

Construction and Building Materials

Electroprecipitation of inorganic borates, with different solubility, within monumental stones to avoid fungal colonization --Manuscript Draft--

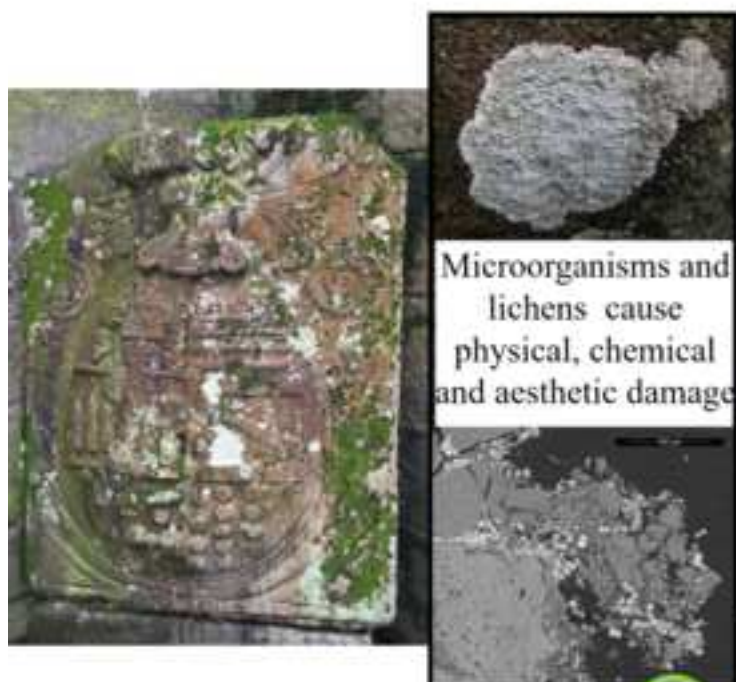
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Abstract:	Biodeterioration is a serious threat to the preservation of cultural heritage. Currently, the chemical treatments used to combat it must fulfil a series of restrictions to ensure that they are not harmful to humans or the environment. Borates satisfy these conditions but due to its high degree of leaching its application is limited to indoor areas. The use of electroprecipitation may to increase the range of applicability by allowing to precipitate, along the entire section of the stony materials, of a mixture of boron salts with different solubility (zinc, magnesium, and sodium borates) to cover a wide range of moisture conditions. The results obtained show that electroprecipitation not only increases the penetration depth of boron compounds but also allows the formation of compounds of different solubility, which allows the treatment to last over time. Furthermore, the treatment increased the mechanical properties and reduced the porosity of the stones treated, all without causing significant aesthetic changes.
Suggested Reviewers:	Ciria Carmen Ascaso national museum of natural history, spain ascaso@mncn.csic.es her research interests have been focused on lichen symbiosis, and have included ultrastructural, ecophysiological, enzymatic and, particularly, thallus-substrate studies. With respect to the latter, she has been involved in the development of new methodologies for the study of microorganism/lithic substrate interfaces and the understanding of the processes of biomineralisation. Elisa Franzoni, PhD University of Bologna Department of Civil Chemical Environmental and Materials Engineering elisa.franzoni@unibo.it Her research interests, in the field of building materials, mainly concern materials for Cultural Heritage conservation L.M. Ottosen, Professor Technical University of Denmark limo@dtu.dk She is specialist in the development of new techniques, especially electrokinetic techniques, for the treatment of deterioration processes affecting stony materials Daniel J Blackwood, PhD National University of Singapore msedjb@nus.edu.sg He has some publications about microbiological degradation on porous materials Shiping Tian, Professor Director of the Key Lab of Plant Resources tsp@ibcas.ac.cn

	Her research area is Pathogenicity and toxin metabolic pathway of fungal pathogens and regulating mechanisms Nidal Hilal, Professor Director of the Centre for Water Advanced Technologies and Environmental Research, Swansea University nidal.hilal@nyu.edu he is the co-author of a new published book by Elsevier entitled 'Boron Separation Processes', so he is a professional in the field of the use of borates.
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Highlights

1. Protection of stony materials against biodeterioration by ecofriendly compounds.
2. Electroprecipitation of borates of different solubility to increase their applicability.
3. The treatment allows the precipitation of different boron compounds.
4. The treatment is effective in preventing the fungal colonization.
5. The crystallization habit and penetrability differ depending on the material to be treated.

Main Problem on Cultural Heritage



Treatment

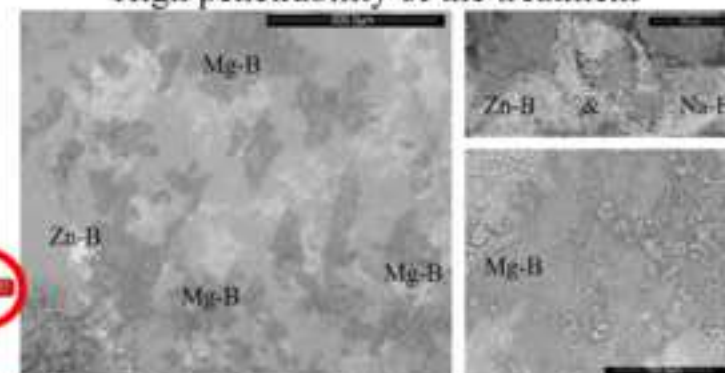


Results

After 60 days of fungi colonization



High and durable protection against fungi
High treatment content in the pores
High penetrability of the treatment



CRedit authorship contribution statement

Jorge Feijoo: Conceptualization, Methodology, Validation, Data curation, Writing- Original draft preparation, Supervision. **L.S. Gomez-Villalba:** Data curation, Writing- Original draft preparation, Methodology, Validation. **A. de los Ríos:** Data curation, Writing- Original draft preparation, Methodology, Validation. **Rafael Fort:** Writing- Original draft preparation, Resources, Supervision, Funding acquisition.

**Electroprecipitation of inorganic borates, with different solubility, within
monumental stones to avoid fungal colonization**

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Abstract:

Biodeterioration is a serious threat to the preservation of cultural heritage. Currently, the chemical treatments used to combat it must fulfil a series of restrictions to ensure that they are not harmful to humans or the environment. Borates satisfy these conditions but due to its high degree of leaching its application is limited to indoor areas. The use of electroprecipitation may to increase the range of applicability by allowing to precipitate, along the entire section of the stony materials, of a mixture of boron salts with different solubility (zinc, magnesium, and sodium borates) to cover a wide range of moisture conditions. The results obtained show that electroprecipitation not only increases the penetration depth of boron compounds but also allows the formation of compounds of different solubility, which allows the treatment to last over time. Furthermore, the treatment increased the mechanical properties and reduced the porosity of the stones treated, all without causing significant aesthetic changes.

Keywords: Electroprecipitation; biodeterioration; boron; borates; stones; fungi.

1. Introduction

Microorganisms and lichens play a major role in stone-built cultural heritage decay, causing irreparable damage and economic losses [1–3]. They induce not only aesthetical alterations, forming extensive colonization and biological patina, but also generating biogeophysical and bio-geochemical changes (biodeterioration processes) in the colonized stone, which contribute to the deterioration of architectural and artworks heritages [4–6].

Several methodologies and products have been used to eliminate and prevent biological settlements, both indirect and direct [7]. Indirect methods, also named as prevention methods, try to control environmental parameters that favor biological colonization, such as humidity, temperature or the availability of organic and inorganic nutrients which promote the microbial growth [8]. However, due to the dimensions of many buildings, their applicability is often challenging. Direct methods, also named as remedial methods, include all treatments aimed at sterilizing or eradicating the agents that cause biodeterioration. These methods include 1) mechanical removal methods, using scalpels, brushes, or abrasive spraying techniques [9,10]; 2) physical methods such as the application of ionizing radiation (beta and gamma [11]) and non-ionizing radiation (ultraviolet [12]), thermal processes [13,14], microwave application [15] and laser cleaning [16,17], among others; 3) biological methods focused on the use of parasitic or antagonistic species to combat invasive species [18–20]; 4) chemical methods based on the application of biocides [21,22], of different nature, either by brush, spraying, injection or through the application of poultices. Many of the compounds used in chemical treatments, whose mission is to inhibit or reduce a specific metabolic activity, have potential unwanted side effects both for the environment and human health. For this reason, the compounds currently in use must meet increasingly stringent requirements.

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Among the biocides that currently satisfy these conditions, it must be highlight boron salts such as borax, disodium octaborate tetrahydrate, and zinc borate, among others. Previous studies showed that borates are much less toxic to mammals and the environment than most common preservatives [23]. These compounds have proven their effectiveness as wood and paper preservatives against most cellulolytic organisms such as fungi and termites, in addition to act as fire retardant ([24–28]). However, the applicability of most of these boron compounds is limited to indoor areas that are not exposed to the weather or in contact with the ground, due to their high susceptibility to leaching, which limits their durability [29,30].

As indicated in [29,30], and in the references included therein, several alternatives have been assessed to limit boron leach ability and improve boron fixation such as formation of insoluble complexes [31–33], formation of protein borates [26,34,35], and formation of organic borates with different polyols [36,37]. Nevertheless, as previously reported, these solutions reduce the biological activity of boron, and especially its fungicidal activity. The use of low solubility borate salts such as zinc borate show a high efficiency under high humidity situations, but not at lower relative humidity since leaching and subsequent release of borate ions does not happen.

The aim of this study is to precipitate, and test its efficacy against fungal colonization, a mixture of boron salts, with different solubility, inside the pore network of a porous material by applying an electrokinetic method. The mobilization and consequent precipitation of inorganic compounds by means of electric field has improved part of the limitations associated with the traditional application method of commercial products, since it allows to increase the penetration depth of the applied treatments, as already demonstrated in previous studies [38,39]. This is achieved by forcing the in-situ synthesis of specific compounds into the pores through which the current flows. Consequently, the

material is left with a lower accessible porosity, which increases its durability against external agents, and a higher mechanical resistance [38,39]. In addition, this type of treatment provides long-lasting protection by allowing the pores of the material to act as a reservoir for the precipitated compound that will be slowly released as the leaching surface of the treatment is restricted to the diameter of the pore [40]. Finally, this type of treatment is more eco-friendly, as there is no release and consequent exposure to toxic gases, such as volatile organic compounds, during its application.

This particular study represents an evolution in the field of biocidal treatments, respectful of current environmental restrictions, since it analyzes the possibility of applying a treatment that increases the fixation of boron salts in stony materials, with the aim of extrapolating its application to outer facades exposed to different humidity conditions.

2. MATERIAL AND METHODS

2.1. Stony substrates and methods used for their characterization

Two different ornamental rocks, widely used in the architectural heritage around the world, especially in Spain, since before the XIXth century [41,42], and with high susceptibility to deterioration due to their high porosity, were selected. A Redueña specimen (cretaceous dolostone extracted from quarries located at Redueña, municipality of Madrid [43,44]), and a Fantasy Bateig specimen (limestone extracted from quarries located between Elda and Novelda, both municipalities of Alicante [42]).

In this study a total of 9 cylindrical samples per stone, of 54 mm in diameter and 30 mm length, were used. From these, twelve specimens (six of Redueña dolostone and six of Fantasy Bateig limestone), were used to evaluate the treatment. The rest of the samples were used as a reference.

111 To characterize both stones, the following properties were determined:

112 - Mineral phase identification carried out by X-ray diffraction using a Philips XPERT-
113 PRO, XCellerator X-ray diffractometer with RTMS detector, operating in a continuous
114 mode, over a 2θ range of 4° to 80° with a 0.0334° step size and a 50.165s count time per
115 step, and Cu-K alpha radiation. The mineral identification was carried out based on the
116 information reported by the Joint committee on powder diffraction standards (JCPDS),
117 the International Center for Diffraction Data (ICDD), and the American Mineralogist
118 Crystal Structure (AMCSD) databases.

119 - Petrographic characterization using the Polarized Light Optical Microscopy (PLOM)
120 technique from samples previously polished and stained with methylene blue. This
121 impregnation allowed the pores identification and possible fracturing of the stones before
122 and after treatments. Thin sections were studied using the Olympus Trans-Ref BX 53
123 petrographic microscope equipped with a fluorescence mercury lamp and filters for
124 obtaining images in bright field (FBF), dark field (FDF), and fluorescence (FBFL and
125 FDFL). Thus, it was possible to use the polarizers and adjust the intensity in transmitted,
126 reflected, and fluorescence modes operating simultaneously with the Olympus Stream
127 Essential software.

128 - Textural properties and chemical composition using environmental scanning electron
129 microscopy (ESEM), and energy dispersive X-ray spectroscopy (EDX) using a FEI
130 Inspect ESEM, equipped with an EDS probe operating in low vacuum mode using
131 secondary (SE) and back scattered electron (BSE) detectors. EDS technique included the
132 detection of chemical elements and its spatial distribution providing the respective
133 mapping images of each element. Image analysis and surface porosity characterization
134 using image J and Digital micrograph software packages.

- Physical properties related to the pore structure such as: water accessible porosity (using 9 samples and following [45]), pore size distribution, and mercury accessible porosity. In the latter two cases, the measurements were conducted, in duplicate, using an Autpore IV9500 porosimeter of Micromeritics, which allows characterize those pores with an access diameter between 360 μm and 3.8 nm. The tortuosity of the pore network was also determined from the porosimeter data using the equation given in [46].

- The anisotropy of a material as well as the presence of fractures or voids within the material that may affect its mechanical behavior was measured as an indirect method by Ultrasonic pulse velocity (UPV) using a PUNDIT CNS Electronics (precision: $\pm 0.1 \mu\text{s}$) and transducers of 1 MHz of frequency and 11.82 mm in diameter. The measurement mode was direct, coupling the transducers on the two surfaces that were in contact with the electrolytic cells during the treatment. A total of 10 measurements for all the nine specimens per stone were taken, taking the average of the eight central values as the accepted value.

