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Detection of the optimal laser fluence ranges to clean graffiti on silicates

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HIGHLIGHTS

- The polymineral characteristic of the granite influences on the laser cleaning effectiveness.
- $Nd:YVO_4$ ns laser at 355 nm cleaned granite of red, blue and silver graffiti.
- The satisfactory cleaning shows a complete extraction of the graffiti without damage in the substrate.
- Quartz and K-feldspar grains were successfully cleaned with 0.1–0.2 $J.cm^{-2}$.
- Plagioclase cleaning depended on the colour of graffiti to be cleaned.
- Biotite at 0.06 $J.cm^{-1}$ started to be cleaned but already damaged.

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ABSTRACT

The polymineralic characteristic of granite implies an additional challenge during the laser cleaning of cultural heritage built of this rock, because the forming-minerals experience different behaviours under the laser radiation, leading to damages of variable nature and intensity.

The aim of this work was to identify the ranges of fluence to satisfactorily and safely clean the four main constituent minerals of granite (quartz, K-feldspar, plagioclase and biotite) painted with three different graffiti colours. The cleaning was performed using a nanosecond $Nd:YVO_4$ laser which works at high pulse rate (kilohertz). The evaluation of cleaning effectiveness was performed in terms of graffiti extraction and mineral damage evaluated by optical, electronic and confocal microscopies and hyperspectral imaging technique.

The results showed that, regardless of the graffiti colour to be cleaned, quartz and K-feldspar grains were satisfactorily cleaned at the same fluence range. However, in case of plagioclase, it depends on the colour of graffiti to be removed. In case of biotite the analytical techniques allowed to confirm that it was already cleaned with the lowest fluence tested and it was the mineral with the highest sensitivity to laser radiation.

Therefore, in order to obtain a satisfactory and safe laser cleaning it would be required the prior identification of the granitic forming minerals to adjust the laser fluence.

1. Introduction

Laser ablation is a well-established cleaning procedure for cultural heritage objects [1,2]. A number of studies focused on the effectiveness of this technique is found in the literature, mainly in carbonate sedimentary and metamorphic stones [3–11]. In a recent review paper, the authors confirmed the lack of scientific research on laser cleaning applied to the granitic cultural heritage [12]. The evaluation of the laser cleaning effectiveness has to be performed considering the extraction of the coating but also the damages induced on the substrate, i.e. changes in physical properties as colour, reflectance, roughness, etc. However, there are not studies focused on the evaluation in detail of the damage induced on the granitic substrate by the laser cleaning in order to find the safe fluence ranges.

On the one hand, regarding the evaluation of coatings extraction on granite, a first study focused on removing bee wax using an excimer laser (ArF) working at 193 nm with fluences between 0.5 J cm^{-2} and 2 J cm^{-2} yielded promising results [13]. Subsequent studies analysing the cleaning effectiveness of other lasers (Nd:YAG, $Nd:YVO_4$ and Ti-sapphire in nanosecond and femtosecond

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domains) confirmed the possibility of using this technique to clean different crusts on granitic substrates: biogenic patina, lichens and graffiti paints [14,15], although the effective removal of gypsum black crust developed on granite continues to be a task unresolved; in a previous work working with a nanosecond Nd:YAG laser (266 nm, 355 nm, 532 nm and 1064 nm) it was not possible to achieve the complete extraction of the gypsum [16]. All those studies confirmed the need to find the suitable laser conditions for each type of crust to be removed, showing a high influence of the nature of the crust or patina on the capacity of the laser to clean.

On the other hand, as occurs in any intervention on cultural heritage aimed to clean materials, the laser cleaning studies must be focused not only on analysing the effectiveness of cleaning but also on the effects of the radiation on the substrate. So, in limestone, carbonate sandstone and marble, much more studied than granite, the side effects, mainly yellowing, have raised discussions that were gradually reduced as the scientific progress in the laser cleaning in these rocks was moving forward. The yellowing has been avoided using simultaneously the first and third harmonic of a Q-switched Nd:YAG laser and the application of water on the crust before to clean [17,18]. This progress allowed defining the operative fluence ranges ensuring the effective discriminations between patinas to be removed and layers underneath to be uncovered, in agreement with the intrinsic parameters of the laser system and types of stone under treatment.

On the contrary, in case of granite, the advancement of knowledge in side effects derived from laser radiation is slower and nowadays very limited; the erroneous consideration that granite is more resistant to degradation than carbonate sedimentary and metamorphic rocks would derive less scientific interest. A first study regarding side effects of laser radiation on granite was performed with a Q-switched Nd:YAG laser working at 1064 nm aplied to different uncoated stones, among them the coarse grained granite commercially known as Rosa Porriño [19]; the results of this first study were later confirmed by Grossi et al. [20]. Different responses of the stones to laser radiation were found conditioned by their chemical and mineralogical composition and, to a lesser extent, by their textural characteristics [19,20]. In those studies, Rosa Porriño granite showed a visual colour change associated to the whitish effect of the laser radiation on the pinkish potassium feldspar grains and the lighting effect on biotite. Also, it was reported melting of biotite and feldspar and cleavage fracture of quartz.

