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Effectiveness and harmful effects of removal sulphated black crust from granite using Nd:YAG nanosecond pulsed laser

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ABSTRACT

Sulphated black crust is a common form of deterioration affecting stone used in monuments, usually occurs in contaminated atmospheres or urban environments. Its origin and cleaning have been studied extensively, for decades, in the case of carbonate rocks. Recent studies show that this form of alteration also affects granites. Scientific research on laser removal effectiveness of gypsum-rich black crust on granites needs to be scientifically addressed considering the inexistent references.

This paper assesses the removal by laser of sulphate-rich black crusts on granite using the different harmonics of a Nd:YAG nanosecond pulsed laser (266 nm, 355 nm, 532 nm and 1064 nm). Effectiveness was evaluated using Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometry (SEM–EDS), X-Ray Diffraction (XRD) and Attenuated Total Reflection-Fourier Infrared Transform Spectroscopy (ATR-FTIR). We also evaluated the effect of the radiation on granite-forming minerals and on the colour of the stone using Scanning Electron Microscopy and spectrophotometry colour measurements respectively.

SEM–EDS, XRD and ATR-FTIR analyses show that the higher the wavelength, the more efficient the cleaning, so samples cleaned using 1064 nm pulsed laser recovered its original colour. Nevertheless, the Nd:YAG laser did not completely eliminate the crust, and gypsum crystals remaining on the rock surface are observed, even at the most effective wavelength.

1. Introduction

Sulphate-rich black crusts are one of the most serious forms of alteration of the building stones used in many constructions constituting the architectural and artistic heritage. The origins of this deterioration have been well studied in carbonated rocks ([1] and references therein). The formation of such a crust is produced by the reaction between atmospheric SO_2 and Ca incorporated in the stone, thus generating a surface layer of gypsum in which carbonaceous particles derived from fossil fuel combustion are incorporated, giving the crust its black colour. The most common intervention for treating this deterioration problem is cleaning by various conventional methods (chemical and mechanical). In recent years, however, there has been considerable progress with respect to crust removal using laser devices, but almost all of the existing published contributions focus on cleaning carbonate rocks. In these studies, the efficacy of the Nd:YAG laser in removing sulphated black crust is confirmed, using either the fundamental wavelength ($\lambda = 1064$ nm) or the different harmonics [2–4]. While this laser is generally found to be acceptably effective in removing black crusts, almost all studies highlight the *yellowing effect* as the main drawback of the technique [5].

In the case of granitic rocks, contributions related to the origins of sulphate-rich black crusts are much less numerous [6,7]. In these studies the morphological differences between sulphated crusts formed on granite, in comparison with those on carbonate rocks, reveal differences in the originating process. Moreover, research on laser cleaning of this type of crust formed on granites is non-existent. From the literature, it can be deduced that the nature of the substrate to be cleaned has a great influence on the efficacy of the laser; important characteristics include properties such as the roughness and porosity of the stone [8,9] and the chemical and physical properties of the patina to be removed [10,11]. In this context, and given the impossibility of extrapolating the results obtained in carbonate stones to granites, it is clear that a specific study of the effectiveness of laser removal of sulphate-rich black crust on granite has become necessary.

In this work, we present the first known contribution to research on the effectiveness of a Nd:YAG laser, working at different wavelengths and fluences, on the removal of a sulphate-rich black crust formed on the surface of a granite building stone.

2. Material and methods

2.1. Sample description

Experiments were carried using a granitic ashlar stone severely affected by sulphate-rich black crust, sampled from a monumental

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building in Vigo (NW Spain). The stone is a fine-grained two mica alkaline granite composed of quartz, K-feldspar, Na-plagioclase, muscovite, and biotite, as the main minerals. The crust is composed of acicular-shaped gypsum and has a thickness of about 70 μm. The boundary between the crust and the underlying stone is net. Micron-sized black particles rich in carbon are observed coating the gypsum crystals, giving the crust its black colour.

2.2. Laser system and cleaning procedure

The laser cleaning was carried out using a Q-switched Nd:YAG laser (Quanta Ray, INDI) operating at 1064, 532, 355 and 266 nm. The laser system delivers pulses of 6–10 ns duration at a constant repetition rate of 10 Hz, and the beam was focused at normal incidence by a spherical plane-convex lens (NewPort).

The cleaning procedure consisted of an initial phase aimed at identifying the suitable wavelength for removing the crust; the fundamental wavelength (1064 nm) and the corresponding harmonics (266, 355 and 532 nm) were tested. This phase was carried out by setting the parameters of spot diameter, power and fluence at 0.06 cm, 0.57 W and 20.16 J cm^{-2} respectively.