- Color characterization, as the main aesthetic property of the material, carried out for all the nine specimens per stone in both cylindrical surfaces. For this purpose, 20 random measurements were made per surface (i.e., 20 measurements per specimen), using a Minolta CM-700d spectrophotometer, and expressing the color in the CIE Lab color space. The measurements were taken including the specular component, with a spot diameter of 8 mm, using a D65 illuminant, and an observed angle of 10° .

2.2. Electrokinetic setup and precursors

The setup and the procedure used to carry out this electrokinetic treatment was similar to that explained in previous studies [38–40], except that the precursors used were different.

Figure 1 shows a schematic drawing of the assembly used, in which there are two compartments, one anodic and the other cathodic, one in front of the other (direct mode of application), separated by the porous material to be treated. To carry out the application of this treatment on the same surface such as a wall, it is only necessary to place the compartments in parallel (indirect mode), as shown in [47,48]. Each of the compartments is formed by three cells (from C1 to C3).

The role of each of the cells within the assembly is as follows:

- Cells C1 placed farther away from the material to be treated house the electrodes, in this case mixed metal oxide-coated titanium electrodes, and the solution containing the precursors selected for the electro-precipitation process.

- Cells C2 house poultices of different composition, depending on the compartment in which are hosted, whose main mission is to buffer the extreme pH values that are expected to reach in the cells C1, due to the electrolysis of water that takes place on the surface of the electrodes. In this study, a poultice made of magnesium carbonate: kaolin: ultrapure water in a proportion 2:1:6 by weight was used in the anode, and a poultice made of kaolin: ultrapure water in a proportion 1.5:1 by weight was used in the cathode. The efficacy of both poultices as pH buffering media has already been proven in previous studies [39,40].

- C3 cells, which are in direct contact with the material to be treated, has only the solutions containing the precursors to be mobilized.

It should be noted that once the electric field is established between the electrodes of the system, the current would be transported in the metals by the electrons, while in aqueous media with soluble ions the transport of the current is due to the mobilization of these ions towards the electrode of opposite polarity. Therefore, a correct disposal of the

precursors in their corresponding compartment will facilitate their entry into the material to be treated, as shown in Figure 1.

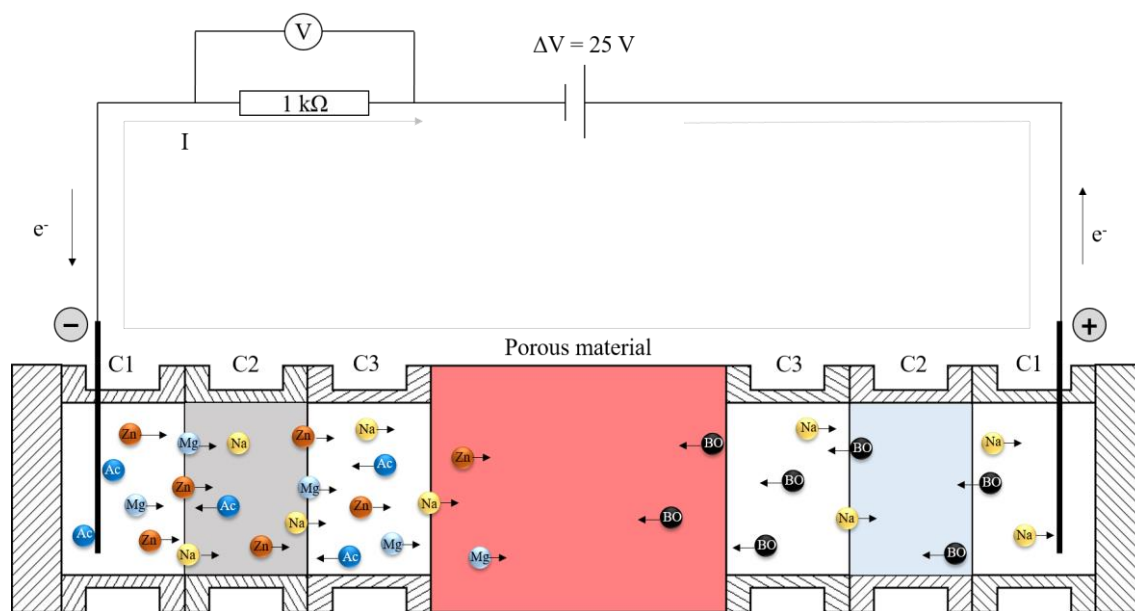


Figure 1. Schematic draw of the assembly used, in direct mode, to precipitate different boron salts into the porous material. The distribution of the cells, which hosted the different elements used (i.e., poultices, solutions, electrodes), can be noted. Also, the initial distribution of the anions and cations used as precursors, and their forced migration, is shown.

The selection of compounds more suitable for the electro precipitation was carried out considering the enormous versatility of the applied procedure. Among its advantages, this method allows the in-situ crystallization of different types of inorganic compounds along the surface through which the electric field circulates, increasing the penetration depth of the treatment and its retention into the material without causing a decrease in biocidal efficacy. The following premises were established for the selection of the compounds: 1) The compounds must not be toxic for humans or the environment. That is why the borates

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200 were chosen; 2) the compounds should release borate under a wide range of humidity
201 conditions. This ensures that, regardless of whether the humidity conditions are low or
202 high, the material is always protected against the possible entry of microorganisms; 3)
203 these compounds must have different solubility in order to increase the durability of the
204 treatment over time. Based on these premises, it was decided to carry out the precipitation
205 of borates of different solubility such as zinc borate (low solubility), magnesium borate
206 (intermediate solubility) and sodium borate (high solubility). For this purpose, the
207 following solutions were prepared:

- 208 - Anode solution (source of the cations supplied to the porous material). A mixture
209 of different acetates solutions (0.5M zinc acetate, 0.5M magnesium acetate, and
210 0.5M sodium acetate), with a 1:2:2.5 molar ratio of Zn^{2+} : Mg^{2+} : Na^{+} respectively
211 was used to facilitate a higher concentration and subsequent precipitation of the
212 most soluble compounds inside the material (compounds that are logically more
213 difficult to precipitate).
- 214 - Cathode solution (source of the anions supplied to the porous material). A
215 supersaturated sodium tetraborate solution was used. This concentration was used
216 since the larger size of the borate molecule influences in its lower mobility with
217 respect to the cations that are being mobilized from the anode. Therefore, as stated
218 in [49], a higher concentration of these molecules should favor a good
219 penetrability of this compound before precipitation begins.

220 The procedure applied to carry out the precipitation of the different boron salts was done
221 in two phases between which both the polarity and the arrangement of the precursors were
222 repositioned in their respective compartment. Detailed information about this procedure
223 is found in [40]. In this study, a constant voltage of 25 V was applied, which corresponds
224 to an initial current density in the range of 1.5-2.5 A/m². During treatment, the current

flowing through the stony materials and their resistance was monitored to determine the moment when the second phase of treatment should be applied (instant at which the current is very low, and the resistance of the material increases considerably). As shown in previous studies, these parameters are usually applied as a measure of the sealing process of the porosity [39,40,49].

2.3. Methods applied to assess the treatment effectiveness

At the end of the treatment, some of the analysis detailed before in section 2.1 were repeated, to assess the variations caused by the electroprecipitation of the boron salts generated into the stony materials, using the same equipment and methodologies. Specifically, the following parameters were evaluated:

a) Post-treatment weight gain (WG), as a measure of the matter that remains precipitated inside the material. For this purpose, the samples were left to dry in an oven at 50°C, both before and after treatment, until a constant weight was reached. The percentage of weight gain was calculated as follows:

$$WG (\%) = 100 \cdot (W_0 - W_f) / W_0$$

where W_0 , W_f correspond to the constant weight before and after treatment respectively.

b) Total boron content. For this purpose, a piece of each treated sample, extracted by hammer and chisel along its entire vertical section, was crushed and homogenized. 1 g of each powder sample was stirred in 25 mL of ultrapure water during 24 h. After filtration, the boron content was quantified by inductively coupled plasma optical emission spectrometer (ICP-OES) using a Spectro Arcos.

c) Ultrasonic pulse velocity (UPV) across the specimens, once dried.

d) Pore size distribution, mercury accessible porosity, and tortuosity. These analyses were carried out, in duplicate, on stone fragments of $2 \times 1 \times 1$ cm. Samples were extracted from both sides of the treated specimens, of 3 cm in length, to evaluate changes over the entire length.

e) Petrography study by polarized light optical microscopy (PLOM), combining transmitted, reflected, and fluorescence light, from thin sections stained with methylene blue, obtained from a cross section of the samples including the two surfaces that were in contact with the C3 cells.

f) Mineralogical identification by XRD.

g) Textural and chemical composition study by environmental scanning electron microscopy (ESEM), energy-dispersive X-ray spectroscopy (EDS), and digital image analyzing (DIA).

h) Color changes caused by the treatment, measuring ΔL^* , Δa^* , Δb^* , ΔC^* , and ΔE^*_{ab} . For this purpose, 20 random measurements were performed on each of the surfaces that were in contact with the C3 cells.

To evaluate the efficacy of the treatment against biodeteriogen agents, small fragments of treated and untreated stones, previously sterilized in an autoclave, were placed on 2% Malt Extract agar (MEA) plates where different fungal isolates were individually transferred. *Aspergillus fumigatus*, *Phoma* sp. and *Epicocom nigrum* isolated previously from Redueña quarry dolostones and identified by ITS rRNA gene sequencing were used for these experiments. Fungi were grown at 20°C until the rock fragments were covered (approximately 60 days). The extension of epilithic and endolithic fungal colonization was evaluated with “SEM-BSE technique” as it is described in [50]. Briefly, stone fragments were fixed in glutaraldehyde (3% v/v), and osmium tetroxide solutions (1%

wt/v), dehydrated in a graded ethanol series, embedded in LR White resin and finely polished. The samples were observed in backscattered electron mode using a FEI INSPECT microscope after being carbon coated.

Finally, a leaching test was performed to assess the durability of the boron salts precipitated inside the stony materials. For this purpose, two treated samples of 3 x 1 x 1 cm per treated stone were completely immersed in 100 mL of ultrapure water for 3 days, under continuous shaking at 150 rpm and 20 °C. At different time intervals (every 30 minutes once the samples were immersed for the first 6 hours and then at 24h, 48h and 72h), 1 mL of the aqueous solution was extracted and replaced with other 1 mL of ultrapure water. The total quantity of boron released into the water was measured again by ICP-OES using the same equipment as mentioned before. In addition, the amount of boron remaining in the stone samples after the leaching test was determined and compared to that exists before the process.

3. Results and Discussion

3.1. Stone properties

Figure 2 displays the textural and mineralogical properties of Redueña dolostone obtained by polarized light optical and electron microscopy techniques, XRD and the processed SEM image. It consists of an oolitic dolostone, with well-preserved ooids in a dolomitic matrix, giving place to the development of intergranular pores as observed by transmitted light images (parallel nicols, Fig. 2a). The enlarged image reveals differences in alteration of ooids with micritic texture in the inner rim and dolo-sparitic cement in the outer rim. Some grains of dolomite appear dispersed in a microcrystalline dolomitic matrix. Ooids have differences in texture between outer rim and center. Outer rim is

denser sparitic dolomite cement while inner preserves dolomicritic texture. The fluorescence image (Fig. 2c) shows differences in contrast due to de-dolomitization of dolomite in the matrix, giving place to Mg rich calcite formation (bluish-green). The ooids of dolomite have yellow and brown color and the pores appear in black. SEM-BSE images (Figs. 2d and 2e) show details of intergranular porosity, and calcite filling pore spaces as product of de-dolomitization. X-ray diffraction analysis confirms the presence of dolomite (D) as the predominant mineral and magnesian calcite (MC) in the dolostone before the treatment (Fig. 2f). The SEM image (Fig. 2g) highlights the surface intergranular porosity of 20 %, with pore spaces around $54 \times 82 \mu\text{m}$ to $50 \times 126 \mu\text{m}$. Chemical composition of Redueña dolostone obtained by SEM-EDS indicate the presence of Ca (58.16 ± 1.3 weight %), Mg (10.03 ± 0.54 weight %), and O (31.82 ± 1.06 weight %).

