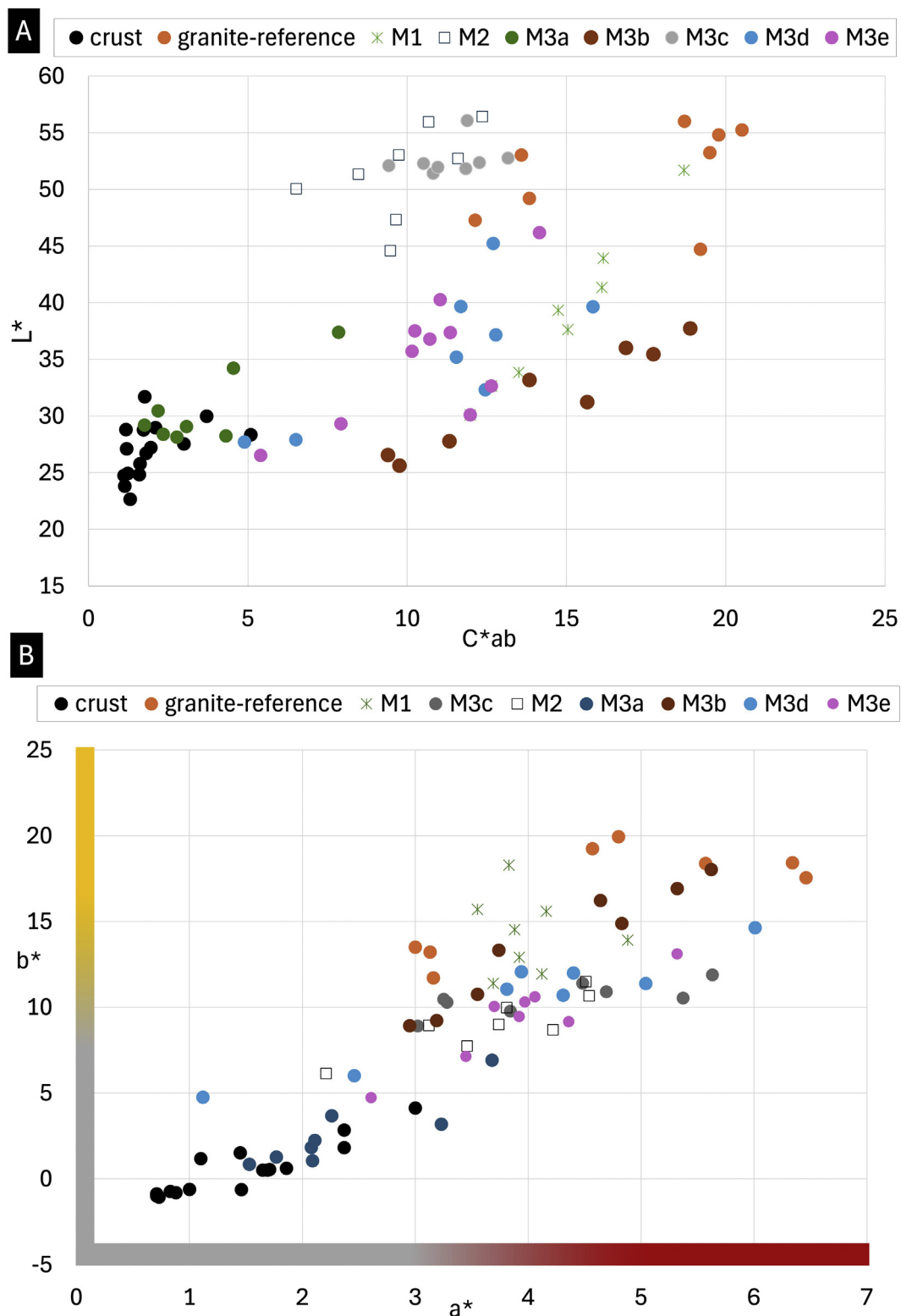


Fig. 6. A) L^* - C^*_{ab} scatter plot of the black crust, the reference granite and test areas of stone cleaned by each of the different methods; B) a^* - b^* scatter plot of the same samples.

ters (a , b , c , etc.) placed above each mean, to provide a compact visual display of pairwise comparisons; so, for each chemical element, areas whose means were not significantly different ($p \geq 0.05$) share the same letter, whereas areas whose means differed significantly ($p < 0.05$) are assigned different letters.

