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Laser versus scalpel cleaning of crustose lichens on granite

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ABSTRACT

This paper addresses the evaluation of the cleaning of crustose lichens developing on granite. The evaluation was performed considering the effectiveness of the cleanings and harmfulness exerted on the granite. The laser cleaning of lichen was compared with the most conventional procedure, scalpel. The combination of both procedures was also tested. The study, which was carried out with two different species of crustose lichen, was also focused on the influence of the intrinsic characteristics of the lichen on the effectiveness.

The cleanings were evaluated by optic and electronic microscopies, FTIR and colour spectrophotometry. A previous characterization of the lichen and its interaction with the granite using those analytical techniques were also performed. The laser cleaning effectiveness depends on the coverage and the colour of the lichen; also, the prior mechanical weakening of the lichen by scalpel seemed to improve the laser cleaning. The darkest lichen was satisfactorily removed by laser and with the combined cleaning. Conversely, the lightest lichen was more difficult to extract with laser than the darkest lichen, being necessary to apply both methods sequentially. Despite laser and the combination of methods cleaned satisfactorily the surface, they were unable to eliminate the thalli into fissures.

1. Introduction

Lichen is a symbiotic association of a mycobiont (a fungus) and a photobiont (an algae or/and cyanobacteria). Unlike to green algae and cyanobacteria, the lichen does not only colonize the stone surface causing an epilithic impact, but also the deeper parts of the stone establishing interactions with the rock forming-minerals developing endolithic damage through physical and chemical alterations [1–5]. The mechanical damage is caused by the penetration of the hyphae into the stone trough the fissures and pores and by the expansion/contraction cycles of the thallus under changes of humidity. Chemical damage is caused by the secretion of oxalic acid, carbonic acid and other acids capable of chelating ions such as calcium [2,5,6]. Furthermore, physicochemical alterations are developed and they lead a faster deterioration of the stone [1,2]. Due to these alterations, the cleaning is more complex for crust composed by lichens than for simple films composed by green algae and cyanobacteria [7–10].

Most of the Cultural Heritage in NW Iberian Peninsula is built with granite, which is a grained and polymineral stone. The temperate and humid climate of NW Iberian Peninsula favours the lichen development on the granitic surfaces, including façades and monuments [11].

In order to remove lichens on Cultural Heritage surfaces, chemical and mechanical procedures are applied, being the scientific publication based on this topic scarcer in granitic stones than in carbonate stones (i.e., limestones and marble) [12]. Biocides, mainly quaternary ammonium-based products, are the most used chemical products [13–15]. Despite Santamaría et al. [16] concluded that the chemical cleaning does not induce a significant mineralogical alteration, Pozo et al. [8] found soluble salts precipitation, even after the neutralization, using biocides such as benzalkonium chloride and hydrochloric acid-solutions involving environmental toxicity issues. A mixture of dead and living microorganisms was found after biocide application [17]. Also, in order to increase their effectiveness, authors advice retreats [18]. Scalpel is one of the most usual mechanical procedures to remove biological colonization in Cultural Heritage because it is controllable (the action can be stopped when the worker decides it), but it can induce damage if it is applied without any caution [19].

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There are no sufficiently consistent studies on the effectiveness of the scalpel as a lichen cleaning technique [10,20]. In a previous study [10], this issue was addressed, but as a case study for the calibration of hyperspectral camera as a non-invasive technique to evaluate the cleaning effectiveness. Therefore, studies are necessary to focus on the effectiveness of the scalpel on removing crustose lichen, on the influence of the lichen specie by itself on the cleaning. Another cleaning method, recently addressed on granite, is the laser [12]. In the last decades, this physical cleaning technique has been deeply investigated mainly in carbonate stones (limestone and marble) [21–26]. Siano et al. [25] tested Q-switched Nd:YAG lasers obtaining successful results to remove biogenic colonization on stones, but they found that the cleaning effectiveness depends on the type of lichen and the mineralogic and petrographical characteristics of the stones. Speranza et al. observed that a Nd:YAG laser at 1064 nm used in order to remove *Verrucaria nigrescens* on dolostone caused the inactivation of endolithic microorganisms and a high extraction level of epilithic colonizers [27]. Osticioli et al., using a Nd:YAG laser, found that the cleaning at 532 nm achieved better results than the cleaning at 1064 nm to clean a crust composed by V*errucaria nigrescens* on Carrara marble [28]. An interesting work centred on the cleaning of epilithic crustose lichen *Caloplaca* sp. colonizing dolostone with the different harmonics at 1064 nm, 355 nm and the sequence of IR followed by UV were developed; the combination of the two harmonics ensured the effective removal of lichen thalli and, even more important, the recolonization was highly reduced [29].

Unlike in carbonate rocks, there are a few studies on laser effectiveness in the removal of lichens on granite. In [10] the removal of *Pertusaria amara* growing on a pre-Variscan granite with a Nd:YVO_4 working at 355 nm was studied. In [30] the cleaning of *Protoparmeliopsis* cf. *bolcana* and *Aspicilia* cf. *contorta* (currently called *Circinaria contorta* (Hoffm.) A. Nordin, Savić & Tibell) growing on a monzogranite with a Nd:YAG working at 1064 nm and 266 nm was also addressed. In both studies it was concluded that, despite the used lasers did not lead to the complete removal of lichen thalli, they induced remarkable damage on the lichens, e.g. loss of the upper cortex and severe effects on the algal layer [10,30]. Comparatively with other cleaning methods, one of these studies [10] stated that laser seemed to be more effective in the removal of *P. amara* than scalpel, one of the mechanical methods most used for this purpose.

From the literature, it is obvious that the degree of knowledge of the efficiency of the laser to remove lichens on granite is insufficient; they are few scientific woks and focused on limited species. Moreover, it is known that the cleaning effectiveness of the laser (and hence the optimal cleaning conditions) depends greatly on the chemical and physical nature of the coating to be cleaned: different composition of the layer to be removed can result in very different results, as can be seen when cleaning graffiti [31] or black crusts [32,33]. This circumstance justifies raising more research on the laser cleaning of lichens on granite, including different type of granite and lichen species of different colour, vegetative body structure and morphology.

In this study, the cleaning of two crustose lichens, *Pertusaria amara* (Ach.) Nyl. and *Pertusaria pseudocorallina* (Sw.) Arnold, developed on a pre-Variscan granite was performed with a Nd:YVO_4 laser working at 355 nm. These two lichen species have different coverage rate and colour; so, the main aim of the work is to clarify the influence of the lichen specie on the laser cleaning effectiveness. Moreover, the cleaning of the same lichens by means of scalpel, one of the mechanical methods most used for cleaning granite, is also performed. Therefore, the comparison of the effectiveness results and harmful effects of both methods, laser and mechanical cleaning, could give information needed to consider the laser cleaning as a realistic alternative method to remove crustose lichen on granite.

2. Materials and methods

2.1. Sampling

For this study, a granite extensively used in the architectural heritage of Galicia (NW Spain) was selected. The granite, called Baiona (Fig. 1A), is an inequigranular two-mica cataclastic granite composed of quartz (30.6 %), microcline (27.3%), plagioclase (24.4 %), muscovite (9.6 %), biotite (8.0 %) and accessory minerals (0.1 %) [34]. It belongs to the alkali affinity group of granite highly represented in Galicia [35,36]. For this reason, they usually have a moderate open porosity (2–4%) which make them easily workable and in consequence extensively used in the Romanesque and Baroque NW Iberian Peninsula heritage.

In the outcrop, lichens extensively colonize this granite. For this study, natural blocks colonized by *Pertusaria pseudocorallina* (Sw.) Arnold and by *Pertusaria amara* (Ach.) Nyl. were collected and cut in 7 cm × 7 cm × 1 cm-slabs easily manageable in order to apply the different analytical techniques for characterization, cleaning and effectiveness evaluation. Fig. 1 depicts the aspect of the thallus of both lichen under different visualization techniques and magnifications. *P. pseudocorallina* thallus (Fig. 1B) is clearer than that of *P. amara* (Fig. 1C); it is also observed a more intense coverage degree in the case of the *P. pseudocorallina* whose thallus seems to be more continuous and homogeneous.

A block of non-colonized granite was collected in the same outcrop in order to be used as the reference surface (Fig. 1A); this block showed the typical weathering patina.

2.2. Cleaning techniques

The cleaning techniques implemented were:

- The laser cleaning performed with a Nd:YVO_4 laser working at 355 nm (Coherent AVIA Ultra 355–2000) and high repetition rate. A frequency of 10,000 Hz, scan speed of 25 mm·s^{-1}, distance between scans of 0.075 mm and regarding the laser trajectory, the beam was applied horizontally and vertically alternated. Due to the roughness of the samples, two fluences were used to ensure that valleys and peaks of the surface receive the same amount of fluence and to achieve a homogeneous ablation process along the surface. Following a previous article [10], the cleaning was performed with two fluences of 0.14 J·cm^{-2} and 0.21 J·cm^{-2} applied alternatively in a total of eight laser scans.
- The mechanical cleaning with a scalpel followed by a smooth brushing in order to eliminate the loose matter. The progress of the cleaning was monitored under optical microscopy (SMZ800 NIKON®). Therefore, it lasted until it was found that more cleaning time did not show any improvement in the cleaning results.

In order to study the combination of both methods, the application of scalpel followed by laser was performed: after the mechanical cleaning with scalpel, four laser scans were applied under the same two fluences previously indicated for the laser cleaning.

The cleaned areas were approx. 6 cm × 6 cm for the three cleaning strategies.

2.3. Analytical techniques

Several analytical techniques were applied in order to (1) characterize the lichen and the lichen–granite interface previously to the cleanings, (2) the effectiveness of the cleanings performed by