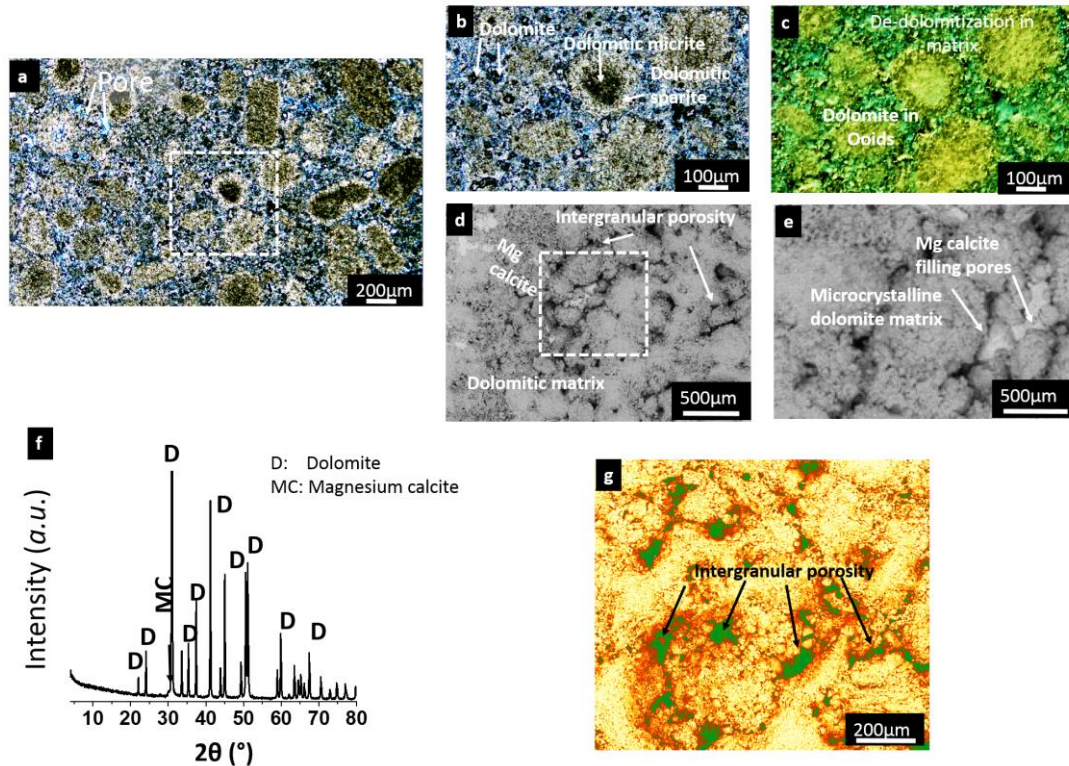


Figure 2. PLOM-ESEM images, XRD and SEM image of Redueña dolostone a) Transmitted light images (parallel nicols) showing an oolitic dolostone, Intergranular pores appear in blue. b) Enlarged image: differences in alteration of ooids c) Difference in contrast due to de-dolomitization of dolomite in the matrix, giving place to Mg rich calcite formation (green), (Fluorescence light) ESEM images (d and e) showing details of intergranular porosity, and calcite filling pore spaces as product of a de-dolomitization process. f) XRD pattern showing the main minerals of the dolostone. g) SEM image highlighting the porosity.

Figure 3 shows the optical and SEM-BSE images, XRD profile and the SEM image for Bateig stone before the treatment. Its textural and mineralogical properties correspond (Figure 3) to a type of limestone, known as biocalcarenite, where the fabric consists of skeletal shell fragments and detrital grains grouped by a calcareous matrix. The transmitted light (FBF) image (Fig. 3a) taken in parallel nicols mode shows several bioclastic fragments cemented by microsparite in a micritic matrix. The zoom image taken in reflected light (FDF) (Fig. 3b) shows some skeletal fragments filled by clay minerals or by detrital calcite and quartz grains. The methylene blue staining allows identifying details as the development of moldic porosity produced by the loss of bioclasts (Fig. 3b). The reflected light image (Fig. 3c) indicates the presence of iron oxides (in red tone) and clay minerals (brown) filling the cavities. SEM-BSE micrographs show details of the moldic porosity and microcrystalline texture of the calcareous matrix (Figs. 3d and 3e). Previous studies describe the Bateig rock as an allochemical calcareous stone composed by foraminifera, mollusks, bryozoan and echinoderm fragments [42]. Similarly, a detailed research identified the clay fraction of the same stone as consisting of glauconite and illite minerals [51]. XRD profile confirms the presence of calcite (C) as

the dominant mineral, and quartz (Q) and dolomite (D) as subordinate compounds (Fig. 3f). The SEM image (Fig. 3g) highlights the surface moldic porosity of 22.7%, generated by the bioclast fragments, developing pores around $290 \times 170 \mu\text{m}$ to $78 \times 75 \mu\text{m}$. Chemical composition of Bateig calcarenite indicate the presence of Ca (36.03 ± 1.19 weight %), Mg (0.7 ± 0.19 weight %), O (53.49 ± 1.52 weight %), C (3.3 ± 1.37 weight %) and Si (6.47 ± 0.37 weight %).

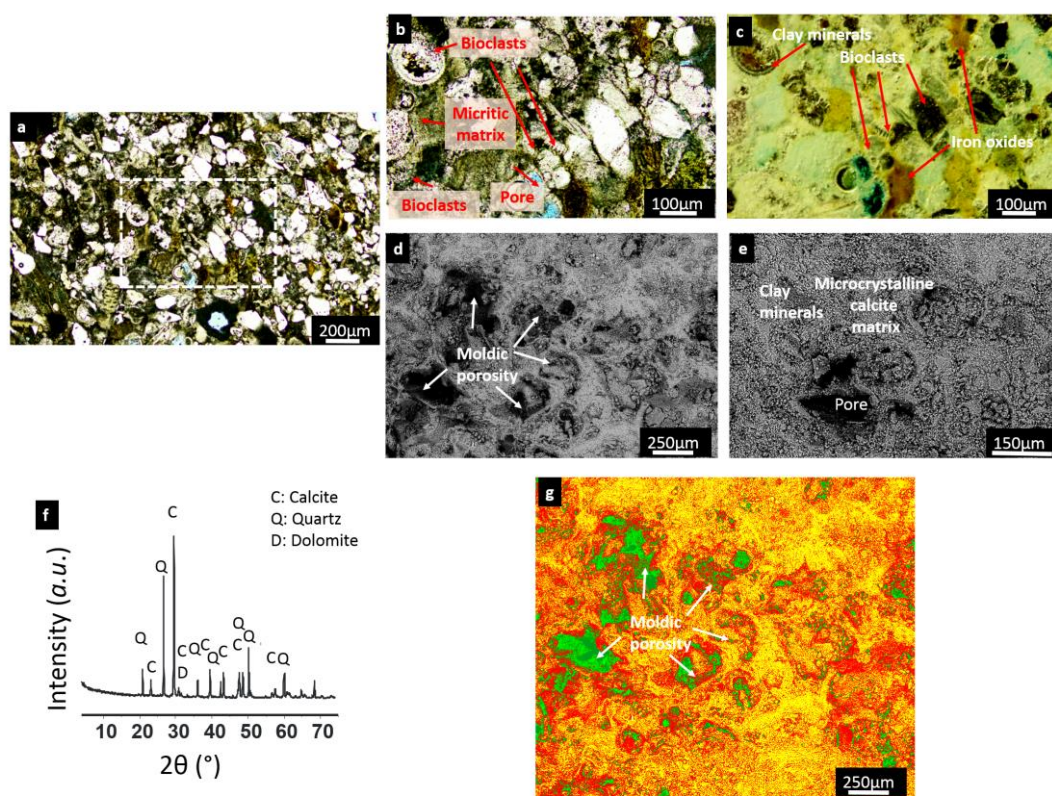


Figure 3. PLOM - SEM -BSE images, XRD profile and BSE image of Bateig calcarenite before the treatment. a) Bioclastic limestone in a micritic matrix (Transmitted light, parallel nicols). b) Zoom FDF image showing some skeletal fragments filled by clay minerals or detrital calcite grains. c) Iron oxides and clay minerals filling the cavities (reflected light image). ESEM micrographs (d and e) show details of the moldic porosity and microcrystalline texture of calcium carbonate of the matrix. f) XRD pattern showing the main minerals of the calcarenite. g) Image highlighting the porosity.

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350 The physical properties (Table 1) of both stones reveals a very high accessible porosity
 351 to both water and mercury, higher than 20% in both cases. This means that both materials
 352 are very susceptible to suffer decay processes promoted or related to the entry of water,
 353 such as the action of soluble salts or biodeterioration. Comparatively, the data indicate
 354 that Redueña dolostone has a higher porosity accessible to water than Bateig calcarenite
 355 and a lower average ultrasound pulse velocity (3506 and 3610 m/s for Redueña and Bateig
 356 respectively), due to the damping generated by higher quantity of empty spaces in its
 357 interior. In addition, its porous network is more tortuous, a negative aspect in terms of the
 358 durability of the materials since the residual moisture that may remain during the
 359 desorption processes is greater.

360

361 **Table 1.** Physical properties of Redueña and Fantasy Bateig stones.

Parameters	Redueña	Fantasy Bateig
Water accessible porosity (% v/v)	23.30 ± 2.54	21.33 ± 0.11
Mercury accessible porosity (% v/v)	21.05 ± 1.92	21.08 ± 1.86
Bulk density (kg/m ³)	2185±75	2129±2
Tortuosity	5.93 ± 1.67	3.25 ± 0.19
UPV (m/s)	3506 ± 284	3610±26

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363 The pore size distributions (see Figure 4 and Table 2) show that Redueña stone has two
 364 main pore families, one between 0.1-4 µm (peaking at 1 µm) and the other between 5-60
 365 µm, with practically all pores within the capillary range between 0.1-100 µm (95%).
 366 Fantasy Bateig, on the other hand, shows a unimodal distribution, with a pore family
 367 between 0.01-5 (peaking at 1 µm). In this case, the range of capillary pores corresponds
 368 to 80% of the detected pore volume.

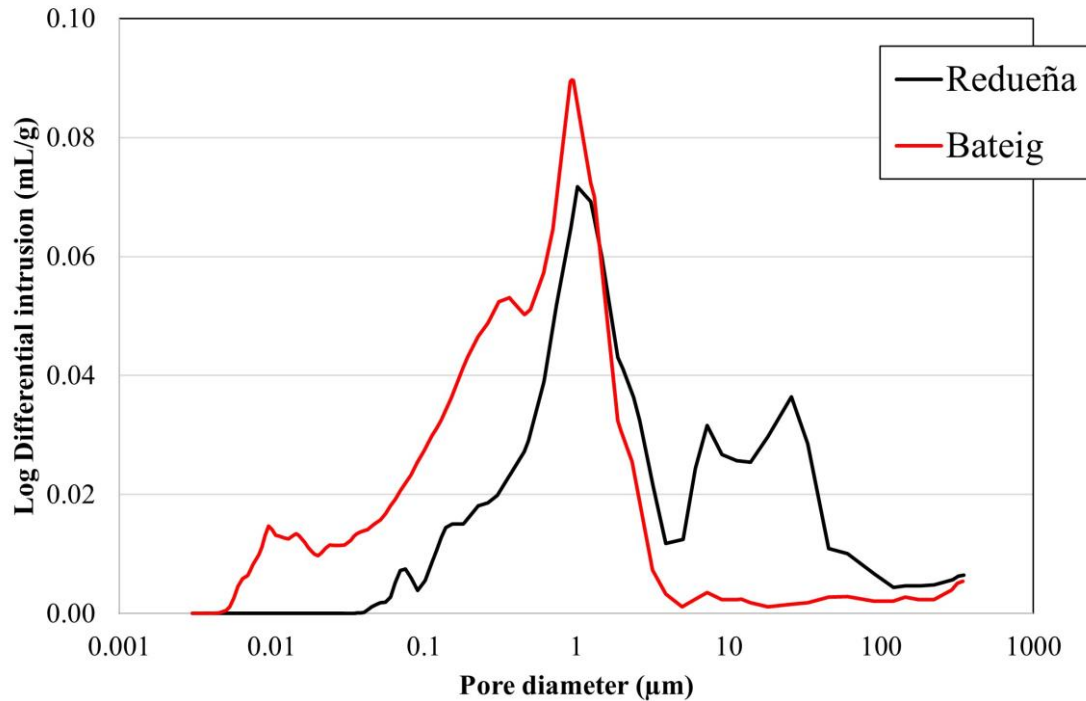


Figure 4. Pore size distribution of both untreated stones: Redueña and Fantasy Bateig.

Analyzing together the values of mercury-accessible porosity with the volume of intruded mercury in the different family ranges (Table 2), it observed that Redueña dolostone hardly presents pores below 0.1 μm , corresponding to pores that are not accessible to water (less than 2%). This fact, considering that the value of accessible porosity to mercury is lower than the value for water, indicates that Redueña stone has a significant volume of pores with an access size greater than 360 μm (upper limit of measurement of the equipment). Bateig, on the other hand, has all ranges of pore sizes, from pores that are not accessible to water (approximately 18% of its pores) to pores that would be outside the measuring range of the equipment. This fact is visible by comparing the water accessible porosity with the mercury accessible porosity value discarding the intruded volume of mercury below 0.1 μm (which would give an approximate porosity of 17.2% lower than the water accessible porosity value of this rock).

Table 2. Intruded mercury volumes for different pore size ranges (in mL/g, upper rows, and %, lower rows) for the both treated and untreated stony materials: Redueña and Fantasy Bateig. The mercury accessible porosity (MAP), the tortuosity (τ), Ultrasonic Pulse Velocity (UPV in m/s), measured from each of the cylindrical surfaces for Redueña and Fantasy Bateig, and the variation of these properties with respect to the initial one (Δ) are also shown.

Stone		Total intruded volume (mL/g 10 ³)	Pore size ranges (μ m)					MAP (%)	[Δ]	τ	UPV	[Δ]
			<0.1	0.1-1	1-10	10-100	>100					
Redueña	Untreated	87.49	0.00	1.44	26.81	35.35	2.69	21.05	-	5.93	3506 $\pm$ 284	-
	Treated	98.01	6.31	18.95	30.12	39.36	3.27	22.46	+6.7%	7.17	4142 $\pm$ 330	+18.1%
Fantasy Bateig	Untreated	94.53	17.14	51.70	22.46	2.03	1.20	21.08	-	3.25	3610 $\pm$ 26	-
	Treated	59.52	0.00	33.12	23.75	1.49	1.15	13.47	-36.08%	7.38	4097 $\pm$ 31	+13.5%
Stone		Total intruded volume (%)	<0.1	0.1-1	1-10	10-100	>100					
Redueña	Untreated	100	1.64	30.64	40.40	24.23	3.09					
	Treated	100	6.44	19.34	30.73	40.16	3.34					
Fantasy Bateig	Untreated	100	18.13	54.69	23.76	2.15	1.27					
	Treated	100	0.00	55.64	39.91	2.51	1.93					

3.2. Changes in the physical properties after treatment

Subsequent to the application of the treatment, and after drying the samples in the oven, the samples showed a certain increase in weight. This weight increasing was somewhat higher in Redueña samples (2.42 ± 0.52 g, which means a percentage increase of 1.43 ± 0.29 %) than in Bateig (1.84 ± 0.04 g, i.e., 1.07 ± 0.02 %). This greater increase in weight seems to indicate that a greater amount of material precipitated in Redueña dolostone than in Bateig calcarenite, possibly due to the greater initial porosity of this stone. This fact was corroborated by comparing the total boron content present in both stones at the end of the test (0.070 for Redueña and 0.055 for Bateig, expressed both in % B g/g).