Having identified the wavelength at which the extraction of the crust is most effective, we proceeded to optimize the cleaning, keeping the spot diameter constant in all experiments for each wavelength, and varying the power between 0.17 W and 2.51 W; this corresponds to a range of fluences between 26.52 and 312.09 J cm^{-2}. The cleaned surfaces evaluated in this second experimental phase were those cleaned at 26.53, 42.44, 79.58, 89.83 and 312.09 J cm^{-2}.

2.3. Evaluation of effectiveness

Viewing the cleaned surfaces by optical microscopy provided an initial qualitative evaluation of laser efficacy in removing the sulphate-rich crust. X-Ray Diffraction (Siemens D5000, grazing incidence) and Fourier Transform Infrared (FTIR) spectroscopy (Thermo Nicolet® 6700) in Attenuated Total Reflectance (ATR) mode were also used to evaluate the existence of gypsum on the cleaned granite surfaces. Scanning Electron Microscopy (SEM)

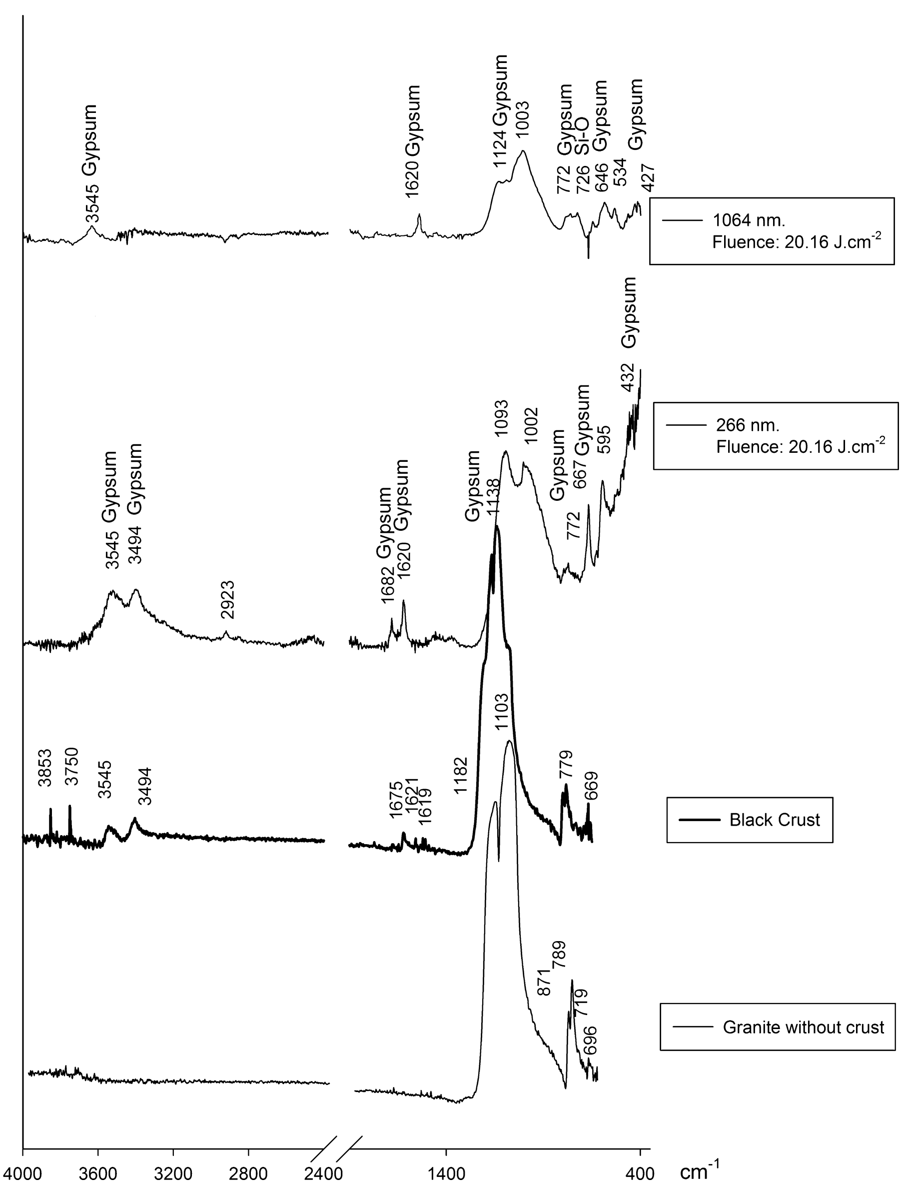

Fig. 1. FTIR spectra (absorbance) of the surfaces cleaned at 20.16 J cm^{-2} and at different wavelengths (266 and 1064 nm); for comparative purposes, spectra of the granite without black-crust and of the black crust are also shown.