Subsequent studies focused on cleaning granites with several kind of patina or crusts. In [21], iron-rich black film developed on a exposed granite was satisfactorily extracted by means of a long Q-switched Nd:YAG laser at 1064 nm with fluences ranged between 0.7 J cm^{-2} and 0.9 J cm^{-2}. In that study, the authors declared the importance to determine the safe fluence range to clean the different silicates; in this sense, the relevant achievement of this research was the performance of the cleaning without undesired spallation of biotite grains.

In other studies, a nanosecond Nd:YVO_4 laser at 355 nm was successfully applied to extract biogenic patina and graffiti paints on several granites [14,15,22–25]; the fluences needed to extract each kind of coating were dependent on the nature of the coating, i.e. biological patina, lichen and graffiti. Also, all those studies confirmed harmful effects on the granite forming-minerals, being the intensity and morphology of these effects different on each silicate mineral. The irradiation conditions were selected to attain the highest extraction level of the coating and the lowest damage on the forming-minerals. Although almost all the coatings were successfully removed, in all cases mineral damage was found. Therefore, the granite, given its polymineralic character and grained texture, shows a specific problem in the field of laser cleaning. The different intensity and morphology of the damage produced in each mineral indicate a different behaviour of each silicate against the laser radiation, also suggesting a different laser-matter interaction or perhaps the predominance, in each silicate to be cleaned, of one of the effects (photothermal, photochemical and mechanical) related to laser radiation.

The apparent different sensitivity of each silicate to be damaged by the same laser radiation lead to orientate the research towards the identification of the laser fluences up to each silicate (quartz, K-feldspar, plagioclase and biotite) can be satisfactorily cleaned without inducing damage. A first approach with that objective tried to identify the extent to which the melting of biotite was produced under different fluences using a Nd:YVO_4 laser at 355 nm, by means of a 3-D finite element model of the heat transfer during the radiation [26]. This study was, nevertheless, performed by irradiating the laser directly on the isolated mineral without any coating.

So, on the one hand, it has been confirmed that the fluence needed to clean granite depends on the nature of the coating to be removed. On the other hand, it is expected that the behaviour of each silicate against laser radiation will be different when it forms part of a polymineral grained rock such as granite than when it is irradiated in isolation; so, the texture (shape, size and spatial relationship of one with respect to others) must undoubtedly influence the individual response of each silicate to the laser radiation.

Taking into account these facts, it is necessary to face a research on the identification of the laser fluence needed to clean each silicate (no isolated) forming a granite without causing damage.

The aim of the current study is to identify the optimal laser fluence ranges to satisfactorily clean the four main granite forming-minerals (quartz, K-feldspar, plagioclase and biotite) covered by three different colour graffiti paints. The cleaning effectiveness is evaluated searching for the maximum extraction with minimal damage to each mineral, and of course, from a practical point of view, with minimal time consumption. It is also intended to check whether the nature of the graffiti paint covering the rock influences the minimum fluence needed to clean completely each mineral without causing damage. The nanosecond Nd:YVO_4 laser working at 355 nm was selected considering its suitability to extract graffiti on granitic objects [12,14]. The evaluation of the graffiti extraction and the damage on each silicate was performed with optical, electronic and confocal microscopies and hyperspectral imaging technique. The achieved knowledge shows the first stage to establish a suitable laser cleaning protocol which will be directly defined not only by the nature of the crust to remove but also by the texture and the mineralogy of the specific granite to be cleaned.

2. Materials and methods

2.1. Granite and graffiti paints

For the present study a coarse grained granite from NW Iberian Peninsula was chosen. This granite, named Rosa Porriño, is one of the most valuable ornamental granites in Europe and its principal characteristic is the pink colour of the feldspar. Its main minerals are quartz, potassium feldspar, calcium plagioclase and biotite. The grain size of each silicate are the following: 0.3–2.0 mm for biotite, 1.2–3.8 mm for quartz and 1.0–10.0 mm for K-feldspar and plagioclase [27]. The coarse grain size of the rock provided the easy location of each silicate during laser application and for the subsequent evaluation of the cleaning and the damages induced. Slabs of 10 cm x 10 cm with cutting disc-surface finish were used. Fifteen slabs were selected to be painted with three different graffiti colours: *Devil red*, *Ultramarine blue* and *Silver chrome* (Montana colours S.L.) (5 slabs for graffiti colour). The characterization of these graffiti paints was addressed in a previous work [14]. Briefly, in the red graffiti painting, traces of rutile (TiO_2) and barite ($BaSO_4$) were found while in the blue graffiti, only rutile and in the silver graffiti, aluminium were identified. All the graffiti paints are organic (53.50 % C for red paint, 62.91 % C for blue paint and 70.36 % C for silver paint). Red and blue graffiti are composed of alkyd and polyester resins or varnishes and silver graffiti is composed of predominance of polyethylene-type polymers.