The precipitation of boron compounds inside the pores caused an increase in the ultrasound pulse velocity of both materials (Table 2), which again indicates the existence of pore filling, similar result to that achieved in previous studies [38]. This increase was higher in Redueña than in Bateig, which is consistent with the greater increase in weight. Comparing the changes caused in the pore size distribution of both stones (see Table 2 and Figure 5), the treatment affected the porosity in different ways.

- At Redueña dolostone, the treatment caused an increase in the mercury-accessible porosity of 6.7%. This increase is due, as shown in Figure 4, to the increase in the volume of pores with access size greater than $5 \mu\text{m}$. This increase is due to the partial filling of pores that were previously larger than $360 \mu\text{m}$ (detection limit of the porosimeter) and are now within the measuring range of the equipment. Furthermore, there is a reduction in the pore volume between 0.1 to $5 \mu\text{m}$, coinciding with the appearance of a family of pores below $0.1 \mu\text{m}$, which are not accessible to water.

- At Bateig calcarenite, the treatment reduced the mercury-accessible porosity considerably (-36%), affecting the volume corresponding to each family of pores existing

in the material. In this case, porosimetry did not allow observing the existence of a partial clogging of large pores, which were not previously detected by the porosimeter.

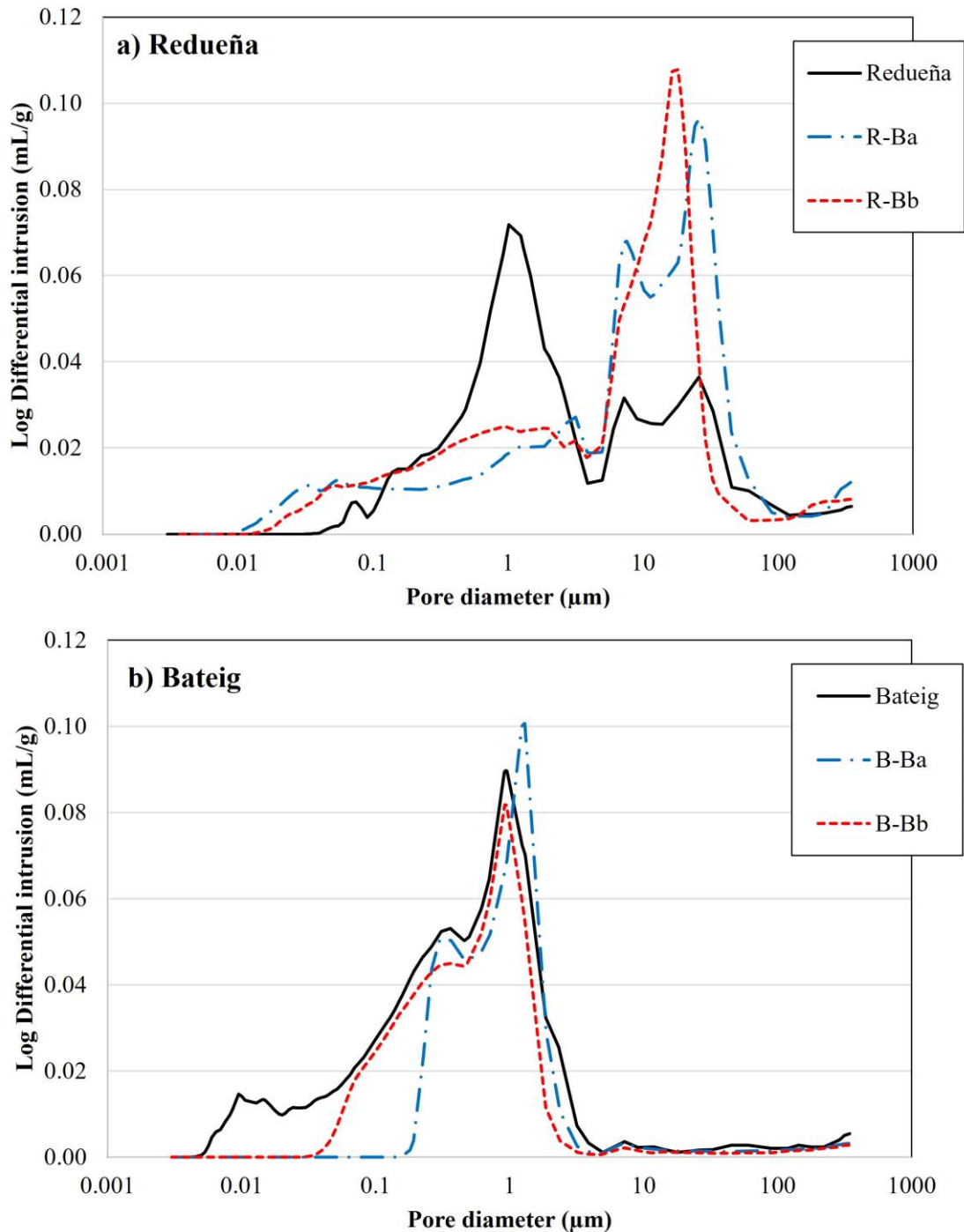


Figure 5. Pore size distribution of both treated stones, obtained from samples taken from each of the surfaces that were in contact with the C3 cells to the rock core (surface “a” in

contact firstly with the anode and during the second phase with the cathode, and surface “b” vice versa). The untreated pore size distribution is also shown.

In both cases, the treatment caused an increase in the tortuosity of the porous network due to the partial clogging of some percolating pathways (Figure 6 for Redueña and 7 for Bateig).

The treatment carried out on Redueña dolostone, as analyzed by SEM-BSE images, modified both texturally and chemically the dolomicritic matrix, as confirmed the EDS spectra of the sample before (Fig. 6d) and after treatment (Fig. 6e, f, and g). The contrast between shades of gray allows identifying different regions in which there are differences in elemental concentrations indicated as 1, 2, and 3 (Fig. 6a). The enlargement of regions 1 and 2 (Fig. 6b) shows the formation of tiny prismatic crystals in region 1, coinciding with the presence of Na (Fig. 6e). Likewise, in zone 2, a crystallization in fibers occurs, where it is detected an enrichment in Mg (Fig. 6f). The high-brightness in zone 3 (Fig. 6c) corresponds to a Zn enriched region where Na is also detected. (Fig. 6g). The contrast provided by the images allows identifying the intergranular porosity with differences in the pore filling by the new precipitates. In the area where Mg-rich compounds crystallize (Fig. 6b') there is a high reduction in intergranular porosity, in addition to generating a new intercrystalline porosity between the lamellar crystals. The local calculated porosity (in green tones) was 4.52%. It consists of intergranular pores varying between 1.32 to 1.78 μm , and intercrystalline pores between 0.84 μm to 1.32 μm . However, in the region where the Zn crystallized (Fig 6c'), the intergranular space is much large with several pore families in the ranges of 76 $\times$ 55 μm , 56 $\times$ 52 μm and 18 $\times$ 8 μm , and there was a minor reduction in porosity. In this case, the calculated porosity was 8.2%.

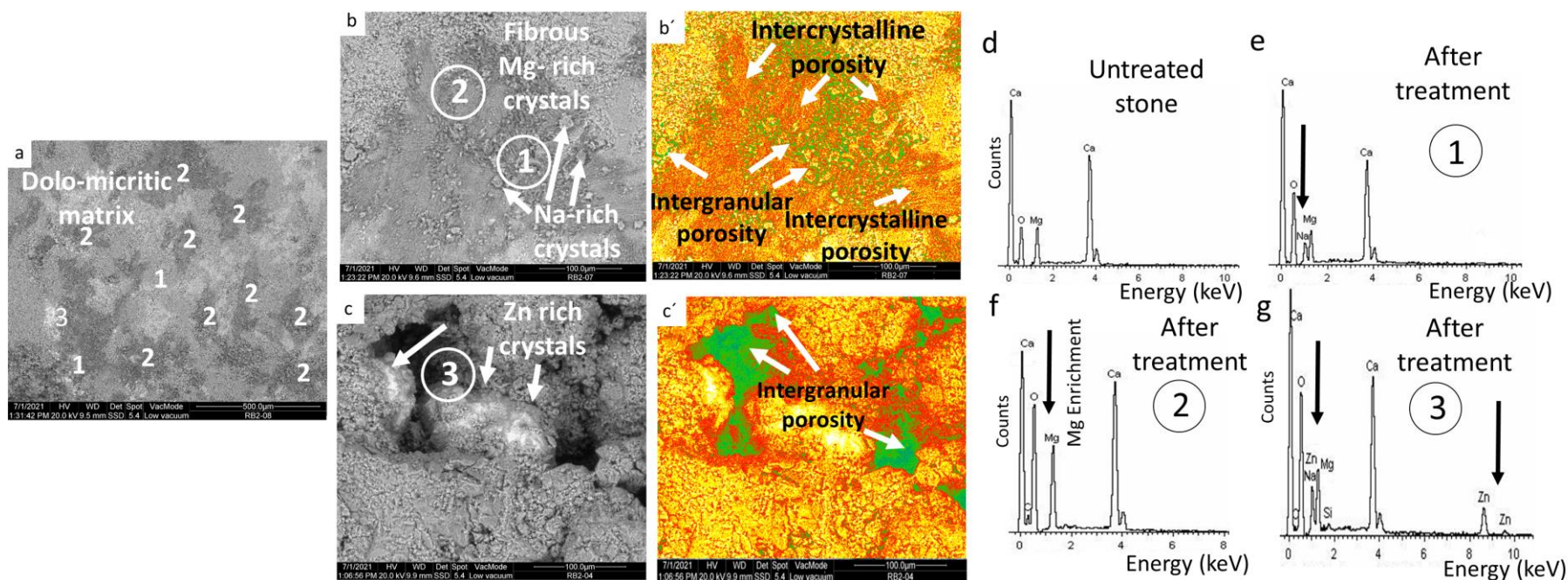


Figure 6. ESEM –BSE micrographs (cross-section) of Redueña after treatment (a), b and c showing the contrast produced by each mineralization in different zones. b' and c': images showing details of the porosity. d, e, f, and g EDS spectra taken in each region.

In the case of Bateig calcarenite, the SEM-BSE images (Figs. 7 a, b, and c) show details of the crystallized compounds beside of changes in porosity after treatment, confirmed by the EDS spectra before (Fig. 7d) and after treatment (Figs. 7e and f). A magnification of the overview shows the formation of well-formed Mg-bearing crystals (Fig. 7b), filling the pore spaces, as well as minute crystals adhering to their surface, as detected by EDS spectra, respectively (Figs. 7e and f). Although the sample initially had a low Mg content (Fig. 7d), an increase in intensity was observed due to the treatment (Fig. 7e). In the same way, the Na signal coincides with the tiny size crystals adhered to the surface of the Mg-bearing crystal (Fig. 7f). Laminar crystals appear packed around the edges of the grains corresponding to phyllosilicates whose composition is iron aluminium silicates (Fig. 7f). The images allowed to identify the existence of two types of porosity, one moldic, produced by the bioclast fragments that do not have any filling (Fig. 7b') and other intergranular porosity between the idiomorphic and sub-idiomorphic Mg-bearing crystals (Fig. 7b'), which, given their morphology, only partially fill the pores (Fig. 7c'). Several families of pores with moldic origin around $29 \times 75 \mu\text{m}$ and $12 \times 22 \mu\text{m}$ appear locally (Fig. 7b'). Similarly, pores around the grains fluctuate between thickness of $57 \mu\text{m}$, $27 \mu\text{m}$ and $6.7 \mu\text{m}$, controlled by the Mg crystal morphology. The calculation of surface porosity obtained a value of 11.6% after treatment.

