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Ultrashort pulsed Femtosecond UV laser for selective cleaning of significant Cretaceous flints

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ABSTRACT

This work reports on studies aimed to evaluate the utilization of ultrashort 238 fs (fs) pulsed UV laser emission at 343 nm for eliminating colored crusts and surface deposits on significant Cretaceous flint surfaces, in an attempt to safeguard its aesthetic appearance and archaeological value. The results indicate that fs UV lasers may be an ideal, non-contact tool for selective surface cleaning of sensitive archaeological artefacts, since they enable contaminant desorption while avoiding photothermal damage.

1. Introduction

Flint, often known as flintstone, is a hard sedimentary rock and a form of microcrystalline quartz. The surfaces of flintstone and most other inorganic materials are extremely reactive after being cut. This is because rupture surfaces disrupt the electrically balanced atomic boundary structure, prompting a quick reaction as the material seeks a new equilibrium state. This might be the first stage in the formation of a flint patina, a form of surface modification brought about by natural processes following initial deposition [12].

The formation of a patina on flints is the consequence of the dissolution and subsequent precipitation of silica by biological and environmental weathering processes [3], which may occur on all flints during their long burial period. The rate at which patination occurs is dependent on a wide variety of factors, including (i) contaminants: type, proportion, and distribution, (ii) feature: texture, microstructure, and permeability, and (iii) environmental factors: temperature, humidity, moisture and soil chemistry etc. The reflectivity and preferred absorption of light are altered by chemical modifications to pigments, dispersion over intergranular surfaces, or elimination by leaching. Several factors can affect the patina's thickness, and hence its ability to be used as a flint patina chronometer: permeability, distribution and composition of contaminants may all be responsible [45]. Carbonates, iron oxides, clay minerals, carbonaceous matter, and iron sulphides are some of the mineral contaminants found in flints [4].

Traditional mechanical and chemical cleaning methods may be considered environmentally unfriendly and cannot always thoroughly clean targeted stone surfaces without inflicting either microdamage, color changes, or prolonged chemical reactivity that may result in long-term damage [6,7]. By contrast, the alternative of developing new laser stone cleaning methods may become increasingly important in the Conservation field [8]. Though the idea of stone or flint patina is still a controversial topic despite the fact that it is of significant relevance to conservation [2], laser cleaning techniques may be included as an outstanding example of how relatively recent technological advances may be applied to improve conservation approaches, at the same time that they are much more environmentally respectful. In laser cleaning, however, emission wavelength and pulse duration play a crucial role in avoiding discoloration [9]. This letter reports on the feasibility of using UV fs lasers to clean flint surfaces avoiding discoloration and other damage phenomena, based on prior laboratory observations of the outcomes of the sub-ns (*n*-IR and UV) and fs UV laser applications [10].

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2. Materials and methods

One Cretaceous flint from *La Paredeja* archaeological site of *Sierra de Atapuerca* (Spain) excavated in 2019 [11], physically 72 mm long ×29 mm wide ×19 mm thick, and dating back to the upper Pleistocene chronology was selected for the present study (Fig. 1). The yellowish-brown patina crusts and surface deposits irregularly covered the surface. Soft brushes were used for post-excavation cleaning to eliminate atmospheric dirt particles.

The laser irradiation was carried out utilizing a Carbide model (CB3-40 W + CBM03-2H–3H, Light Conversion, Lithuania) diode-pumped Yb: KGW solid-state laser (238 fs UV laser emission at 343 nm), with a linearly polarized output coupled with a galvanometric mirror configuration (Direct Machining Control, UAB, Lithuania). The maximum power for this laser was measured at 9.33 Watt, and its output beam waist focus at 30 μm. Irradiation of the surface was accomplished by a continuous laser beam scanning mode, ensuring a minimum pulse-to-pulse spatial overlap of 70 %.

Microstructure and surface morphology were studied by optical and Scanning Electron Microscopies (SEM). Chemical and mineralogical compositions were studied by EDS (SEM, semi-quantitatively) and XRD, respectively. Phase identification was carried out by comparison with the standard PDF references.

3. Results and discussion

EDS was used to identify the chemical composition of the flint sample by analyzing the flint's cross-section (Fig. 2). The presence and distribution of Si and O, which correspond to silica -the main component of flint, appear to be approximately uniform throughout the observed surface (Fig. 2a and b). Contaminants, specifically crusts and surface deposits, are thus restricted to the outermost layers of several μm. K is detected within the dark yellowish-brown patina area (ca. 5–15 μm) and follows a similar trend as Al. Both Al and Fe are consistent with the fact that the flint surface had long been in contact with clay, as their presence is significantly reduced below a depth of ca. 5–15 μm.