One-way ANOVA and *Tukey's post-hoc test* confirmed that there were no statistically significant differences ($p > 0.05$) regarding Si, Al, Fe, K and Mg content in the different measurement areas, but there were statistically significant differences regarding Mn, Ca and Na.

Table 3

Elemental composition (means, $n = 3$, and standard deviations) of the black crust, the unaffected granite and the cleaned areas, determined by LIBS (relative values, %); the concentrations of the main elements are shown. For each chemical element, means with the same superscript letter do not differ significantly according to the *post hoc* Tukey test ($p < 0.05$).

	Al	Si	Ca	Mn	Fe	Na	Mg	K
Crust	7.4 ± 1.3 ^a	5.5 ± 1.9 ^a	32.5 ± 3.6 ^a	9.1 ± 2.4 ^a	1.4 ± 0.8 ^a	9.0 ± 2.3 ^a	3.4 ± 0.9 ^a	4.1 ± 1.4 ^a
Unaffected granite	10.0 ± 2.2 ^a	7.4 ± 1.6 ^a	31.9 ± 4.0 ^a	0.7 ± 1 ^b	1.6 ± 0.9 ^a	10.4 ± 3.1 ^a	3.8 ± 0.8 ^a	4.3 ± 2.2 ^a
M1-laser	8.1 ± 1.2 ^a	7.1 ± 1.1 ^a	30.4 ± 8.7 ^a	7.2 ± 1.5 ^a	3.9 ± 5.2 ^a	9.0 ± 3.8 ^a	5.5 ± 4.2 ^a	3.7 ± 1.5 ^a
M2-microab.	9.0 ± 3.8 ^a	9.4 ± 3.0 ^a	32.1 ± 2.4 ^a	2.8 ± 2.5 ^b	1.7 ± 2.5 ^a	12.2 ± 2.8 ^b	3.6 ± 1.8 ^a	5.6 ± 2.9 ^a
M3a-aqua regia	6.5 ± 2.3 ^a	3.6 ± 0.5 ^a	31.1 ± 1.2 ^a	7.4 ± 0.4 ^a	1.4 ± 0.6 ^a	6.3 ± 2.4 ^a	3.6 ± 0.7 ^a	5.4 ± 1.8 ^a
M3b-EDTA	8.6 ± 2.4 ^a	6.9 ± 1.9 ^a	26.4 ± 3.5 ^a	8.0 ± 2.0 ^a	1.7 ± 1.1 ^a	13.9 ± 1.4 ^b	3.8 ± 1.4 ^a	3.8 ± 0.6 ^a
M3c-oxalic sat.	8.5 ± 0.3 ^a	7.3 ± 1.3 ^a	43.6 ± 7.0 ^b	1.7 ± 0.4 ^b	1.8 ± 1.5 ^a	13.5 ± 2.0 ^a	3.7 ± 2.0 ^a	4.3 ± 2.1 ^a
M3c-oxalic 0.1M	7.6 ± 0.9 ^a	6.0 ± 0.9 ^a	39.5 ± 3.2 ^b	3.1 ± 0.2 ^b	3.2 ± 1.1 ^a	10.9 ± 1.7 ^a	5.7 ± 0.7 ^a	3.5 ± 0.5 ^a
M3d-gallic	10.8 ± 2.8 ^a	6.8 ± 0 ^a	37.5 ± 4.5 ^a	3.8 ± 1.3 ^b	1.4 ± 0.5 ^a	14.7 ± 1.1 ^b	3.3 ± 0.5 ^a	2.5 ± 0.7 ^a
M3e-formic	9.2 ± 1.5 ^a	8.5 ± 1.0 ^a	28.3 ± 4.1 ^a	6.8 ± 2.8 ^a	1.7 ± 0.7 ^a	14.6 ± 3.5 ^b	4.1 ± 0.5 ^a	4.4 ± 1.2 ^a

Regarding Mn content, *Tukey test* denotes statistically significant differences ($p < 0.05$) among the black crust and the unaffected granite, the oxalic acid cleaned area (M3c), the gallic acid (M3d) cleaned area and the area cleaned by microabrasion (M2). Indeed, the average Mn content in the black crust was around 9 % in contrast to much lower values in the unaffected area (0.7 %), in the area cleaned with the saturated solution of oxalic acid (1.7 %) and in the areas cleaned with 0.1 M oxalic acid, gallic acid and by microabrasion (around 3 %). *Tukey test* would also confirm a lower efficacy of laser (M1), aqua regia (M3a), EDTA (M3b) and formic acid (M3e) since no statistically significant differences were detected among the means of the Mn content after cleaning with these four methods and the Mn mean of the crust; indeed, the content of Mn in these areas are the most similar to those corresponding to the crust, reinforcing the limited effectiveness of these methods.

In addition, *Tukey test* shows that the means of Na content after cleaning with M2-microabrasion, M3b-EDTA, M3d-gallic acid and M3e-formic acid differ significantly ($p < 0.05$) from the means of Na content for the remaining areas (Table 3). This finding may indicate that Na contamination has occurred after these cleaning interventions. In the treatment with EDTA (M3b) this is not surprising as EDTA is a sodium salt. In the areas treated with gallic acid (M3d) and formic acid (M3e), the presence of Na may be due to impurities associated with the chemical processes involved in producing both agents. Nonetheless, the difference, although significant, involved very low percentages of Na. On the other hand, the mineralogical composition of the stone also strongly influences the results. Thus, the Na content of the test area cleaned by microabrasion was very similar to that of the area cleaned with EDTA; given that microabrasion is a mechanical cleaning method, the presence of more Na in the test area than in the unaffected granite can only be explained because the LIBS measurements were made in an area of the granite surface with a higher proportion of sodium plagioclase.

Finally, *ANOVA-Tukey test* denotes statistically significant differences in the average Ca content in the areas cleaned with oxalic acid comparatively to the rest of the areas; this may indicate the possible calcium oxalate precipitation after the application of this chemical method.

The most representative Raman spectra of the unaffected granite and the areas cleaned by the different methods are shown in Fig. 3a and b; these figures also include the Raman spectrum of the black crust corresponding to sample CN1. In the spectrum of the unaffected granite, bands typical of the Si-O functional group [41,42] were detected, corresponding to the different silicates of the granite: 127, 279, 202, 285 and 475 cm^{-1} . No bands representing the Si-O group were detected in the spectra of the black crust, but a series of peak at 591, 631, 644, 740 and 770 cm^{-1} were observed, and which can be attributed to pyrolusite and hausmannite-type Mn (IV) oxides [39,40].

In the Raman spectra of the area cleaned with saturated oxalic acid, typical peaks of silicates, but not of the Mn(IV)-O functional group were detected, indicating that this method was effective. The Raman spectra of the areas cleaned by laser and by microabrasion included the peak attributed to the Mn(IV)-O group, i.e. the band at longest wavelength (771 cm^{-1}), indicating a lower effectiveness than that achieved by oxalic acid. In the spectra of the areas cleaned with the other chemicals, the fluorescence observed, which complicates the identification of peaks, requires these results to be considered with caution, although the identification of the Mn(IV)-O peaks in the M3a-aqua regia spectra is clear.

No peaks that could be assigned to Na-rich compounds that could explain the slightly higher contents of this element detected by LIBS in the areas treated with gallic acid, formic acid and EDTA were detected by Raman spectroscopy. The typical peaks associated with calcium oxalate were also not detected in the areas cleaned with oxalic acid.

5. Discussion and conclusions

The characterization of the samples collected from the building confirmed that the black crust did not correspond to a gypsum black crust, a type of alteration form that is very common in granites in old buildings and has a similar appearance. The crust studied here is also an inorganic crust but is rich in Si, Al and with a high and unexpected content of Mn. The presence of trace amounts of S and Ba (probably forming BaSO_4) was also detected. The presence of Mn, S and Ba suggest that the crust was not produced by weathering of the stone. The granite of this monastery, which is most likely the one that outcrops in the vicinity, and which has been characterized chemically and petrographically, did not contain enough Mn to generate such a crust nor S and Ba. Furthermore, as the granite contains these chemical elements in trace amounts, intense weathering (by the action of water) of a large volume of rock beneath the crust would be necessary for the Mn to be released in soluble form for subsequent precipitation. There is no evidence that weathering processes related to water action have occurred in the granite ashlar of this church: the black crust is the only severe deterioration form observed except for biological colonization on the outside and occasional losses of relief due to sand disaggregation. On the other hand, it is known that weathering of granite, which occurs via hydrolysis, does not progress at the same rate in buildings and in nature, as there is much less contact with water in buildings and the dynamics of the process are very different from those in natural environments; thus, scientific literature confirms that the main deterioration forms of granite in buildings (sand disaggregation, surface detachments) are not caused by hydrolysis processes but due to crystallization-dissolution of soluble salts [43], thermal shock [44] and/or thermal stress [45], playing

an important role in this physical processes the inherited alteration features of the granites [46,47].

One possible hypothesis regarding how the black crust is formed involves mobilization of the soluble form of Mn (Mn II) from a source under acid environment, in accordance with the pH-Eh stability diagram. The soluble Mn (Mn II) would be mobilized to another environment in which the pH increases to above 8, thus favouring precipitation of the unstable oxidised phase of Mn (Mn IV) in the form of the typical black concretions. The stone itself can be ruled out as a possible source of Mn, at least in these Galician Romanesque buildings affected by this pathology because these buildings are constructed with Hercynian granites that do not contain Mn-rich accessory minerals. The subsoil and foundations of the churches can also be ruled out as sources of the Mn, as the crusts also appear in vaulted ceilings at heights that would not be reached by capillary movement from the soil; also, in the present case, the joint mortar can also be ruled out as the source of Mn as this element was not detected in the samples analysed. Thus, the most likely hypothesis is that the Mn originates from old cleaning treatments or from the remains of previous coatings. This hypothesis is supported by the presence of S and Ba, chemical elements not associated with the geochemistry of the Hercynian granites described but sometime present in conservation treatments reagents or formulations. It is also important to identify the factors determining the precipitation of Mn in the black, oxidised (Mn IV) form; the alkaline environment characterizing the ashlar joints (lime mortar and/or Portland cement) and the remains of historical lime coatings may favour the precipitation of soluble Mn. All these questions must be addressed in future studies that would also provide interesting historical and archaeological information about these buildings.

The efficacy of seven different cleaning methods were evaluated by means of four non-destructive, *in situ* analytical methods: optical microscopy, colour spectrophotometry, LIBS and Raman spectroscopy. The results of these evaluation techniques coincide regarding identification of the most effective method of removing the crust, i.e. a saturated solution of oxalic acid densified with carboxymethylcellulose. This method completely removed the black crust from the stone surface. The four analytical techniques were also consistent regarding the order of efficacy of the cleaning methods: saturated oxalic acid > 0.1 M oxalic acid > microabrasion = laser > formic acid and gallic acid > EDTA > aqua regia. The saturated solution of oxalic acid and microabrasion were the only cleaning methods that restored the colour of the stone to a colour very similar to that of the unaffected granite.

These analytical techniques also enable detection of some damaging effects of the cleaning methods, including the following: 1) slightly greater roughness after cleaning by laser and microabrasion; 2) Na enrichment after cleaning with gallic acid, formic acid and EDTA and 3) Ca enrichment after cleaning with the saturated solution of oxalic acid. The increase in these chemical elements after cleaning is not noticeable and in fact calcium oxalate is not detected by Raman spectroscopy; however, these data indicate the importance of completely neutralizing the chemicals used in the cleaning methods; rinsing the treated surfaces after cleaning not only prevents the neoformation of precipitates, but also removes the carboxymethylcellulose remains, which would otherwise leave a whitish halo on the stone. Regarding laser cleaning, the present study highlights the need to extend research on the cleaning of manganese crusts on granite to a broader range of laser systems, including both solid-state lasers (testing alternative gain crystals) and fiber lasers. Future work should systematically evaluate not only the crust removal efficiency but also the potential effects on the stone substrate, considering key operational parameters—fluence, energy per unit area, repetition rate, wavelength, and pulse duration—under controlled experimental condi-

tions. Such comparative analyses will provide a more comprehensive basis for selecting the most suitable laser configuration for future cleaning interventions on granitic monuments affected by this manganese crusts. Of all of the methods evaluated, cleaning with a saturated solution of oxalic acid proved the best, as it enabled removal of most of the crust without affecting the surface of the granite.

Data availability

Data will be made available upon reasonable request.

CRediT authorship contribution statement

T. Rivas: Conceptualization, Investigation, Resources, Methodology, Data curation, Supervision, Writing – review & editing. **L. Espiño:** Conceptualization, Investigation, Methodology, Data curation, Writing – review & editing. **S. Pozo-Antonio:** Conceptualization, Investigation, Resources, Methodology, Writing – review & editing. **C. López:** Resources, Methodology, Data curation, Supervision, Funding acquisition.

Acknowledgments

SEM EDS analyses were performed using the University of Vigo's own equipment available at the Centro de Apoyo Científico y Tecnológico of the University of Vigo-CACTI facilities. Thanks are also due to the Dirección Xeral de Conservación e Restauración de Bens Culturais, of the Galician Autonomous Government (Xunta de Galicia) which allowed to dispose these data to be published. Funding for open access charge: Universidade de Vigo/CISUG.

References

- [1] W.S. Broecker, T. Liu, Rock varnish: recorder of desert wetness? *GSA Today* 11 (8) (2001) 4–10, doi:10.1177/09596836211011655.
- [2] B.M. Tebo, J.R. Bargar, B.G. Clement, G.J. Dick, J. Karen, K.J. Murray, D. Parker, R. Verity, S.M. Webb, Biogenic manganese oxides: properties and mechanisms of formation, *Annu Rev. Earth. Planet. Sci.* 32 (2004) 287–328.
- [3] W.B. White, C. Vito, B.E. Scheetz, The mineralogy and trace element chemistry of black manganese oxide deposits from caves, *J. Cave Karst Stud.* 71 (2) (2009) 136–143.
- [4] A.J. Friedrich, E.A. Hasenmueller, J.G. Catalano, Composition and structure of nanocrystalline Fe and Mn oxide cave deposits: implications for trace element mobility in karst systems, *Chem. Geol.* 284 (1–2) (2011) 82–96, doi:10.1016/j.chemgeo.2011.02.009.
- [5] D.S. Macholdt, K.P. Jochum, C. Pöhlker, B. Stoll, U. Weis, B. Weber, M. Müller, M. Kappel, S. Buhre, A.L.D. Kilcoyne, M. Weigand, D. Scholz, A.M. Al-Amri, M.O. Andreae, Microanalytical methods for in-situ high-resolution analysis of rock varnish at the micrometer to nanometer scale, *Chem. Geol.* 459 (2017) 91–118, doi:10.1016/j.chemgeo.2015.06.023.
- [6] P. Bugini, M. Laurenzi Tabasso, M. Realini, Rate of formation of black crusts on marble. A case study, *J. Cult. Herit.* 1 (2) (2000) 111–116, doi:10.1016/S1296-2074(00)00161-8.
- [7] R. Fort, M. Álvarez De Buergo, F. Mingarro, M.C. López De Azcona, Chemical processes of alteration on the surface of building stones by anthropogenic causes, *Afinidad* 60 (507) (2003) 450–457.
- [8] C. Saiz-Jimenez, P. Brimblecombe, D. Camuffo, R.A. Lefèvre, R. Van Grieken, Damages caused to European monuments by air pollution: assessment and preventive measures, *Air Pollut. Cult. Herit.* (2004) 91–109.
- [9] P. Brimblecombe, C.M. Grossi, Aesthetic thresholds and blackening of stone buildings, *Sci. Total Environ.* 349 (1–3) (2005) 175–189, doi:10.1016/j.scitotenv.2005.01.009.
- [10] P. Maravelaki-Kalaitzaki, Black crusts and patinas on Pentelic marble from the Parthenon and Erechtheum (Acropolis, Athens): characterization and origin, *Anal. Chim. Acta* 532 (2) (2005) 187–198, doi:10.1016/j.aca.2004.10.065.
- [11] C.A. Grissom, E.P. Vicenzi, R.A. Livingston, E. Aloiz, N. Little, J. Giaccai, W. Freedman, Manganese in black crusts on Seneca sandstone, *Microsc. Microanal.* 20 (2014) 2044–2045, doi:10.1017/S1431927614011957.
- [12] E. Uchida, R. Watanabe, S. Osawa, Precipitation of manganese oxides on the surface of construction materials in the Khmer temples, Cambodia, *Herit. Sci.* 16 (4) (2016), doi:10.1186/s40494-016-0086-1.
- [13] E.P. Vicenzi, C.A. Grissom, R.A. Livingston, Z. Weldon-Yochim, Rock varnish on architectural stone: microscopy and analysis of nanoscale manganese oxide deposits on the Smithsonian castle, Washington, DC, *Herit. Sci.* 4 (1) (2016), doi:10.1186/s40494-016-0093-2.

- [14] D.S. Macholdt, S. Herrmann, K.P. Jochum, A.L.D. Kilcoyne, T. Laubscher, J.H.K. Pfisterer, C. Pöhlker, B. Schwager, B. Weber, M. Weigand, K. Domke, M.O. Andreae, Black manganese-rich crusts on a Gothic cathedral, *Atmos. Environ.* 171 (2017) 205–220, doi:[10.1016/j.atmosenv.2017.10.022](https://doi.org/10.1016/j.atmosenv.2017.10.022).
- [15] B. Campos, A. Marco, D.M. Freire-Lista, N. Durães, J. Silvestre-Albero, E.F. da Silva, E. Vieira, M. Pintado, P.R. Moreira, Rare Biogeochemical Phenomenon Associated to Manganese Patinas on Mural Painting and Granite Ashlars, *Coatings* 11 (2021) 917, doi:[10.3390/coatings11080917](https://doi.org/10.3390/coatings11080917).
- [16] B. Prieto, N. Aira, B. Silva, Comparative study of dark patinas on granitic outcrops and buildings, *Sci. Total Environ.* 381 (1–3) (2007) 280–289 ISSN 0048-9697, doi:[10.1016/j.scitotenv.2007.04.002](https://doi.org/10.1016/j.scitotenv.2007.04.002).
- [17] J. Sanjurjo Sánchez, C.A.S. Alves, J.R. Vidal Romaní, D. Fernández Mosquera, Origin of gypsum-rich coatings on historic buildings, *Water Air Soil. Pollut.* 204 (2009) 53–68, doi:[10.1007/s11270-009-0025-9](https://doi.org/10.1007/s11270-009-0025-9).
- [18] B. Silva, N. Aira, A. Martínez-Cortizas, B. Prieto, Chemical composition and origin of black patinas on granite, *Sci. Total Environ.* 408 (1) (2009) 130–137 ISSN 0048-9697, doi:[10.1016/j.scitotenv.2009.09.020](https://doi.org/10.1016/j.scitotenv.2009.09.020).
- [19] T. Rivas, S. Pozo, M. Paz, Sulphur and oxygen isotope analysis to identify sources of sulphur in gypsum-rich black crusts developed on granites, *Sci. Total Environ.* 482–483 (2014) 137–147, doi:[10.1016/j.scitotenv.2014.02.128](https://doi.org/10.1016/j.scitotenv.2014.02.128).
- [20] J.S. Pozo-António, T. Rivas, A.J. López, M.P. Fiorucci, A. Ramil, Effectiveness of granite cleaning procedures in cultural heritage: a review, *Sci. Total Environ.* 571 (2016) 1017–1028 ISSN 0048-9697, doi:[10.1016/j.scitotenv.2016.07.090](https://doi.org/10.1016/j.scitotenv.2016.07.090).
- [21] A. Martínez-Cortizas, *Zonas agroecológicas de Galicia; zona climática FAO*, An. Edafol. Agrobiol. 46 (1987) 521–538.
- [22] A. Martínez-Cortizas, A. Pérez (Eds.), *Atlas Climático de Galicia, Consellería de Medioambiente, Xunta de Galicia*, 1999.
- [23] M. Kottek, J. Grieser, C. Beck, B. Rudolf, F. Rubel, World Map of the Köppen-Geiger climate classification updated, *Meteorol. Z.* 15 (2006) 259–263, doi:[10.1127/0941-2948/2006/0130](https://doi.org/10.1127/0941-2948/2006/0130).
- [24] Instituto Geológico y Minero de España-IGME, Mapa geológico de España (Geological map of Spain) Servicio De Publicaciones Del Ministerio De Industria, 1st ed., 1981 Hoja 154 Lalin. Open access <https://info.igme.es/cartografiadigital/geologica/Magna50Hoja.aspx?language=es&id=154>.
- [25] R. Capdevila, Le métamorphisme régional progressif et les granites dans le segment hercynien de Galice Nord-orientale NW Espagne PhD thesis, University of Montpellier, France, 1969.
- [26] R. Capdevila, P. Floor, Les différents types de granites hercyniens et leur distribution dans le Nord Ouest de L'Espagne, *Bol. Geol. Minero t. LXXXI-II-III* (1970) 215–225.
- [27] J.C. Fernández-Caliani, E. Galán, P. Aparicio, A. Miras, M.G. Márquez, Origin and geochemical evolution of the Nuevo Montecastelo kaolin deposit (Galicia, NW Spain), *Appl. Clay. Sci.* 49 (3) (2010) 91–97, doi:[10.1016/j.clay.2010.06.006](https://doi.org/10.1016/j.clay.2010.06.006).
- [28] J. Escuder, R. Carbonell, D. Martí, Pérez-Estaún A. Interacción fluido-roca a lo largo de las superficies de fractura: efectos mineralógicos y texturales de las alteraciones observadas en el Plutón Granítico de Albalá, SO del Macizo Hercínico Ibérico, *Bol. Geol. Min.* 112 (3) (2001) 59–78.
- [29] R. Jiménez Martínez, E. Díaz Martínez, in: *Las piedras del Camino de Santiago en Galicia*, Instituto Geológico Y Minero de España, 2013, p. 268. ISBN 978-84-7840-910-5.
- [30] B. Silva, M. Casal, B. Prieto, T. Rivas, F. Guitián, Forms and factors of weathering in the Cathedral of Santiago de Compostela, in: *Proceedings of III International Congress on Deterioration and Conservation of Monuments in The Mediterranean Basin*, Venecia, 1994, pp. 743–748.
- [31] J. Feijoo, I. de Rosario, T. Rivas, M.J. Mosquera, R. Benavides, Influence of a pre-consolidation treatment on the desalination effectiveness of a highly deteriorated granite façade of medieval age, *Int. J. Architect. Herit.* 17 (12) (2022) 1965–1983, doi:[10.1080/15583058.2022.2086506](https://doi.org/10.1080/15583058.2022.2086506).
- [32] S. Siano, M. Giamello, L. Bartoli, A. Mencaglia, V. Parfenov, R. Salimbeni, Laser cleaning of stone by different laser pulse duration and wavelength, *Laser. Phys.* 18 (2008) 27–36, doi:[10.1134/S10546660x08010064](https://doi.org/10.1134/S10546660x08010064).
- [33] S. Siano, J. Agresti, I. Cacciari, D. Ciofini, M. Mascalchi, I. Osticioli, A.A. Mencaglia, 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, *Appl. Phys. A* 106 (2012) 419–446, doi:[10.1007/s00339-011-6690-8](https://doi.org/10.1007/s00339-011-6690-8).
- [34] Y. Lu, H. Ma, R. Huang, A. Yuan, Z. Huang, Z. Zhou, Reductive leaching of low-grade pyrolusite with formic acid, *Metallurg. Mater. Trans. B* 46 (4) (2015) 1709–1715, doi:[10.1007/s11663-015-0380-4](https://doi.org/10.1007/s11663-015-0380-4).
- [35] J. Li, G. Xiao, C. Chen, R. Li, D. Yan, Superior dispersions of reduced graphene oxide synthesized by using gallic acid as a reductant and stabilizer, *J. Mater. Chem. A* 1 (4) (2013) 1481–1487, doi:[10.1039/C2TA00638C](https://doi.org/10.1039/C2TA00638C).
- [36] B. Prieto, P. Sanmartín, B. Silva, F.M. Martínez-Verdú, An effective methodology to colour characterization for contact colour measurement in granitic rocks, *Optica Pura Apl.* 41 (4) (2008) 389–396.
- [37] CIE S014-4/E:2007, Colorimetry Part 4: CIE 1976 L*a*b* Colour Space Commission Internationale de L'eclairage, CIE Central Bureau, Vienna, 2007.
- [38] Zar, J.H. *Biostatistical Analysis*. 5th edition. Pearson New International Edition. Edinburgh Gate Harlow Essex CM20 2JE. 761 pp.
- [39] N. Mironova-Ulmane, A. Kuzmin, V. Skvortsova, G. Chikvaidze, I. Sildos, J. Grabis, D. Jankoviča, A. Dindune, M. Maiorov, Synthesis and vibration spectroscopy of nano-sized manganese oxides, *Acta Phys. Polonica A* 133 (4) (2018) 1013–1016, doi:[10.12693/APhysPolA.133.1013](https://doi.org/10.12693/APhysPolA.133.1013).
- [40] J.E. Post, D.A. McKeown, P.J. Heaney, Raman spectroscopy study of manganese oxides: tunnel structures, *Am. Mineral.* 105 (8) (2020) 1175–1190, doi:[10.2138/am-2020-7390](https://doi.org/10.2138/am-2020-7390).
- [41] P.F. McMillan, B. Piriou, Raman spectroscopic studies of silicate and related glass structure: a review, *Bull. Minéral.* 106 (1) (1983) 57–75, doi:[10.3406/bulmi.1983.7668](https://doi.org/10.3406/bulmi.1983.7668).
- [42] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, 3rd ed., John Wiley and Sons, 2001, doi:[10.1021/ja0153520](https://doi.org/10.1021/ja0153520).
- [43] B. Silva, T. Rivas, B. Prieto, Soluble salts in granitic monuments: origin and decay effects, in: J.L. Pérez (Ed.), *En Applied Study of Cultural Heritage and Clays*, 2003, pp. 113–130.
- [44] M. Gómez-Heras, M. Hajpál, M. Alvarez de Buergo, A. Török, R. Fort, M.J. Varas, Evolution of porosity in Hungarian building stones after simulated burning, in: R. Fort, M. Alvarez de Buergo, M. Gomez-Heras, C. Vazquez-Calvo (Eds.), *Heritage Weathering and Conservation*, Rotterdam, Balkema, 2006, pp. 513–519.
- [45] D.M. Freire-Lista, R. Fort, M.J. Varas-Muriel, Freeze-thaw fracturing in building granites, *Cold Reg. Sci. Technol.* 113 (2015) 40–51 ISSN 0165-232X, doi:[10.1016/j.coldregions.2015.01.008](https://doi.org/10.1016/j.coldregions.2015.01.008).
- [46] J. Delgado Rodrigues, D. Costa, The conservation of granite in Évora Cathedral. From laboratory to practice, in: J. Delgado Rodrigues, J.M. Mimoso (Eds.), *Proceedings Int. Symp. Stone Consolidation in Cultural Heritage. Research and Practice*, Lisbon, 2008, pp. 101–110. Published by LNEC.
- [47] A. Dionísio, E. Martinho, J.S. Pozo-António, M.A. Sequeira Braga, M. Mendes, Evaluation of combined effects of real-fire and natural environment in a building granite, *Constr. Build. Mater.* 277 (2021) 122327 ISSN 0950-0618, doi:[10.1016/j.conbuildmat.2021.122327](https://doi.org/10.1016/j.conbuildmat.2021.122327).