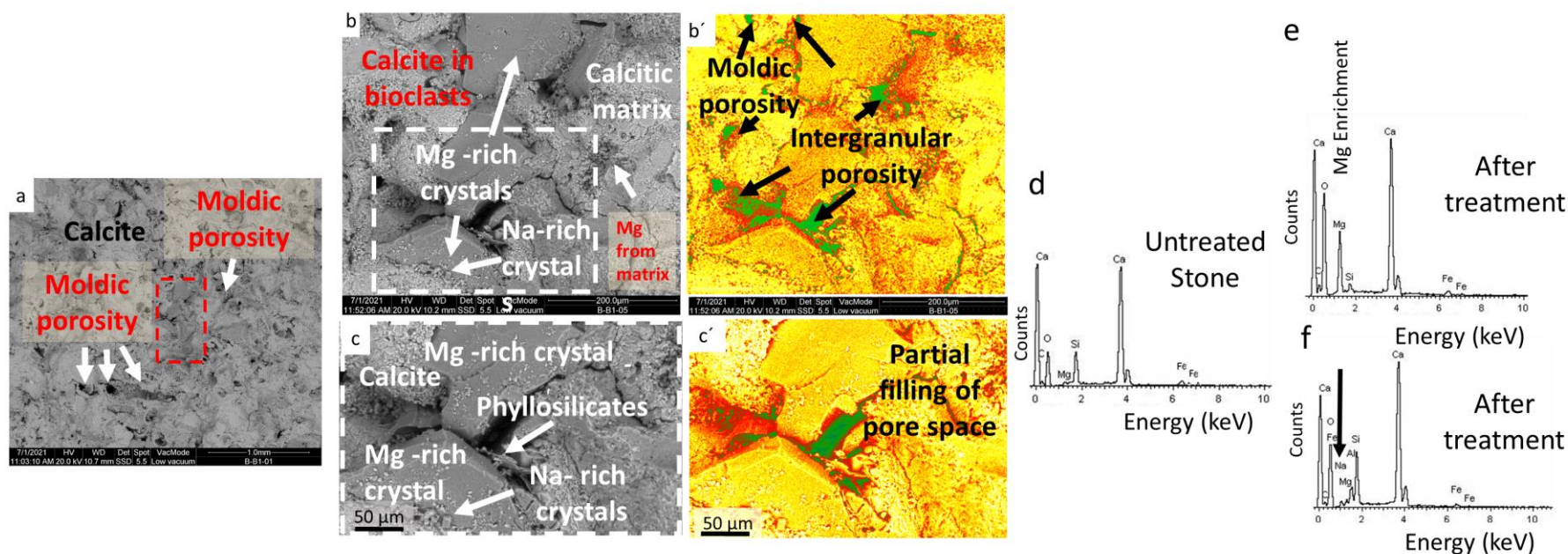


Figure 7. ESEM- BSE micrographs (cross-section) of Bateig calcarenite after treatment a, b details of the mineralization. b' and c' images obtained from b and c showing the porosity. d, e, and f EDS spectra taken in each region

The petrographic analysis of the treated Redueña dolostone (Figure 8) showed differences between the low magnification image in transmitted light (FBF) (Fig. 8a) and its corresponding image obtained by fluorescence (Fig. 8a'). While the FBF image shows a similar texture to the untreated dolostone, the enlarged fluorescence image (FBFL) shows black prismatic crystals (60-100 μm) and occasional white prismatic crystals (100-200 μm). Details of crystallization in fibers (Fig. 8b) is visible in the enlarged images taken by fluorescence and SEM-BSE (Fig. 8b'). The acicular crystals appear scattered and preferentially oriented, filling the pores or superimposed on the dolomitic matrix (Fig. 8b), in yellow tone, sometimes acquiring a blue hue probably by the blue methylene impregnation. The SEM-BSE image confirms this type of crystallization, coinciding with an increase in Mg content, in addition to occasional minute crystals rich in Zn (Fig. 8b'). The average size of needle-like crystals is 20 μm x 1 μm . The acicular crystals give a light-yellow tone in the fluorescence image (Fig. 8c), while non fluorescent minute crystals exhibiting black color (Fig. 8d) correspond to prismatic Na-bearing compound (Fig. 8d'). Based on XRD results (Fig. 10a), the acicular crystals could correspond to the magnesium borate hydroxide, of which the natural counterpart is known as Wightmanite [52] and non-fluorescent prismatic crystals to sodium boron hydroxide. Table 5 summarizes the morphological and chemical specifications of each mineralization. The high brightness contrast observed in the SEM-BSE images taken in the Zn-rich region confirms the formation of Zn borates on dolomite (Figs. 8c' and 8d'). These crystals form a layer of aggregated made up of individual tiny crystals. XRD measurements (Fig. 10), as described below, confirm the formation of Zn borate hydrate. The respective selected area EDS analyses confirm the energy signals for Mg, Zn and Na compounds (Table 3).

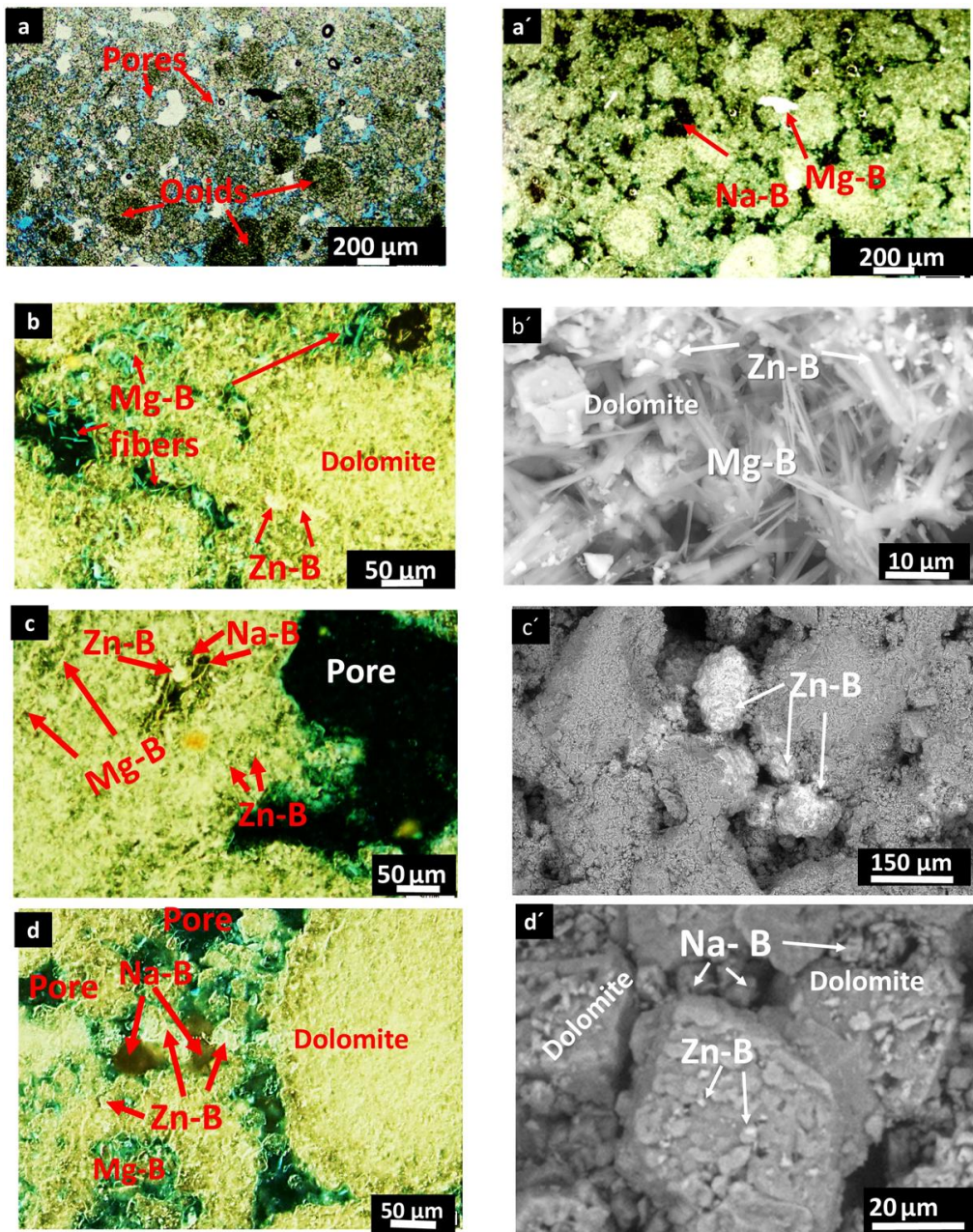


Figure 8. PLOM and ESEM (BSE) images of Redueña dolostone after treatment. Low magnification PLOM image in transmitted light (a) and fluorescence mode (b) mineralization of prismatic (black) and columnar crystals (white) in the dolomicritic matrix (fluorescence light) b) Fibrillar and short prismatic crystals growing on dolomite grains, pores and filling intergranular space. b') acicular crystals in Mg-rich zone, and small crystals in Zn-rich area (SEM-BSE). c) Details of acicular, dark prismatic and pale-yellow crystals (fluorescence light). c') bright grey crystal in a Zn-rich zone forming a

layer of tiny agglomerates on the dolomite (SEM-BSE) d) F Zn borate, Na and Mg borate fibers growing on the matrix (fluorescence light) d') mineralization in Na and Zn rich zones (BSE). (Mg-B, Zn-B, and Na-B correspond to the respective borate compounds).

Table 3. EDS analyses obtained for Mg, Zn and Na compounds crystallized in Redueña dolostone.

Element	Weight%	Weight% Sigma	Compound
Ca	27.88	1.72	Mg compound (Fig 8 b')
O	61.11	2.21	
Mg	11	1.02	
Si	0.64	0.15	
Ca	11.8	0.49	Zn compound (Fig 8 c')
O	43.76	1.38	
Zn	36.21	1.3	
C	2.09	1.79	
Ca	17.21	0.57	Zn, and Na compounds (Fig 8 d')
O	53.4	1.28	
Mg	8.31	0.46	
Na	0.5	0.17	
Zn	17.38	0.92	
C	1.29	0.495	

In Bateig calcarenite, the treatment leads to the crystallization of new compounds, as observed by transmitted light and fluorescence images (Figure 9). FBF image allows identifying textural and mineralogical features, as well as details of the porosity highlighted in dark blue due to methylene blue staining (Fig. 9a). The contrast provided by the fluorescence image indicates the presence of black prismatic crystals and regions of yellowish coloration on a highly porous surface. The micritic matrix produced an intense bluish green coloration (Fig. 9a'). Similarly, the contrast produced by the fluorescence image (Fig. 9b) indicates the presence of non-fluorescent prismatic crystals

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513 embedded in the calcitic matrix. The same sight shows a layer of pale yellow to white
514 massive and short prismatic crystals covering the matrix. The SEM-BSE image (Fig. 9b')
515 shows a well-crystallized Mg-rich prismatic crystal, and tiny Zn-rich crystals. The
516 development of porous surfaces with light yellowish contrast obtained by fluorescence
517 (Fig. 9c) coincides with the presence of Zn-enriched crystals with bright grey tones
518 deposited in highly porous areas as shown in the BSE image (Fig. 9c'). These crystals
519 appear as patinas on the surface of the micritic matrix. In general, Zn-rich crystals appear
520 in neighboring areas where non-fluorescent prismatic compounds crystallize as visible in
521 dark color in the FBFL image (Fig. 9d). The same region in SEM- BSE mode shows
522 prismatic crystals (Fig. 9d'), coinciding with Zn rich zones, and rhombohedral crystals
523 where Na was centered. XRD results confirmed the formation of Mg borate hydrate,
524 with a structure similar that of the mineral known as Admontite, reported to form well
525 crystallized euhedral crystals depending on the synthesis conditions [52]. The bluish
526 green coloration fluorescence emission of calcite in this kind of biocalcarene could be
527 produced by the presence of organic activators or electron defects in the crystal structure
528 [53,54]. The respective selected area EDS analyses confirm the energy signals for Mg,
529 Zn and Na compounds (Table 4).

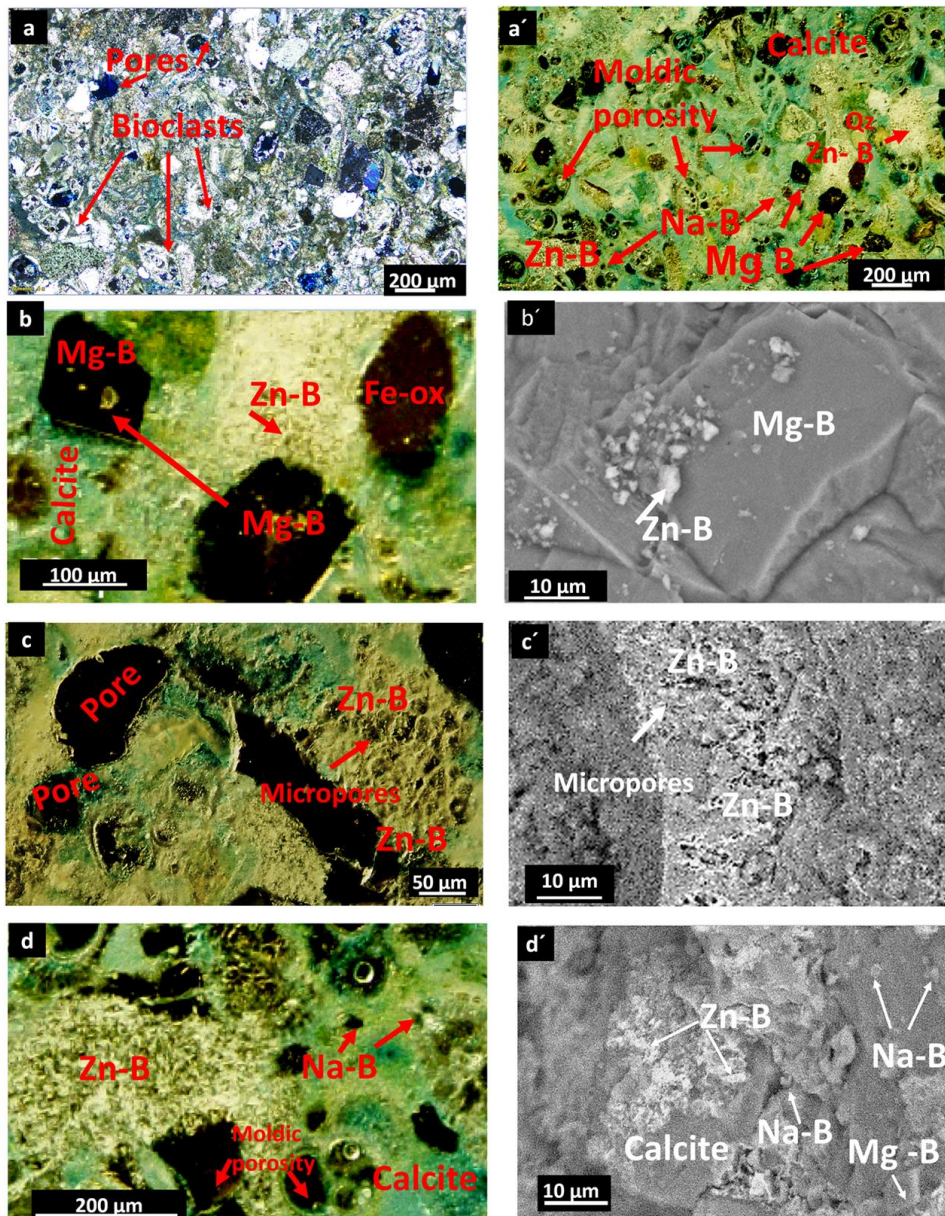


Figure 9. PLOM and ESEM (BSE) images of Bateig calcarenite after treatment. Low magnification images in transmitted light (a) showing pores (dark blue, crossed nicols) and the texture of the calcarenite. (a') Different crystals in dark color and yellow in a micritic matrix green colored (Fluorescence light) b) Fiber like crystals growing attached on the bioclasts, over micritic matrix and on pores. Calcite looks in green tone. (Fluorescence light b') BSE image showing fibers in Mg-rich zone. c) Mineralization in pale yellow areas with development of highly microporous surface (Fluorescence light) c')

BSE image showing bright grey contrast mineralization in Zn-rich zone. d) Black prismatic and pale-yellow crystals in a calcitic matrix green colored (Fluorescence light) d') BSE image showing a Zn-rich area and prismatic well-defined crystal in a Na-rich area. (Mg-B, Zn-B, and Na-B correspond to the respective borate compounds).