In order to explore a useful set of irradiation parameters, variation of laser power, pulse duration, and spatial distribution of the laser irradiation were explored to enable effective control of laser-flint interactions. Relevant parameters are summarized in Table 1. No discoloration was observed upon laser irradiation with crusts and surface deposits, thus confirming that this laser may effectively remove dark-colored overlayers from flint substrates (Fig. 3). Since ultrashort duration pulses are not expected to significantly contribute to input heat into the irradiated surface [12], this laser is expected to provoke very limited photothermal effects on the substrate surface during crust removal; however, higher irradiance values usually result in undesirable phenomena, such as discoloration, darkening, cracks and melting [Table 1].

Fig. 3 (top) shows optical (left) and SEM micrographs (center) obtained on selected areas of the samples, accompanied by their corresponding EDS spectra. These micrographs were obtained on the original encrusted dark-colored region before (Fig. 3a) and after (Fig. 3b – e) laser irradiation, and the presence of Si, O, Al, K and Fe was confirmed by EDS. Some regions also exhibited trace amounts of Mg, Ca, Na, and Ti. The analysis indicates that the observed flint material mainly consists of silica (SiO_2), accompanied by other major and minor trace elements which appear specifically on the original, nonirradiated surface. This is not surprising, since these elements usually appear associated to distinctive geographical location factors and are largely affected by soil composition [13].

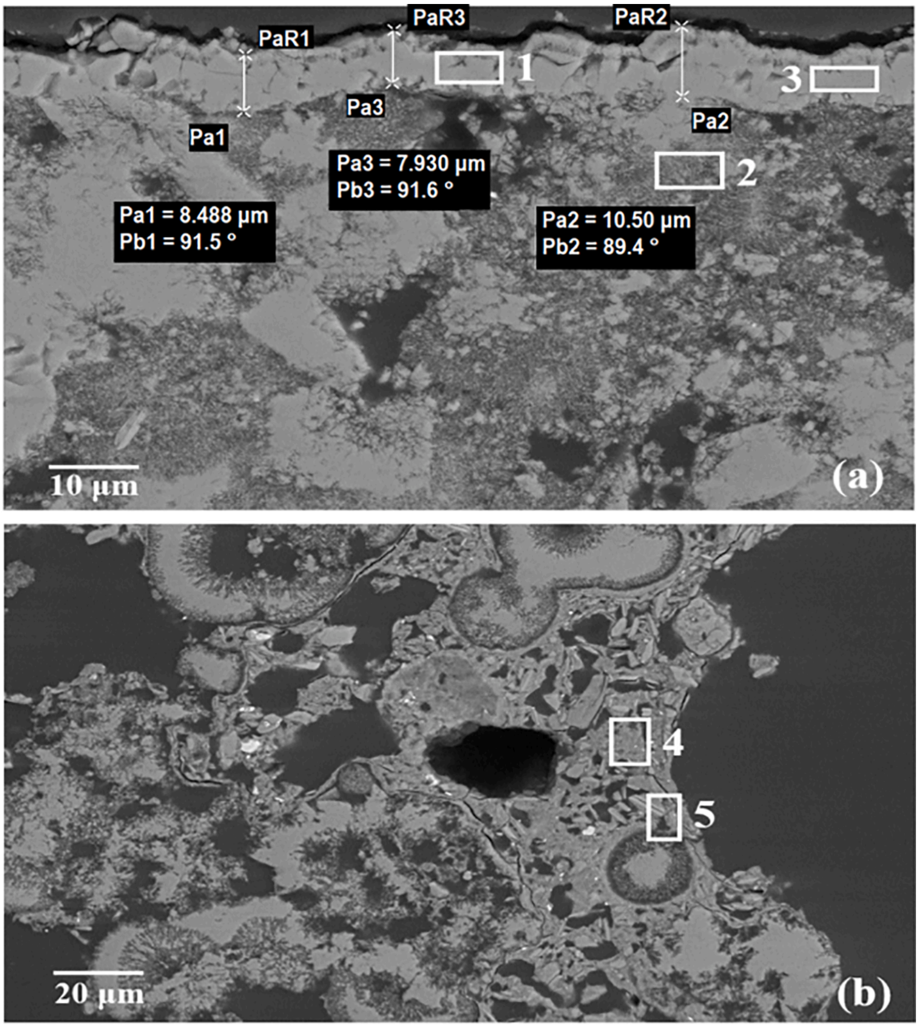
Moreover, the micrographs presented in Fig. 3b and d correspond to the ablation (0.68 $TWcm^{-2}$) and Fig. 3c and e to the cleaning thresholds (1.24 $TWcm^{-2}$), respectively, within the identified laser treated surfaces referenced in Table 1. According to Fig. 3c and e, laser irradiation removes almost all iron compounds, as well as those of most other elements associated to the presence of contaminants. At least minor amounts or traces of Al still remain, however, according to these analyses.

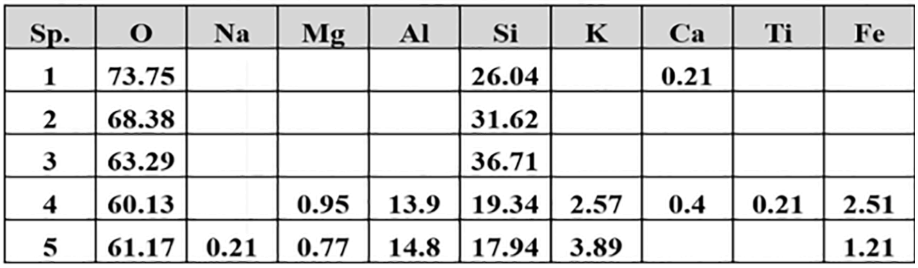
XRD patterns obtained on the flint surfaces 'before and after' laser treatment (Fig. 3: lower inset) exhibited double diffraction lines at low angles, probably due to the presence of different quartz allotropes. The diffraction pattern in 'As-received' corresponds to the original yellowish-brown patina crusts before laser treatment; two lines at 2θ 20.45° and 26.25° are assigned to quartz (SiO_2). The diffraction line at 2θ 29.15° is assigned to calcite ($CaCO_3$). In contrast, diffraction pattern in 'Laser-cleaned (e)' exhibits quartz diffraction lines from the satisfactorily laser-cleaned surface. The line at 2θ 21.57° corresponds to the most intense cristobalite diffraction line, although no other diffraction lines are observed corresponding to this allotrope. Only quartz lines were observed in the pattern shown in 'Laser-cleaned (c)'.

4. Conclusions

This letter reports on the use of a UV fs pulsed laser for the removal of

Fig. 1. Top and side surface photographs of the flint artifact.





Sp.	O	Na	Mg	Al	Si	K	Ca	Ti	Fe
1	73.75				26.04		0.21		
2	68.38				31.62				
3	63.29				36.71				
4	60.13		0.95	13.9	19.34	2.57	0.4	0.21	2.51
5	61.17	0.21	0.77	14.8	17.94	3.89			1.21

Fig. 2. Non-irradiated flint cross-section observed on FE-SEM micrographs. EDS analysis performed on the indicated representative outer surface areas, which contain yellowish-brown patina crusts and surface deposits. The Table summarizes atom percent compositions found in the marked areas.

Table 1
Laser emission parameters employed in this study. Beam scan was set at 150 mm/s for a single, complete surface scan.

Nominal Power (W)	Effective Frequency (kHz)	Pulse Energy (µJ)	Fluence (J/cm^2)	Irradiance (TW/cm^2)	Observations
0.23	10	1.15	0.16	0.68	Ablation threshold (Fig. 3b and d)
0.42	10	2.10	0.29	1.24	Satisfactorily cleaned; no damage, no discoloration (Fig. 3c and e)
0.80	10	4.00	0.56	2.37	Damage threshold; melt, cracks and discoloration

natural contaminants on archaeological flint samples. The laser was applied to the surface of the sample which originally contained incrustations and other undesired forms of contaminants. After laser irradiation under a low pulse frequency of 10 kHz, the contaminant ablation, substrate cleaning and damage thresholds were determined (irradiance values) as 0.68, 1.24 and 2.37 TW/cm^2, respectively. According to optical and electron microscopy observation and consistent with XRD results, encrustation removal appeared successful and the results achieved suggest that fs UV lasers may be effective and safe tools for cleaning flint surfaces.

CRediT authorship contribution statement

Md. Ashiqur Rahman: Investigation, Writing – original draft. **Germán F. de la Fuente:** Conceptualization, Methodology, Writing – review & editing. **José Miguel Carretero:** Writing – review & editing. **Mª Pilar Alonso Abad:** Conceptualization, Writing – review & editing. **Marta Navazo Ruiz:** Writing – review & editing. **Rodrigo Alonso**

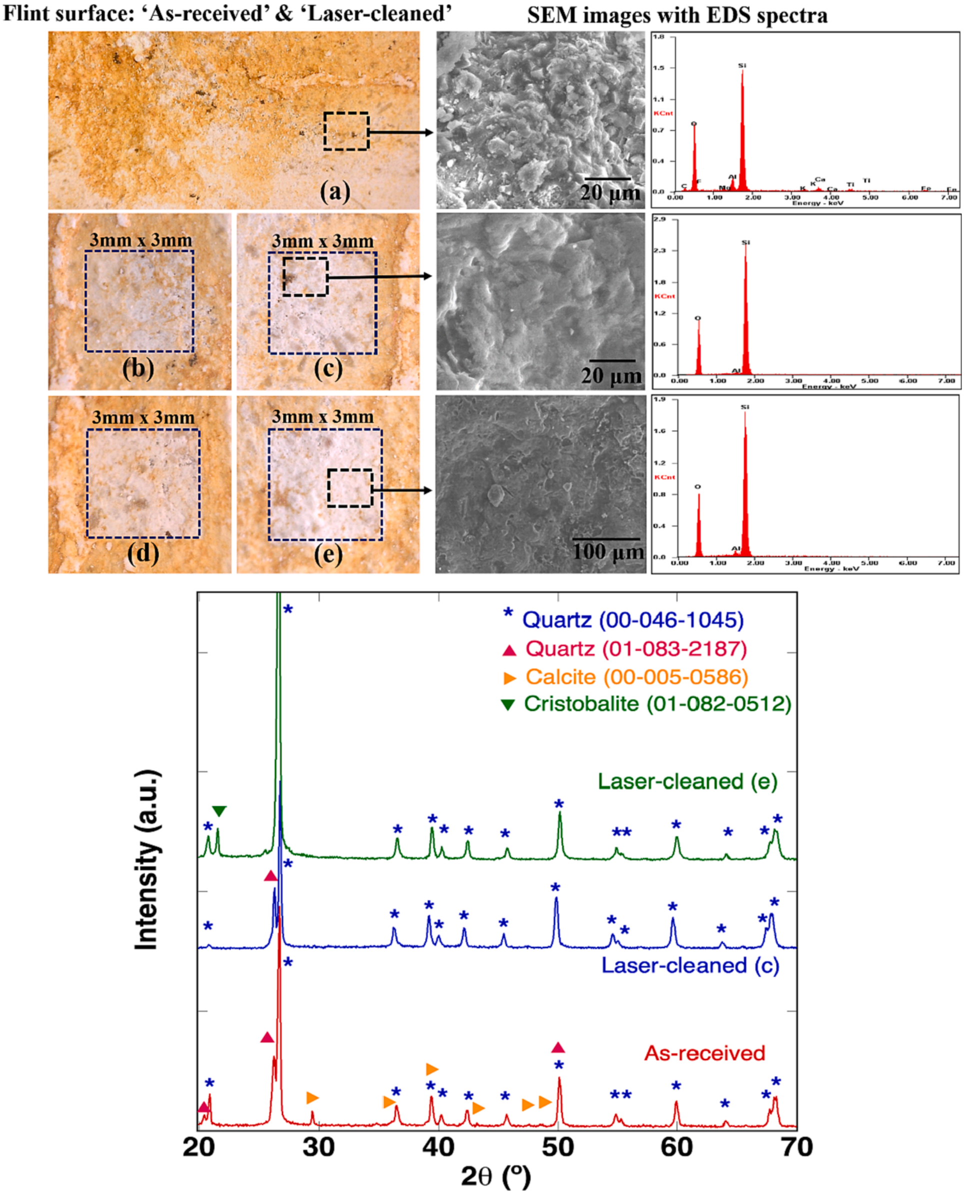


Fig. 3. Optical (left top) and SEM micrographs (center top) with EDS spectra (top right) for 'As-received (a)' and 'Laser-cleaned flint (b, d: ablation threshold; c, e: cleaning threshold)' using the parameters given in Table 1. XRD patterns (bottom) obtained for 'As-received', Laser-cleaned (c) and Laser-cleaned (e) from the above areas marked by dotted black rectangles in Fig. 3a, c and e, respectively.

Alcalde: Conceptualization, Writing – review & editing. **Rémy Chapoulie:** Writing – review & editing. **Nick Schiavon:** Methodology, Writing – review & editing. **Luis A. Angurel:** Conceptualization, Methodology, Writing – review & editing.

Declaration of Competing Interest

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.

Data availability

Data will be made available on request.

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