Ultrashort pulsed laser cleaning in the conservation of archaeologically significant bones and flints

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Introduction

Laser cleaning techniques could be considered amongst the most noteworthy contributions of Physics towards the conservation of artworks[1,2]. Although having established themselves as a striking field of research for the last three decades, these techniques have attracted limited attention by the archaeological conservation community. Laser-assisted removal of contamination and deterioration products in archaeological bones[3] and flints is a subject of great interest to improve recovery and conservation of these most valuable museum artifacts, and may highlight the use of laser cleaning methodology in this field. This research work reports on studies aimed to evaluate the application of two different ultrashort pulsed lasers for the elimination of contaminants on significant Pleistocene bone and Neogene flint surfaces from *Sierra de Atapuerca*(Spain)[3,4] in an attempt to safeguard their archaeological value and origin.

Materials

Material: Pleistocene bone (Bear rib)
Archaeological site: Sima de los Huesos
Chronology: Pleistocene (430,000 years)
Objective: Remove the hard blackish stains without altering the surface.

Material: Cretaceous flint
Archaeological site: La Paredeja
Chronology: Upper Pleistocene
Objective: Clean the dark brownish - yellowish encrustations without damaging the original surface.

Laser Cleaning Systems and Parameters

	Femtosecond (fs) Laser	Sub-nanosecond Laser
Wavelength	343 nm	1064 nm
Pulse duration	238 fs	800 ps
Pulse repetition rate	200 kHz – 1 MHz	200 – 800 kHz
Average power	9.33 W	8 W
Maximum pulse energy	46.6 μJ	40 μJ
Beam diameter	30 μm	80 μm
Distance bet. adjacent laser passes	15 μm	20 μm

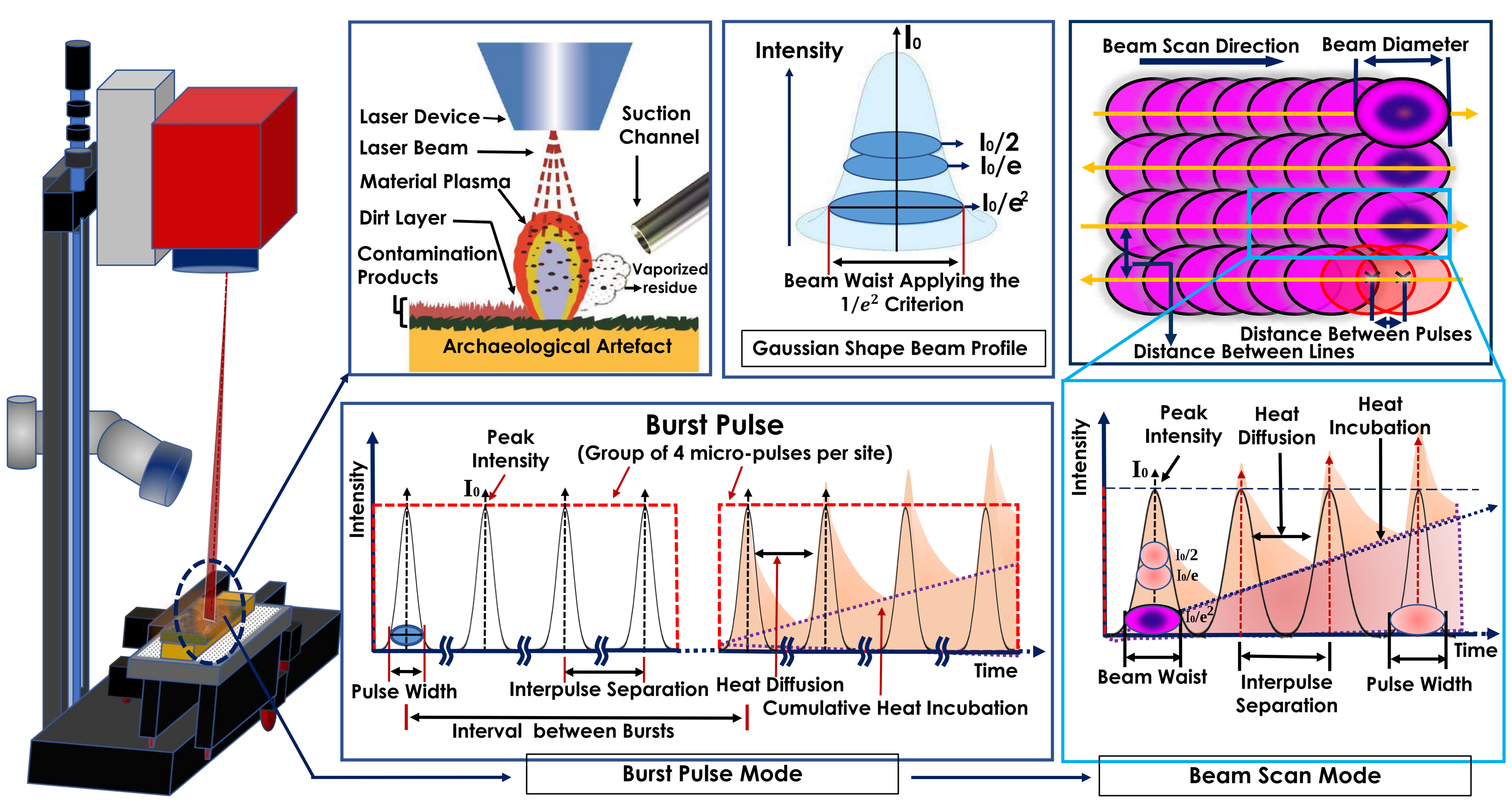

Fig. 1: Illustration of the laser cleaning apparatus used for the present study (left), where the laser x-y scanner head is shown above the archaeological artifact sample and a fume extraction device. The upper left inset illustrates the ideal sample behavior under laser irradiation, where the contaminant layer is removed, while the protective patina (green) is preserved. The upper middle inset depicts the connection between laser intensity and various definitions of beam waist for a Gaussian beam profile, emphasizing the 1/e² criteria utilized in this investigation. The lower and right side inset illustrations depict the laser output intensity at a specific place as a function of time for the burst pulse and beam scan mode used to control thermal damage. These insets visually depicts the pulse width, pulse-to-pulse (interpulse) spacing and how thermal incubation occurs during the subsequent pulse irradiation procedure.

Results and Discussion

Table 1: The cleaning threshold ranges and damage threshold values observed in the study.

Material	Region	Laser	Application mode	Cleaning thresholds		Damage thresholds	
				Fluence (J/cm²)	Irradiance (GW/cm²)	Fluence (J/cm²)	Irradiance (GW/cm²)
Bone	Fig. 2b	800ps n-IR	Beam Scan	0.20 – 0.31	0.25 - 0.39	0.36	0.45
	Fig. 2d	800ps n-IR	Burst pulse	0.14 – 0.16	0.18 – 0.20	0.17	0.22
	Fig. 2f	238fs UV	Beam Scan	0.29 – 0.56	1248.27 – 2377.66	0.66	2793.75
Flint	Fig. 2h	238fs UV	Beam Scan	0.29 – 0.47	1248.27 – 1961.57	0.66	2793.75

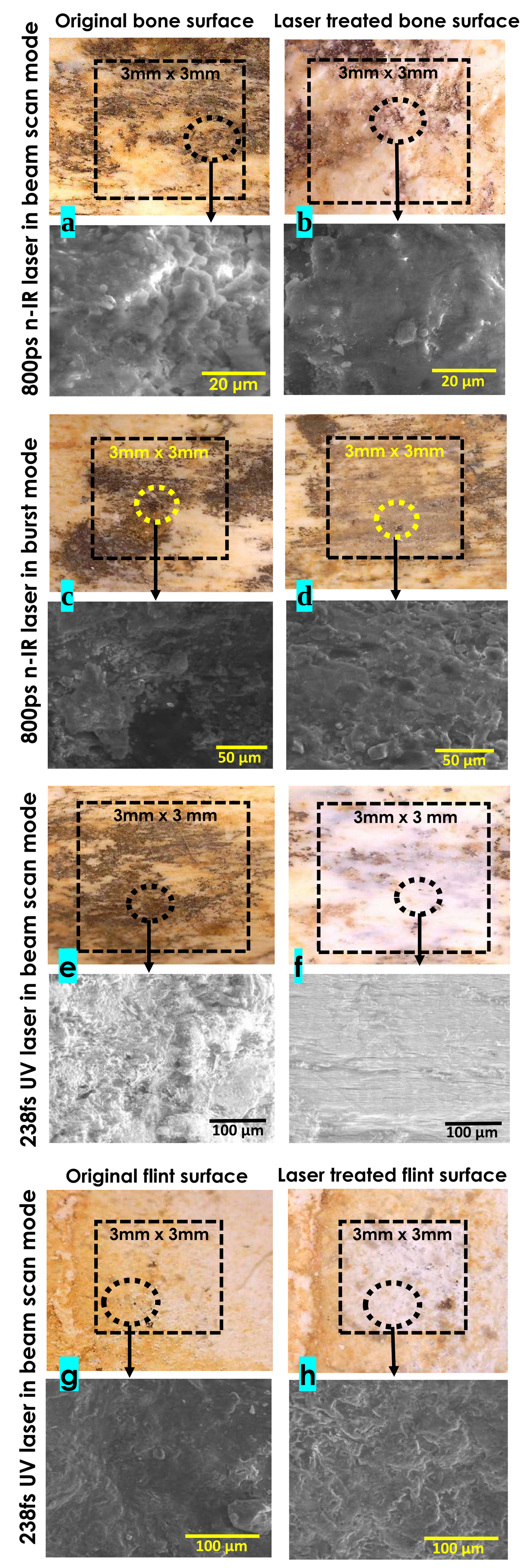

Fig. 2: Optical microscopy and SEM images of the bone and flint cleaned by both 238fs UV laser and 800ps n-IR laser, associated with Table 1: 'a, c, e, and g' presents the original outlook of the sample, where 'b, d, f and h' presents the best cleaning threshold outcomes. In all cases, only 1 treatment has been executed.

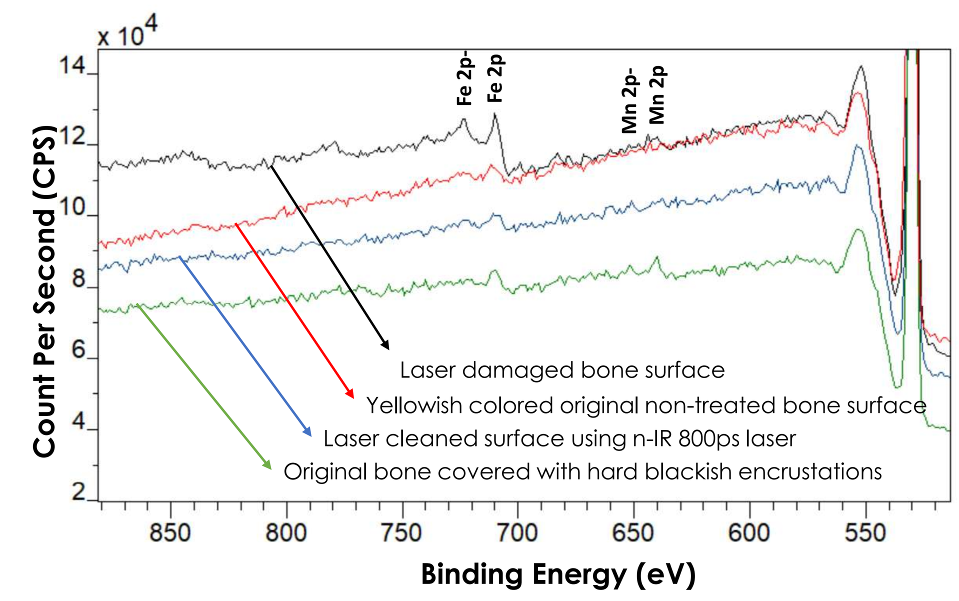

Fig. 3: Representative raw XPS survey spectrum of the Bear rib bone: green & red colored bands obtained from the 'as received non treated' surface, where blue & black colored bands correspond to the 800ps n-IR laser-treated cleaned and damaged surface accordingly.

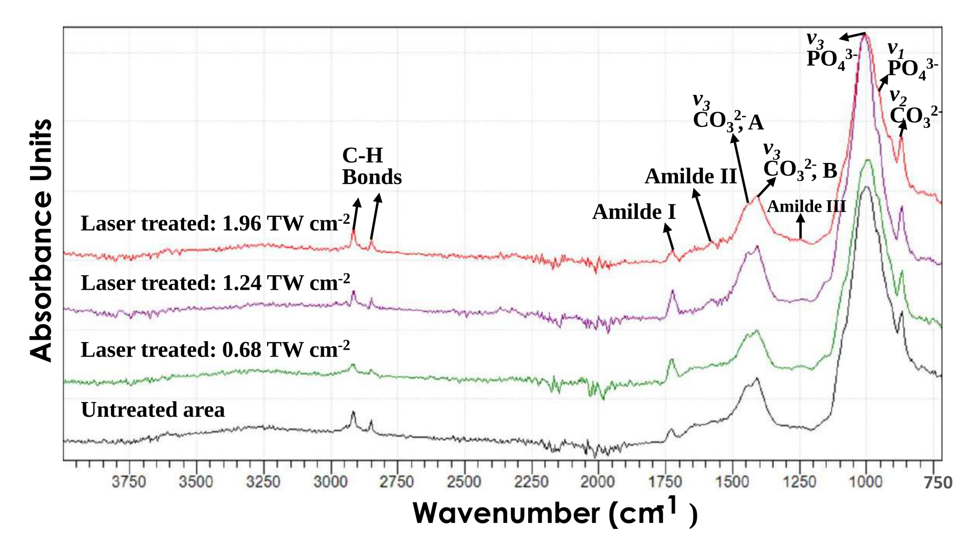

Fig. 4: ATR-FTIR spectra of untreated & laser treated bone area with irradiance levels of 0.68, 1.24 and 1.96 TW cm⁻².

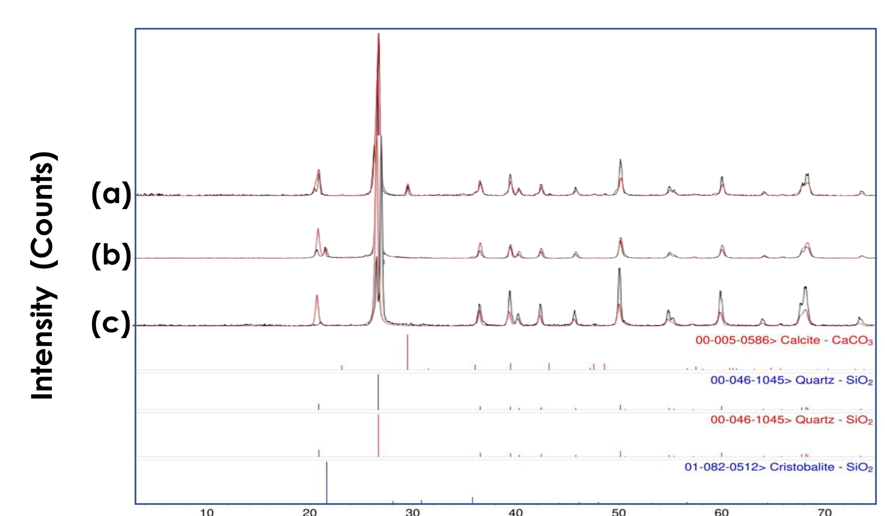

Fig. 5: Representative XRD peak identification of the flint sample with and without treatment of fs UV laser: 'a' presents the original flint surface and 'b & c' presents the satisfactorily cleaned laser treated surface. The JCPDS-2000 database utilized to determine the phases.

Conclusion and Future Perspectives

The results indicate that fs UV laser irradiation is significantly safer and more efficient at cleaning than sub-nanosecond laser irradiation, owing to the controllability of laser irradiation parameters, which allow for a systematic and accurate parameter description of an actual laser cleaning intervention. Further research on ultrashort pulsed laser-surface interaction using a variety of pulse durations and emission wavelengths, based on the advancements achieved within this study will pave the way towards future respectful and environmentally advantageous conservation practices.

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