Table 4. EDS analyses obtained for Mg, Zn and Na compounds crystallized in Bateig calcarenite.

Element	Weight%	Weight% Sigma	Compound
Ca	60.08	0.78	Mg compound (Fig 9 b')
O	30.80	0.7	
Mg	7.031	0.46	
Zn	1.99	0.19	
Ca	21.79	2.01	Zn compound (Fig 9 c')
O	41.46	3.82	
Zn	27.51	3.54	
Si	9.23	1.3	
Ca	27.89	0.69	Mg, Zn, and Na compounds (Fig 9 d')
O	56.63	1.06	
Mg	2.94	0.34	
Na	1.16	0.19	
Zn	1.09	0.23	
Si	6.73	0.28	

Figure 10 shows the comparison between XRD profiles obtained for Redueña dolostone (Fig. 10a) and Bateig calcarenite (Fig. 10b), before and after treatments. These XRD results confirm the formation of different borates after treatment. In Redueña dolostone, low intensity peaks appear to be associated to the dolomite, calcite and quartz visible in the zoom image. The Bragg peaks are ascribable to those of magnesium borate hydroxide, Na borate hydrate and Zn borate hydrate. In all cases, the new compounds are hydrated

phases, with variable content of hydroxyls. In the case of Bateig calcarenite, additional Bragg peaks to those of calcite (C), quartz (Q), and dolomite (D) occur, ascribable to new precipitates. The zoom image shows intensity peaks concerning to Mg borate hydroxide, Na borate hydrate and Zn borate hydrate. Table 5 summarizes the reference code of each crystalline compounds with good agreement with the experimental data. However, it is not ruled out the presence of intermediate phases below the XRD detection limit.

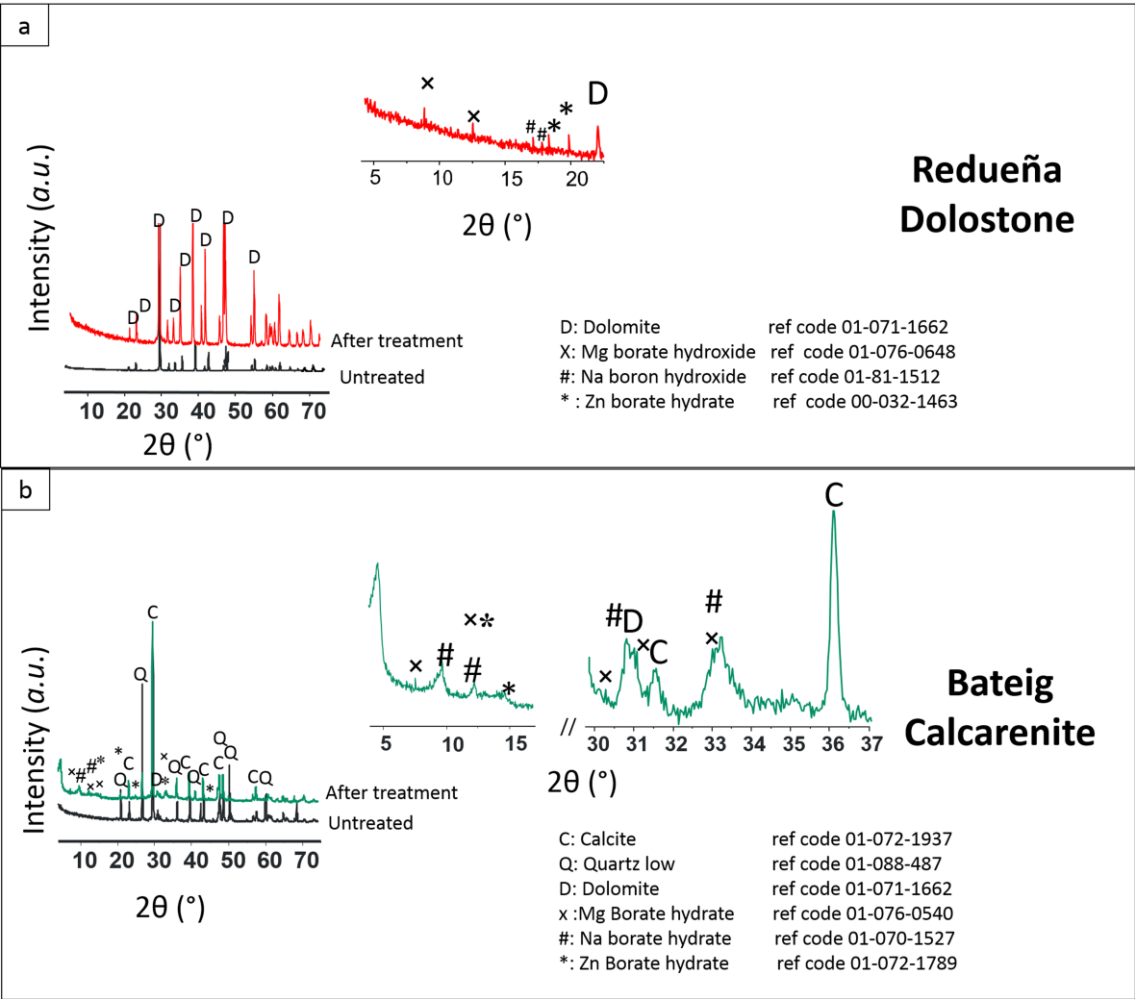


Figure 10. XRD analysis of Redueña dolostone (a) and Bateig limestone (b) after and before the treatment.

Table 5. Crystalline compounds identified by polarised light optical microscopy, SEM, and XRD, before and after the treatment.

Mineral Compound	Mineral name (Ref. code)	Specifications
REDUEÑA DOLOSTONE		
Calcium Magnesium Carbonate $\text{CaMg}(\text{CO}_3)_2$	Dolomite (01-071-1662)	Dominant phase forming the dolomicritic matrix
Calcium Carbonate CaCO_3	Calcite (01-072-1937)	Product of de-dolomitization of Ca-Mg carbonate
Mg borate hydroxide $\text{Mg}_5(\text{BO}_3)\text{O}(\text{OH})_5 \cdot 2(\text{H}_2\text{O})$	Wightmanite (01-076-0648)	Radiated and isolated acicular fibers filling pores ranging from $20 \mu\text{m} \times 1 \mu\text{m}$ to $36 \times 6 \mu\text{m}$
Na boron hydroxide $\text{NaB}(\text{OH})_4$	(01-81-1512)	Non fluorescent prismatic crystals $\sim 23 \times 21 \mu\text{m}$ to $40 \times 40 \mu\text{m}$ growing near Zn enrichment areas
Zn borate hydrate $\text{Zn}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$	(00-032-1463)	Aggregates of $140 \times 110 \mu\text{m}$ including crystals around $12.7 \times 7.4 \mu\text{m}$
BATEIG CALCARENITE		
Calcium Carbonate CaCO_3	Calcite (01-072-1937)	Bluish green fluorescence massive and microcrystals in matrix and sparitic cement in bioclasts
Calcium Magnesium Carbonate $\text{CaMg}(\text{CO}_3)_2$	Dolomite (01-071-1662)	Massive crystals giving low grey tones in SEM-BSE included in matrix
Silicon dioxide SiO_2	Quartz low (00-005-0490)	Sub-angular to sub-rounded grains of $73 \times 51 \mu\text{m}$ to $67 \times 67 \mu\text{m}$ randomly dispersed in the matrix
Mg borate hydrate $\text{MgO}(\text{B}_2\text{O}_3)_3(\text{H}_2\text{O})_7$	Admontite (01-076-0540)	Non fluorescent prismatic crystal from $150 \times 115 \mu\text{m}$ to $15 \times 10 \mu\text{m}$
Na borate hydrate $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2(\text{H}_2\text{O})_3$	Kernite (01-070-1527)	Non fluorescent short submicronic prismatic crystals $< 1.2 \mu\text{m}$ with predominant particle sizes $\sim 580 \times 340 \text{ nm}$
Zn borate hydrate $\text{Zn}(\text{B}_3\text{O}_3(\text{OH})_5)\text{H}_2\text{O}$	(01-072-1789)	Yellowish fluorescence massive and short prismatic crystals $0.82 \times 0.97 \mu\text{m}$ to $0.47 \times 0.6 \mu\text{m}$

Figures 6 and 11 show SEM micrographs of Redueña. The results previously observed, when analysing the variation caused in the physical properties of the treated materials, are refuted when observing under the microscope the changes caused by the treatment in the porosity of the material.

In Redueña, the treatment caused a substantially reduction in the porosity, especially through the precipitation of compounds rich in zinc and magnesium, which were not original to the untreated dolostone. Sodium-enriched compounds were the ones that developed smaller particles dispersed throughout the matrix or concentrated in the areas with Zn enrichment. Although the crystallization is poorly visible, due to the particle size and limited by the SEM resolution, it can be more effective during cell interaction as observed in specific procedures.

Considering the XRD results (Fig 10), the boron-sodium compound identified corresponds to a boron-sodium hydroxide with formula $\text{NaB}(\text{OH})_4$ (Table 5), reported as highly soluble in low boron concentrations [55–57]. Its high solubility could justify the dispersion of Na throughout the entire surface, which can concentrate in the areas surrounding the crystallization of Zn-enriched compounds, which would act as a barrier for its dispersion.

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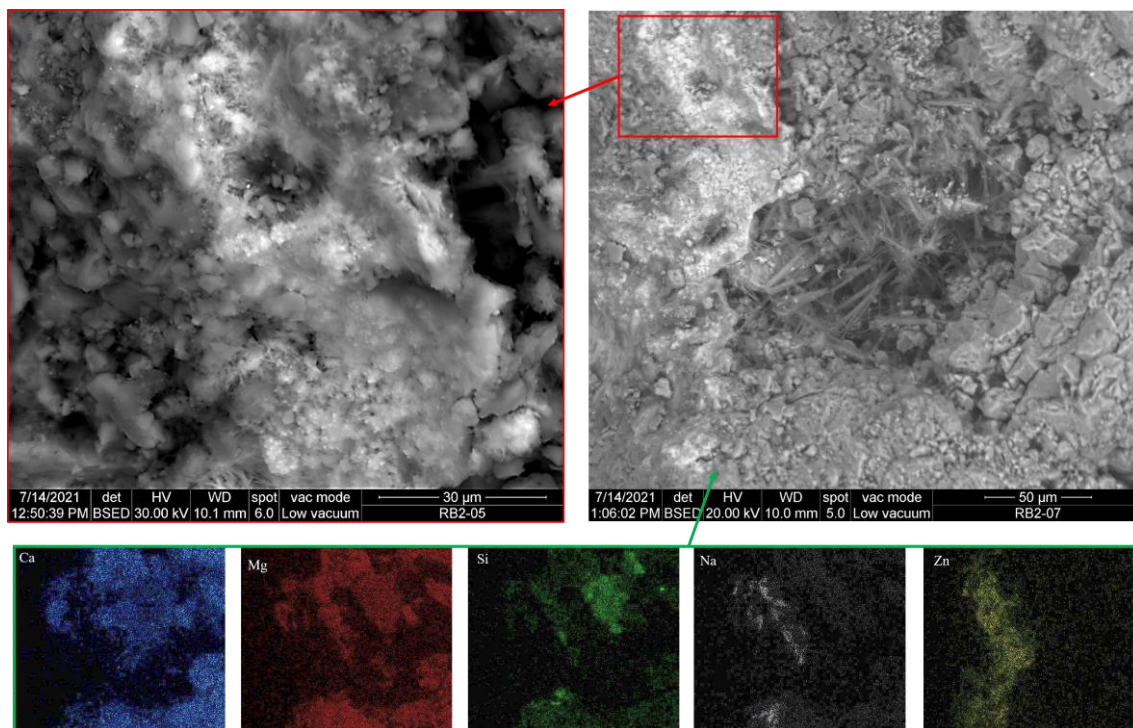


Figure 11. ESEM micrographs (cross-section) of Redueña dolostone treated with borates of different solubility and the corresponding EDX mapping.

As mentioned above, the crystallization habit of the precipitated magnesium salts was mainly acicular. These crystals not only filled the large pores, but also formed in narrow pores and even between the gaps left by the precipitation of other precipitated compounds, as observed at high magnification in the precipitation zone of the Zn enriched boron crystals, (Figure 11). In Redueña, the zinc boron salts form granular crystals, precipitating mainly in certain areas of the dolostone forming columns as a barrier.

With respect to Bateig calcarenite (Figures 7 and 12), it was also observed that the treatment caused a reduction in porosity through the neoformation of new crystalline compounds mainly composed of magnesium and zinc. Similar to Redueña stone, the presence of sodium appeared associated with the zones where zinc also precipitated. Furthermore, low magnification mappings showed evidence of Na dispersion throughout

the entire sample. In this rock, the magnesium was distributed along the whole section of the treated sample, forming euhedral and subhedral crystals. Due to developing well-defined shapes, there is not complete filling of the pore surface, leaving gaps, with a consequent low reduction in porosity. The zinc salts again presented a granular habit, accumulating in this case in the areas closest to the surface.

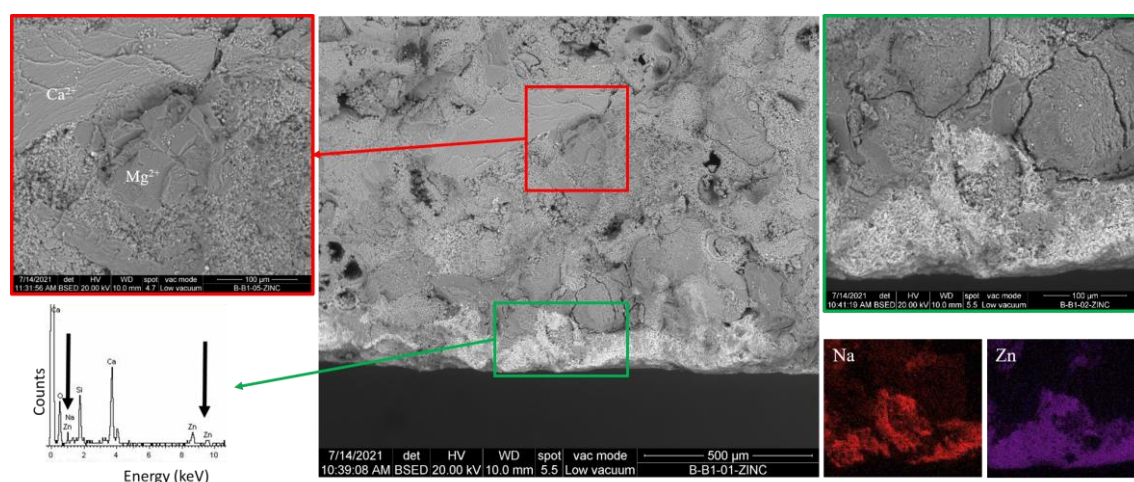


Figure 12. ESEM micrographs (cross-section) of Bateig limestone treated with borates of different solubility and the corresponding EDX mapping.

Comparing the two rocks, the penetration depth and the consequent precipitation of zinc compounds seem to be lower in Bateig than in Redueña dolostone. Combining the surface porosity results obtained from digital image analysis, and the elemental distribution mapping results by SEM, it is possible to establish a comparison between both types of rocks. As observed, the treatment's effect on Redueña dolostone reduced the porosity from 20% to 8.2%, conditioned by the type of crystallized compound. However, there is a notable difference between the zone with fibrous crystals rich in Mg, with the generation of an intercrystalline porosity, and that rich in Zn, where intergranular porosity

predominates. Considering that the original pores range between 50 x 80-120 μm , the zones occupied by Mg-salts reduced pore spaces to values around 1 μm thick, helped by smaller crystals enriched in Na. While, in the Zn-rich zones, the arrangement of the crystals failed to significantly reduce the pores (predominantly around 50x70 μm), despite the crystallization of tiny Na crystals in neighbouring zones.

The treatment of the Bateig calcarenite reduced the surface porosity from 22% to 11.6%.

Due to local filling by Mg-rich crystals, the pore dimensions decreased from 290 x 170 μm to 29 x 75 μm . However, as previously mentioned, the filling of pores with euhedral or subhedral crystals proved to be morphologically dependent, which limits the effectiveness of the precipitated crystals. In the case of Zn-enriched crystals, their dispersion is limited to covering the edge of the rock, which does not contribute to reducing porosity.

These results suggest that either the connection between the pores, the ion mobility during the treatment (which will influence the penetrability especially of the less mobile ions), and the pH characteristic of the stones might influence on the crystallization process of the boron salts. As previous researches report, there is a pH dependence resulting in a clue factor to maintain the equilibrium of the system [58], even changing its dispersion mechanism [55] or by the temperature fluctuations [59,60]. Similarly, the chemical properties depend on their morphology and particle size [55].

Furthermore, based on the porosity study by SEM, in both cases it is possible to deduce that the treatment does not generate fractures in the rock. The in-situ electrochemical precipitation occurs within the stone's pores without exceeding the surrounding spaces as observed in previous works [61]. Besides, no new fractures appear around the precipitation zones, which rules out that the compounds can generate excessive pressures when formed. In this case, the current continually circulates through less-resistance areas.

Therefore, as the compound's precipitation occurs, the empty space begins to block, increasing the resistance to the passage of the current. This situation causes the mobilization of the ions to continue through other pores and favours precipitation to occur in different spaces. Therefore, no excessive super-saturation could push overpressures against the walls of the pores.

3.3. Color changes

Table 6 shows the color changes detected after the treatment. These data suggest that the most noticeable changes in both stones mainly affect the luminosity coordinate, decreasing in general with respect to its original value. Although in some cases the overall color changes (ΔE^{*ab}) were greater than 3, a value established by [62] as appreciable by an unexperienced observer, these were not really noticeable.

Table 6. Colorimetric variations (ΔL^* , Δa^* , Δb^* , ΔC^*), and total color difference ΔE^{*ab} detected on the two surfaces that were in contact with cells C3: (Surface “a” in contact firstly with the anode and during the second phase with the cathode, and surface “b” vice versa).

Stone	Surface	ΔL^*	Δa^*	Δb^*	ΔC^{*ab}	ΔE^{*ab}
REDUEÑA	a	-2.8	0.6	-0.64	-0.5	2.9
	b	-4.4	0.9	2.1	2.2	5.2
FANTASY BATEIG	a	1.5	-0.1	-1.6	-1.6	2.2
	b	-3.4	0.3	-0.1	-0.1	4.2

3.4. Efficacy test

Figure 13 shows the differences between fungal isolates growth in presence of treated and untreated Redueña and Bateig stone fragments. Both types of stone were observed

extensively colonized for untreated fragments (Fig. 13, above row) and without apparent colonization for treated samples (Fig. 13, bottom row).

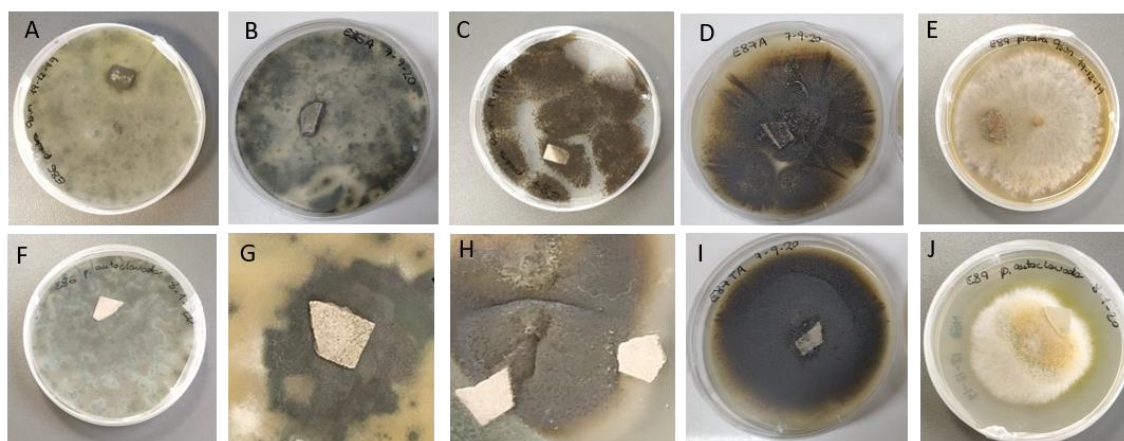


Figure 13. Effect of borates mixture treatment on the mycelial growth of *Aspergillus fumigatus*, *Phoma* sp. and *Epicoccum nigrum* in Redueña and Bateig stones. A-B *Aspergillus fumigatus* in presence of untreated Redueña (A) and Bateig (B). C-D *Phoma* sp. in presence of untreated Redueña (C) and Bateig (D). E *Epicoccum nigrum* in presence of untreated Redueña. F-G *Aspergillus fumigatus* in presence of treated Redueña (F) and Bateig (G). H-I *Phoma* sp. in presence of treated Redueña (H) and Bateig (I). J *Epicoccum nigrum* in presence of treated Redueña.

Analysis with “SEM-BSE technique” of the stone fragments immersed in the fungal cultures confirmed the less intense colonization of stone surface in treated than in untreated stones (Figures 14, 15, and 16) and revealed how borates treatment does not completely inhibit fungal penetration through internal stone (Fig 15 and 16). Endolithic colonization was observed in stone fragments in presence of *Phoma* sp. and *Epicoccum nigrum*, but this was always less extensive in treated stones (Fig. 15D and 16C), than in untreated ones (Fig. 15A and 16B). In addition, multiple spores were observed on the

stone surface in presence of *Aspergillus fumigatus* and *Phoma* sp. (Fig. 14A, 14B), but it showed lack of spores in proximity to treated stones (Fig. 14C, 14D) which could be the result of sporicide and/or sporostatic effects previously attributed to borate compounds [63,64]. Fungal hyphae of *Phoma* sp. and *Epicoccum nigrum* in the proximity of the stone surface and especially in endolithic positions showed also morphological and ultrastructural changes indicating cellular damage (Fig. 15 and 16). Fungal cells with high content in lipid bodies, and consequently high backscattered signal (Fig. 14A, 14B and 15A), are substituted by hyphae with low backscattered signal. Distorted morphological cells were also detected in treated stones (Fig. 15D). These damaged hyphae could correspond to the cells with high amount of small vacuoles and degraded cytoplasm harboring empty spaces, reported for fungal spores and hyphae exposed to borates [63,65,66]. Hence, the tested borate treatment showed also hyphal toxic effect which could be associated to the induction by borates of physiological disorders leading eventually the leakage of cytoplasmic materials and cellular death [66,67].

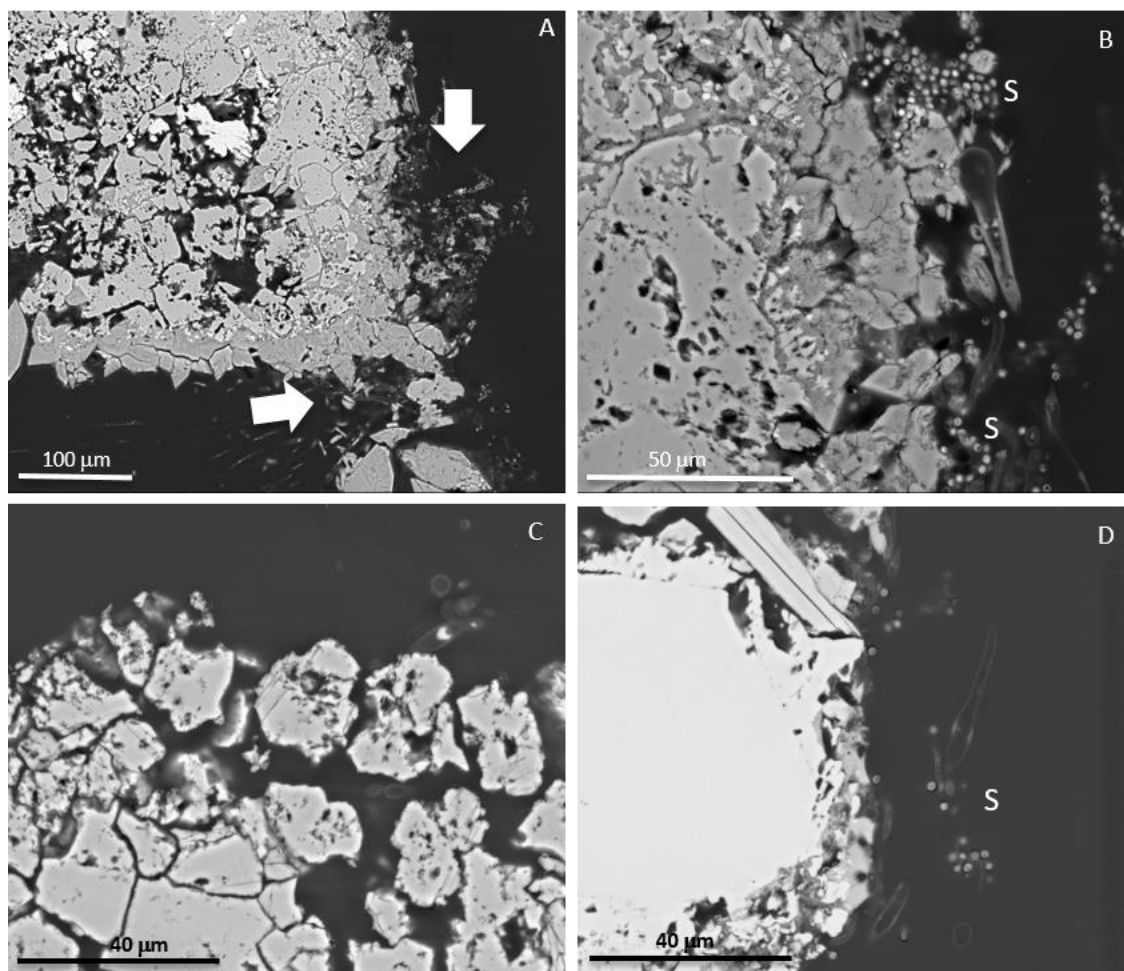


Figure 14. SEM-BSE images of Redueña and Bateig stone fragments from *Aspergillus fumigatus* in vitro experiments. A, Untreated Redueña colonized in surface (white arrows). B, Untreated Redueña showing presence of spores (s) on the stone surface. C, Treated Redueña showing lack of epilithic and endolithic colonization. D, Treated Bateig stone showing lack of epilithic colonization and presence of spores (s) only at certain distance of the stone surface.

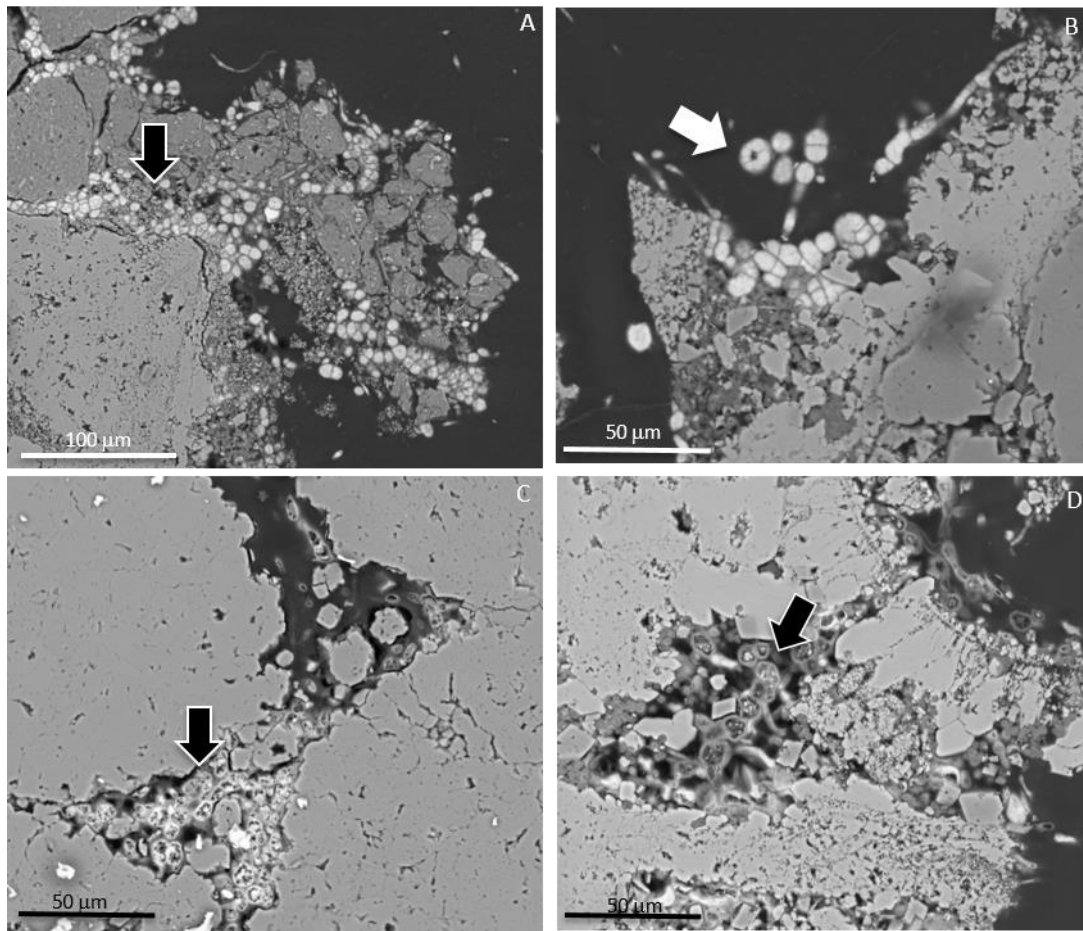


Figure 15. SEM-BSE images of Redueña and Bateig stone fragments from *Phoma* sp. in vitro experiments. A, Untreated Bateig showing intensive endolithic colonization (black arrow). B, Untreated Bateig showing extensive epilithic colonization. (white arrow) C, Treated Redueña showing endolithic growth composed of damaged cells (black arrow). D, Treated Bateig showing endolithic growth. Arrow notes distorted hyphae.

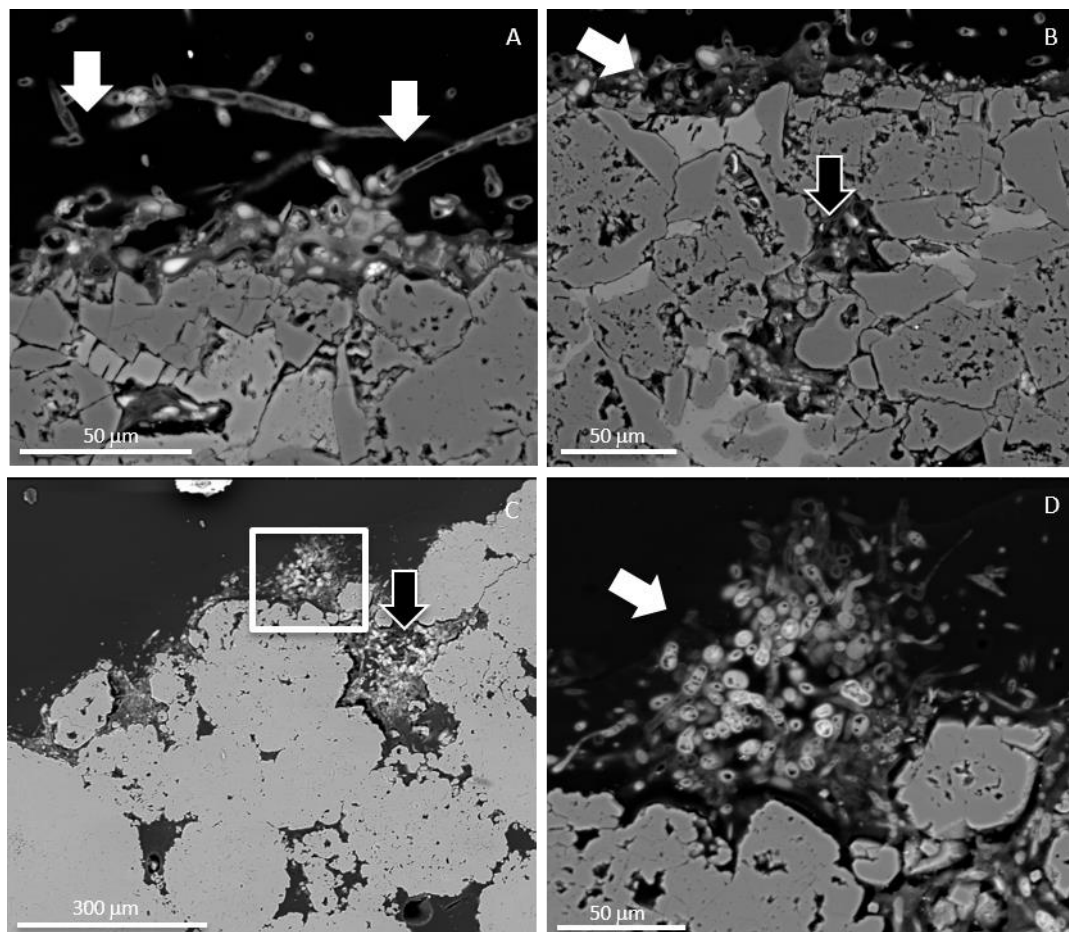


Figure 16. SEM-BSE images of Redueña dolostone fragments from *Epicoccum nigrum* in vitro experiments. A, Untreated stone showing extensive epilithic growth (white arrows). B, Untreated stone showing epilithic (white arrow) and endolithic colonization (black arrows). C. Treated stone showing damaged fungal cell in endolithic position (black arrow). D, Enlargement of the area noted by a square in C, showing damaged fungal cells in stone surface (white arrow).

3.5. Leaching test

Boron leaching occurred very quickly during the first 24 hours, being higher in Redueña dolostone than in Bateig calcarenite (see Figure 17). However, after this period, the leaching rate decreased being very low in both stony materials after 3 days. This behavior

was similar to that observed in a previous study performed on sandstone [40]. In this case, it was evident that despite the loss of part of the precipitated compound after accelerated leaching cycles of the stone samples, the amount of product remaining in the pores after leaching was still high. It is noteworthy that the accelerated leaching process is an uncommon situation of finding under real conditions, when materials are put into service. So in these conditions it is expected that the durability of the treatment will be longer. At the end of the leaching process, the total boron content analysis obtained by ICP-OES indicated a reduction of 77% for Redueña (from 0.070 % g/g to 0.016 % g/g) and 47% for Bateig (from 0.055 % g/g to 0.029 % g/g). This difference behavior may be related to the larger pore size of Redueña samples and the higher accessible porosity after treatment (22.46% and 13.47% for Redueña and Bateig respectively). Both aspects favor the leaching conditions of the precipitated compound.

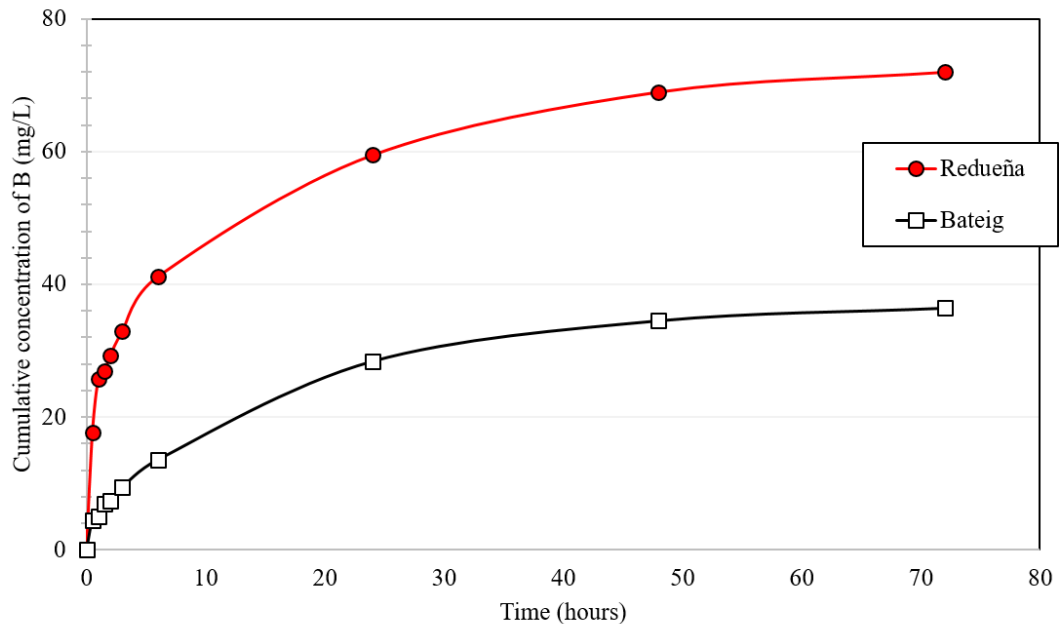


Figure 17. Average concentration (n = 2) of boron (in mg/L) released during the leaching process in water.

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742 The leaching of boron compounds does not generate any damage to the stone samples.
743 Although part of the leached ions, that do not come out completely from the stony
744 material, may precipitate again in other pores during the drying of the stones, the behavior
745 would be similar to that already indicated during the precipitation process (this fact was
746 demonstrated in [40]).

747 **4. Conclusions**

748 The main conclusion to be drawn from this study was to demonstrate the efficacy of an
749 electrokinetic technique for the precipitation of different soluble boron phases for its
750 application in antifungal procedures in building materials.

751 1) The electroprecipitation treatment allows the formation of boron compounds of
752 different solubility along the entire section of both rocks.

753 2) The precipitation of borate phases within the studied dolostone and calcarenite, as well
754 as their morphological and granulometric properties, depends on the nature and pore
755 distribution of the original rock.

756 3) Borates with different degrees of hydration and crystal morphology modifies the
757 intergranular porosity and develop intercrystalline porosity. The filling of pores with
758 euhedral or subhedral crystals proved to be morphologically dependent, which might limit
759 the effectiveness of the precipitated crystals depending on their specific shape. The
760 treatment reduced the surface porosity from 20% to 8.2% in Redueña dolostone and from
761 22% to 11.6%.in Bateig stone locally conditioned by the type of crystallized compound.

762 4) Within the three types of mineralization, larger crystals of Mg borate develop in both
763 types of stones. The smallest are Na borates, which decrease to a submicron scale as
764 observed in calcarenite stone. These criteria suggest the possibility of significant crystal-
765 cell interaction, especially with small crystals. However, to accurately determine which

mineralization best interacts with the cell wall, it is necessary to carry out a study with high-resolution tools.

5) As seen in previous studies about this technique, the precipitation of crystalline phases along a porous section of a building material improves its mechanical properties by increasing the velocity of ultrasound propagation due to a reduction inside the material the number of empty spaces or pores (i.e., the skeleton of the stone has become more massive). Moreover, this is achieved without causing significant changes in the color of its surface.

6) The treatment is effective in preventing fungal colonization. Although some endolithic growth especially of *Phoma* sp. and *Epicoccum nigrum* were detected, their hyphae showed cytoplasmic degradation that could progress to cell death.

7) Although a rapid release of borate occurs during the first day (particularly in Redueña, which has wider pores than Bateig), the release of these compounds stagnates after the third day, leaving a high amount of precipitate in the stones. Consequently, this treatment improves the durability of the current borate treatments, especially considering that the samples were subjected to accelerated leaching cycles that are unlikely to be found under real conditions.

Summarizing, the procedure established in this paper allows borates to be applied in areas exposed to high humidity conditions, such as building facades.

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Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: