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A STUDY OF TEMPERATURE CHANGES IN THE CLEANING OF FOSSIL BONES BY ER:YAG LASER (2940 NM)

Alessia Andreotti[1]*, Alessio Ceccarini[1], Maria Perla Colombini[1], Adele De Cruz[2] and Mark Norell[2]

1 - Chemistry and Industrial Chemistry Department, Pisa University, Italy
2 - American Museum of Natural History, New York, USA

Emails: alessia.andreotti@unipi.it (AA); alessio.ceccarini@unipi.it (AC); maria.perla.colombini@unipi.it (MPC); adecruz@amnh.org (ADC); norell@amnh.org (MN)

ABSTRACT

This work examines the feasibility of monitoring temperature changes during laser cleaning to ensure the safe removal of unwanted materials from fossil bones. The use of laser technology for cleaning fossils originated from the need to clean a vast collection of fossil finds from the American-Mongolian Expedition (2017) of the Museum of Natural History in New York. One of the steps in the conservation of fossils involves removing the residues of soil and unwanted materials such as consolidation or restoration products that have degraded over time. The main aim of this study was to optimize the Er:YAG Laser parameters for the effective and safe cleaning of different rock matrices, unwanted organic remains, and past conservation materials such as Paraloid B72, which can be very cohesive to the surface of the fossil. The museum collection provided an opportunity to test for the first time the Er:YAG Laser for cleaning a large variety of bones from dinosaurs and animals from hundreds of millions of years ago: fossils of *Coryphodon* (Paleocene-Eocene, 66-33My), *Psittacosaurus* (Cretaceous, 123-100My) and also *Hapalemur simus* and *Hyrax*. To fully understand the effects of the laser cleaning, the chemical characterisation of the unwanted material and residues of biological tissue was performed using infrared spectroscopy and chromatographic techniques. Pyrolysis analysis was also carried out on the ablated material and on the fossils after cleaning. The laser tests were executed in the presence or absence of various auxiliary wetting agents and by irradiating the samples with different energy fluences, repetition rates and number of consecutive pulses. The temperature measurements were performed with an infrared sensor system (FT-H10 Sensor Head, by Keyence, U.S.A) with the appropriate setting, avoiding any interference. The IR measurement system was tested on model specimens comparing the surface temperature (infrared sensor) with the bulk temperature measured with a Type T (copper-constantan) thermocouple inserted into the reference material. The experimental set up was then applied to the fossil bones with the right working conditions for safe laser cleaning. Experimental results demonstrated that the irradiation with an Er:YAG long pulse duration (300 μs) laser induced a limited temperature increase on the surface, when working with a threshold fluence under 2.5 J/cm2, and using ethanol as a wetting agent during the irradiation.

Keywords: fossils; laser cleaning; surface temperature; spectroscopic; chromatographic techniques

RESUMO [in Portuguese]

Este trabalho examina a viabilidade de monitorar as mudanças de temperatura de ossos fósseis durante a limpeza a laser para assegurar a remoção segura de materiais indesejáveis. A utilização da tecnologia laser para a limpeza de fósseis teve origem na necessidade de limpar uma vasta colecção de achados fósseis da Expedição Americana-Mongoliana (2017) do Museu de História Natural de Nova Iorque. Uma das etapas na conservação de fósseis envolve a remoção dos resíduos de solo e materiais indesejados, tais como produtos para consolidação ou restauração que se degradaram ao longo do tempo. O principal objectivo deste estudo foi optimizar os parâmetros do Laser Er:YAG para a limpeza eficaz e segura de diferentes matrizes rochosas, restos orgânicos indesejados, e materiais de conservação passados, como o Paraloid B72, que pode estar muito coeso à superfície do fóssil. A colecção do museu proporcionou uma oportunidade de testar pela primeira vez o Laser Er:YAG para a limpeza de uma grande variedade de ossos de dinossauros e animais de centenas de milhões de anos atrás: fósseis de *Coryphodon* (Paleoceno-Eoceno, 66-33Ma), *Psittacosaurus* (Cretáceo, 123-100Ma) e também *Hapalemur simus* e *Hyrax*. Para compreender plenamente os efeitos da limpeza a laser, a caracterização química do material indesejado e dos resíduos de tecido biológico foi realizada utilizando espectroscopia de infravermelho e técnicas cromatográficas. A análise de pirólise também foi realizada no material ablacionado e nos fósseis após a limpeza. Os testes com laser foram executados na presença ou ausência de vários agentes molhantes auxiliares e por irradiação das amostras com diferentes fluências energéticas, taxas de repetição e número de pulsos consecutivos. As medições de temperatura foram realizadas com um sistema de sensor infravermelho (FT-H10 Sensor Head, por Keyence, E.U.A) com a configuração apropriada, evitando qualquer interferência. O sistema de medição de IV foi testado em amostras-modelo comparando a temperatura da superfície (sensor de infravermelho) com a temperatura a granel medida com um termopar do tipo T (cobre-constantan) inserido no material de referência. A configuração experimental foi então aplicada aos ossos fósseis com as condições de trabalho adequadas para uma limpeza a laser segura. Os resultados experimentais demonstraram que a irradiação com um laser Er:YAG com pulso de longa duração (300 µs) induziu um aumento limitado da temperatura na superfície, quando se trabalha com uma fluência de limiar inferior a 2,5 J/cm2, e utilizando etanol como um agente molhante durante a irradiação.

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INTRODUCTION

The conservation protocols following the excavation, preparation and transport of fossils, involve various steps, such as cleaning and consolidation. When cleaning is necessary, the main issues are related to the similarity in the physical properties of the fossil bones and the unwanted materials. The hardness of the soil or other residues can make removal difficult without damaging the substrate. The fossils may also contain residuals from previous cleaning procedures, as well as natural or synthetic organic materials used as preservatives and consolidants. Another issue is associated with the removal of degraded glues, resins, waxes, or synthetic polymers in palaeontological finds which in the past have already been inadequately prepared. The characterization of the materials and the investigation and optimization of the cleaning procedure require close collaboration among palaeontologists, chemists, physicists, conservators, and curators.

Lasers are commonly used to clean archaeological artefacts. The cleaning (removal of the matrix) of paleontological artefacts, such as fossil bones, requires a thorough understanding of the short and long-term effects of laser irradiation. Nd:YAG laser cleaning has been performed on fossils (Sokhan et al., 2003: 230–236), on the fossil bones of dinosaurs and whales (Asmus, 2008:1), Pleistocene period fossils (López-Polin et al., 2008:477), and also mammal fossils (Landucci et al., 2003: 106–110). Another study examined the Nd:YAG-Laser application on bones, but from the recent Roman period (Al Sekhaneh et al., 2015:157).

Although the Er:YAG laser has been successful in a variety of cases, including the removal of thin layers of varnish from paintings or overpainting on stone surfaces (Pereira-Pardo . and Korenberg, 2017), to date it has not been used on fossils. Moreover, investigating the thermal, and photomechanical mechanisms related to the temperature increase induced by mid-infrared laser irradiation, is of primary importance. The Er:YAG laser wavelength (2940 nm) is absorbed by a large variety of materials, and together with the longer pulse length compared to other Q-switch lasers, it induces a heating effect in wider surrounding areas.

In addition to wavelength, fluence applied, frequency, as well as the nature of the treated material and its reflectance, the pulse duration needs to be carefully evaluated before choosing a laser source for cleaning. Many of the studies in the field of cultural heritage have investigated the increase in temperature during laser cleaning with ultraviolet nanosecond sources (Matteini et al., 2003:147; Osticioli et al., 2017: 772-778; Rockstroh and Mazumder,1985; Siano et al., 2012: 419), but only a few have used the near infrared source, or those operating in Free-Running (FR: pulse duration 100-500 µs) or Short Free Running Mode (SFR: pulse duration 20-50 µs) (De Cruz et al., 2014;Salimbeni et al., 2003:72-76; Striova et al.,2021:3354). Furthermore, most have evaluated the maximum and instantaneous value of the peak temperature induced by the laser pulse, which is of fundamental importance for the extensive understanding of the laser technique. Although the average thermal state or the transient of the target area under laser irradiation may also be of interest, especially for quick monitoring during cleaning, only a few studies have been reported (De Cruz et al., 2014; Siano and Salimbeni, 2001:269-281; Striova et al., 2021:3354).

A study on the photomechanical effects using a variable pulse width Nd:YAG laser, established the capability of the safe SFR laser removal of encrustation from Pliocene sandstone and limestone. Although the thermal diffusion length was higher for a longer pulse duration, it was possible to safely laser clean the stone, with a thermal heating zone confined to a few tens of microns (Salimbeni et al., 2003:72-76).

When an Er:YAG laser operates in a range of 200-300 µs, the laser absorption is confined to a surface depth of a few microns (Andreotti et al., 239:2007). The side effects due to thermal overheating of such photothermal ablation with a longer pulse duration need to be investigated.

As the removal of the superficial deposits is achieved through melting and evaporation, the main problem is how much energy is adsorbed by the underlying layer and how the related heat is dissipated.

In this study we evaluate the best working parameters for using an Er: YAG laser to clean fossil bones, with the real-time control of temperature variations on the treated area.

The temperature of the irradiated area was monitored with an infrared sensor system (FT-H10 Sensor Head, by Keyence, U.S.A) that enables real time remote measurements without the need for a probe in contact with the surface. Since the IR sensor response depends on the surface emissivity of the irradiated surface, a calibration model was set up. Model specimens, simulating low and high emissivity material, were prepared with a copper-constantan thermocouple, positioned a few microns beneath the surface and sufficiently small to minimize any perturbation in temperature. During the laser irradiation of the reference materials, the temperature measured by the IR sensor, representative of the surface of the specimen, was compared with that measured by the TC, which was representative of the bulk.

The same system setting was then applied on fossil bones from the American Museum of Natural History collection in New York. The fossil finds came from the American-Mongolian Expedition, particularly from 2017 (Hong and Norell, 2013; Napoli et al., 2019), and were mainly covered by a thick encrustation of soil and salt deposits, which are often treated with synthetic polymers as a protective or consolidant.

Infrared spectroscopy and chromatographic techniques were performed to investigate the composition of the unwanted material on the fossil surface. Evolved gas analysis by mass spectrometry (Orsini et al., 2017:643) and pyrolysis gas chromatography were used to characterize the synthetic polymers and provided information on the nature of the unwanted material.

To further investigate the chemical transformations induced by the laser irradiation, pyrolysis analyses were also performed after the cleaning test, or on the ablated material when possible, thus controlling the safety of the laser cleaning system.

EXPERIMENTAL SET-UP AND METHODOLOGY

Instrumentation

Laser system

The laser system was a high power Er:YAG CriystaLase (by Schwartz Electro-Optics, Inc; Orlando FL 32819, United States) with a wavelength of 2.94 μm and a pulse length of 300 μsec (Fig. 1A).
The maximum repetition frequency used was of 9 Hz. The energy laser output from the articulated arm of the laser was measured using an OPHIR Starlite LASER power meter.

Temperature measurement devices

The temperature measurements were performed with an infrared sensor (FT-H10 Sensor Head by Keyence, Corporation of America, Itasca, IL 60143, U.S.A., Fig. 1A-B) and a thermometer equipped with a type T thermocouple (TC, Fig. 1A). The detection wavelength of the IR sensor was 8-14 μm, the rated temperature range of 0 to 500°C and the emissivity correction was possible from 0.1 to 1.99 (0.01 step). The IR sensor is equipped with two red laser pointers that control the area where the temperature is being measured. The copper-constantan resistivity ($49.0 \times 10^{-8}\ \Omega \cdot m$) is sufficiently high to achieve suitable resistance values in even very small grids, and its temperature coefficient of resistance is fairly low. This experimental setting does not evaluate the maximum value of the temperature induced by the laser radiation because the pulse duration of 300 µs is several orders of magnitude less than the response time of the sensor. The temperature values obtained represent the real time average surface temperature measured (with a speed response of 10 ms) during the tests.

The IR and the TE sensors provided voltage responses, which were acquired with an Arduino Nano A/D converter circuit (Fig. 1A). The system was calibrated by simultaneously comparing the two measurement devices. The IR sensor was positioned (Fig. 1B) above the tested area to measure the average temperature of a surface as close as possible to the laser spot (a circular spot with a diameter of 1-1.5 mm). The temperature measurement needs to be performed exactly inside the Er:YAG laser spot.

We fixed the sight of the sensor so that the area for which we wanted to detect the temperature, fell in between the two laser pointers. For a highly accurate reading, a view width that is at least 1.5 times smaller than the measurement target must be used. When the laser pointer distance of the sensor is 3.5 cm, the view width is 1.5 mm in diameter, which was exactly the dimension of the Er:YAG laser spot used for these tests. This measurement view and sight parameters are reported in the Keyence user manual (see References). They were also tested during preliminary experiments, described in the 'System set-up and model specimen preparation' section.

Evolved gas analysis, coupled with mass spectrometry (EGA-MS)

A few milligrams of the sample were scraped from the surface of the fossil and placed in a stainless-steel cup of the micro-furnace Multi-Shot Pyrolizer EGA/Py-3030D (Frontier Lab) coupled with a gas chromatograph 6890 Agilent Technologies (Palo Alto, USA) equipped with a 5973 Agilent Mass Selective Detector (Palo Alto, USA) single quadrupole mass. More details of the instrumental set-up are described in Orsini et al, 2017.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC-MS)

The same Multi-Shot Pyrolizer EGA/Py-3030D (Frontier Lab) and GC-MS system were used for the pyrolysis analysis of the fossil samples (about 500 µg) which were placed in a stainless-steel cup and pyrolyzed at 550 °C. The products of the thermal degradation are chromatographically separated and identified by the quadrupole mass device. Experimental conditions are described in the literature (Bonaduce and Andreotti, 2009, Degano et al, 2018).

Attenuated Total Reflection (ATR) Fourier Transform Infrared Spectroscopy (FT-IR)

The FTIR spectra were recorded with a Thermo Fischer Nicolet iS50 FT-IR instrument interfaced with an ATR ITX accessory equipped with a diamond crystal (radiation penetration of about 2 µm at 1000 cm^{-1}). Spectra were recorded between 4000 and 650 cm-1 using 16 scans and a resolution of 4 cm-1 (Castelvetro et al, 2021).

System set-up and model specimen preparation

Model specimens were prepared by depositing different reference materials onto glass microscope coverslips, and a thermocouple was positioned a few microns (10-20 µm) beneath the surface before curing the material. In order to verify the correspondence between the surface temperature read by the IR sensor and the bulk temperature, these models were prepared for the laser irradiation test with different combinations of black charcoal and titanium (Fig. 1A-B), and also soil residue from the fossil excavation (Fig. 1C). These black and white reference materials were prepared in order to obtain a grey-scale with different light absorption indices and consequently, dissimilar responses to the laser irradiation. The soil residue from the fossil excavation used for the reference specimens enabled us to test the temperature set-up on a system as similar as possible to real fossils (Fig. 1C).

The glass specimens were prepared by inserting the hot joint of the thermocouple into the following mixtures:

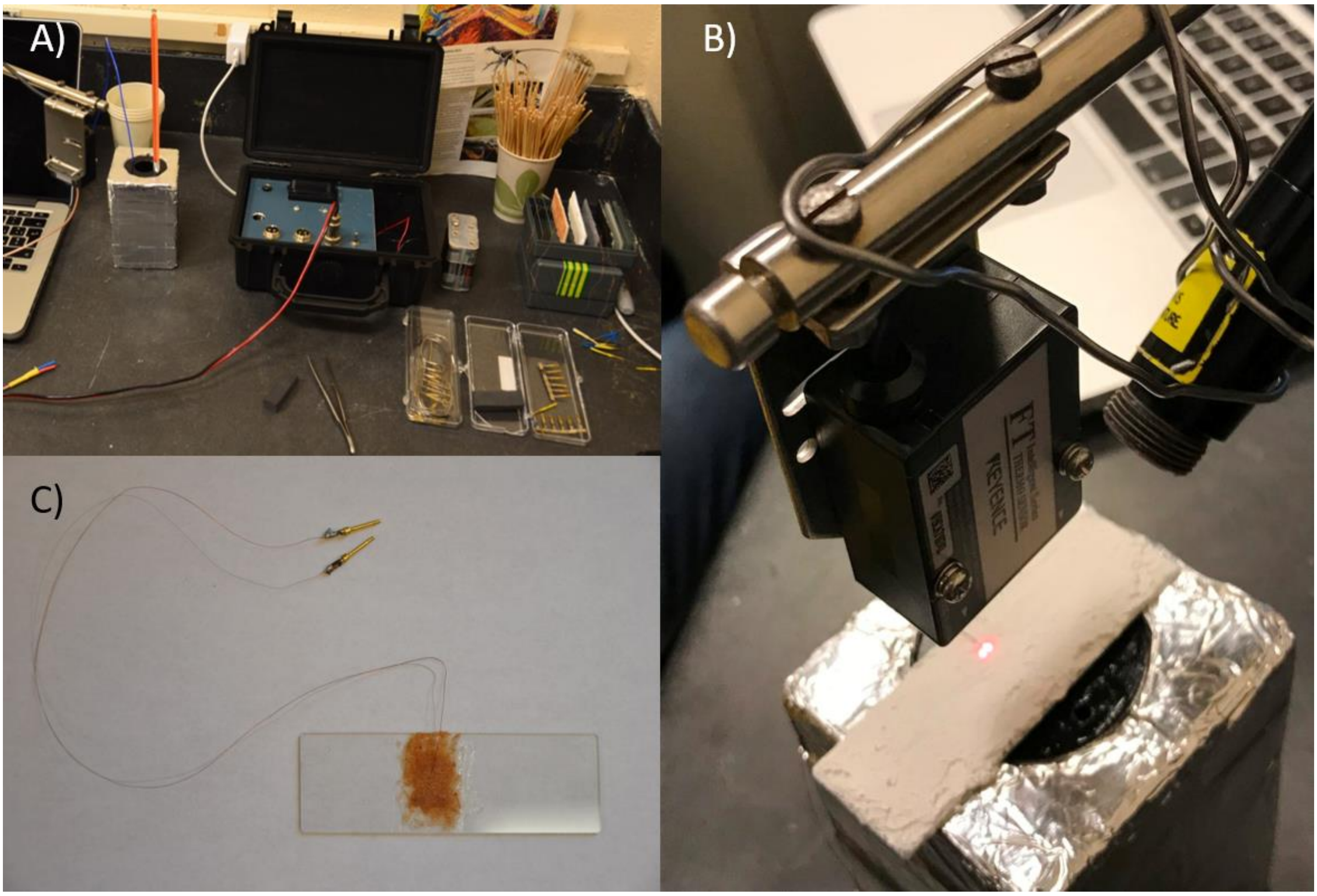

Figure 1. Experiment set-up with the IR sensor, the set of reference specimens with the TE, the cylinder with the thermometer and the Arduino Nano (A). Details of the Er:Yag laser irradiation and IR temperature measurements on the white specimen (B), and the fossil reference material specimens with the thermocouples (C).

- black reference material: charcoal and vinyl glue;
- white reference material: titanium oxide and vinyl glue;
- grey reference material: mixture of charcoal and titanium oxide
- fossil reference material: powder residue of the soil covering the fossil bones and Paraloid B72 in 50% acetone. Another layer of soil powder was applied immediately before drying.

We used synthetic acrylic resin (Paraloid B72) and vinyl glue as binders, because they are commonly used by preparators as a fixative on paleontological materials and therefore have a similar glass transition temperature and response to laser radiation.

For an accurate measure of the temperature, the emissivity of the materials was determined using the model specimens for a correct calibration of the sensor. The emissivity can be automatically calculated by entering the temperature of the measuring target on the FT-H10 display. For each reference specimen and for an aluminium block, or a black spray surface acting as a non-blackbody or a blackbody irradiator respectively, the temperature value measured by a digital thermometer connected to the TC positioned on the surface was set on the display, and the emissivity automatically calculated and set by the sensor before conducting the increase in temperature tests. The IR and the TC sensor voltage responses were acquired with an Arduino Nano for the signal calibration. For this first calibration, a device was built for the thermal heating and temperature measurement. This consisted of an aluminium cylinder, with a central hole with diameter 2 cm and depth 8 cm, and with the internal wall coated with a black spray paint (Fig. 1A). Two holes drilled into the cylinder were used to hold a bulb thermometer and the TC sensor. The cylinder was heated on a heating plate to a temperature of ~60 °C and then inserted into an insulating sheath. The blackened walls of the central hole cause it to emit in the infrared analogously to a blackbody. Once the aluminium cylinder reached a stable temperature, the temperature reading from the bulb thermometer, the voltage signals produced by the TE sensor, and the signal produced by the IR sensor positioned immediately above the central hole were recorded simultaneously.

The results of the digital conversion were translated into temperature values using a linear calibration, which enabled the signal of both measuring systems to be calibrated. The maximum analogical output of the IR sensor (20mA) was set at 150°C.

After setting up the Arduino converter, to verify the agreement of the TC and IR sensor response, a second system calibration was performed. Each type of glass specimen was placed on a heating plate and brought to a temperature of over 60°C. The heating plate was then turned off. The TC and IR signals were monitored during cooling. Experimental results showed that the surface temperature of the specimens, measured by the IR sensor, exactly followed the same cooling profile as the bulk (TC sensor).

RESULTS

Temperature measurements on reference materials

The two sensor signals were registered during the laser irradiation of the reference specimen surface. For each measure of the surface temperature increment, a continuous stream of pulses from the Er:YAG laser was delivered, until a constant value of the signal of the two measurement devices was reached. The maximum temperature value obtained is thus representative of the maximum average surface temperature reached (with a speed response of 10 ms) during laser irradiation.

Table 1: Er:YAG laser operating parameters for the tests performed on the reference specimens.

Frequency	9 Hz
Energy/pulse	15-30 mJ
Spot diameter	1.5 mm
Fluence	0.8-1.7 J/cm^2

The working conditions of the laser are shown in Table 1. The same laser parameters were used for all the specimens, however the number of pulses varied and whether or not ethanol was used as wetting agent. The surface temperature was measured after a stable value was reached during continuous laser irradiation.

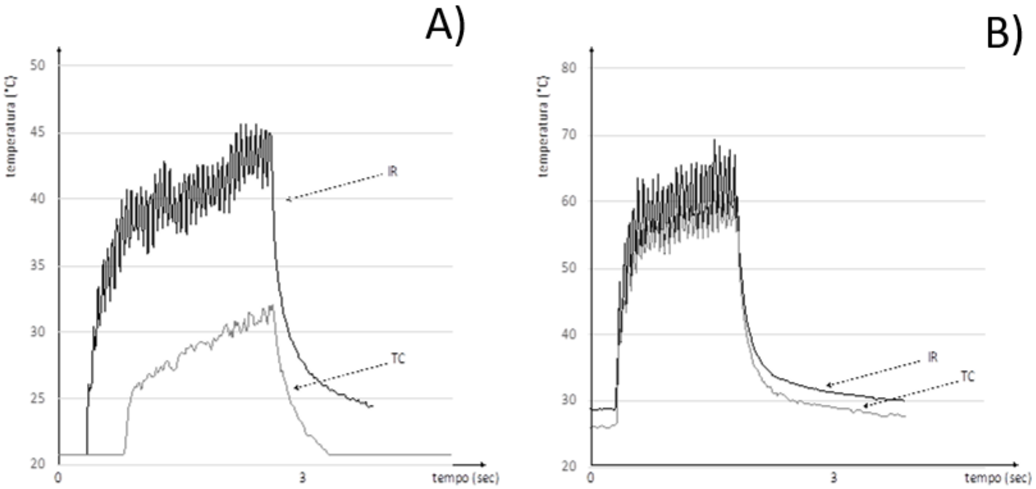

Figure 2. Temperature measurements for the specimen: (A) white reference material; (B) black reference material.

During the laser irradiation, the TC sensor registered a slighter lower temperature than the IR one, since the TC sensor is located a few microns under the surface. Typical profiles of temperature increases are shown in Fig.2A-B) compare the IR and TC signals for the irradiation of specimens, with white and black reference material respectively, for about 3 secs of consecutive laser pulses on the same area, which was necessary to reach a constant value of the average temperature recorded by the two sensors.

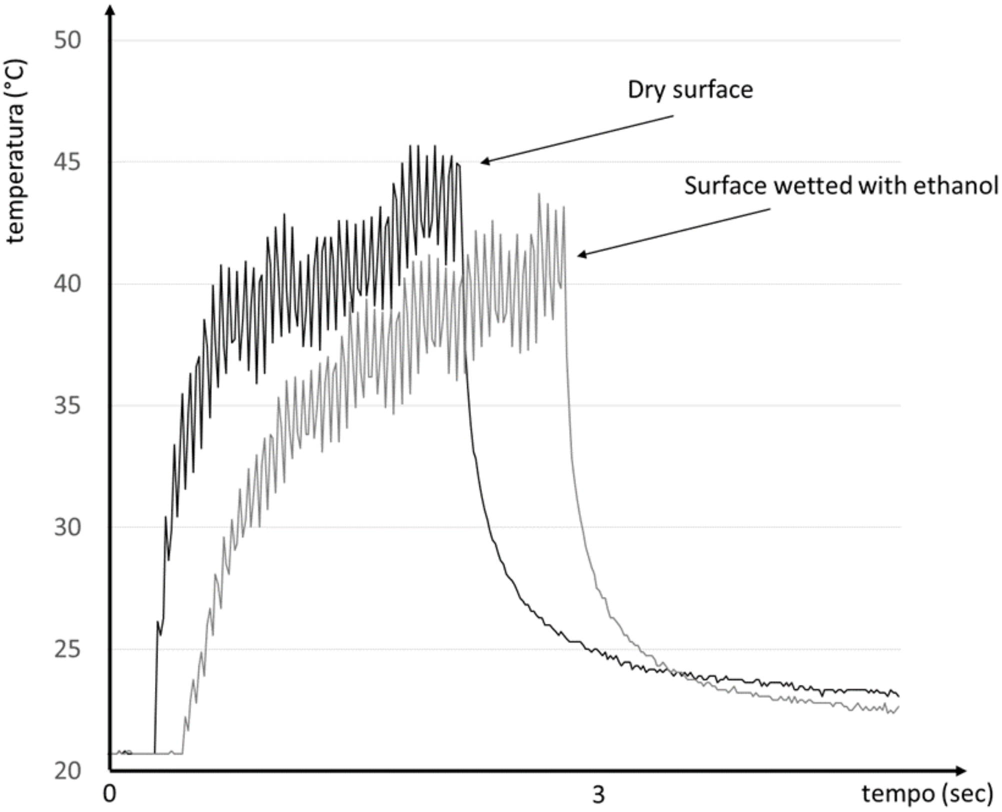

Figure 3. Temperature measurements for the white reference material specimen (IR - sensor) in dry or wet condition (ethanol).

As expected, the white surface reached a lower temperature than the black one. In fact, the maximum surface temperature was approximately 45°C for the white specimen, and approximately 60°C for the black one. Lastly, the two plots show how a lower absorption of laser radiation enhances the difference between bulk (TC sensor) and surface temperature (IR sensor). This thus confirms that the thermal diffusion of temperature of the laser with highly reflective materials is limited to a depth of a few microns.

The application of ethanol as wetting agent before the laser irradiation, which is a common practice in laser cleaning of artworks, mitigates the temperature rise of the surface as shown in Fig. 3 in the case of white reference material.

As regards the fossil reference material, the specimen covered with the soil matrix and Paraloid B72, a significant difference between the surface temperature and the bulk temperature (about 80°C vs about 40°C respectively, Fig. 4) was observed during the first irradiation. This difference drastically decreased when a second laser passage was applied. This can be explained by the high IR absorption of the organic superficial layer, which was completely ablated during the first passage.

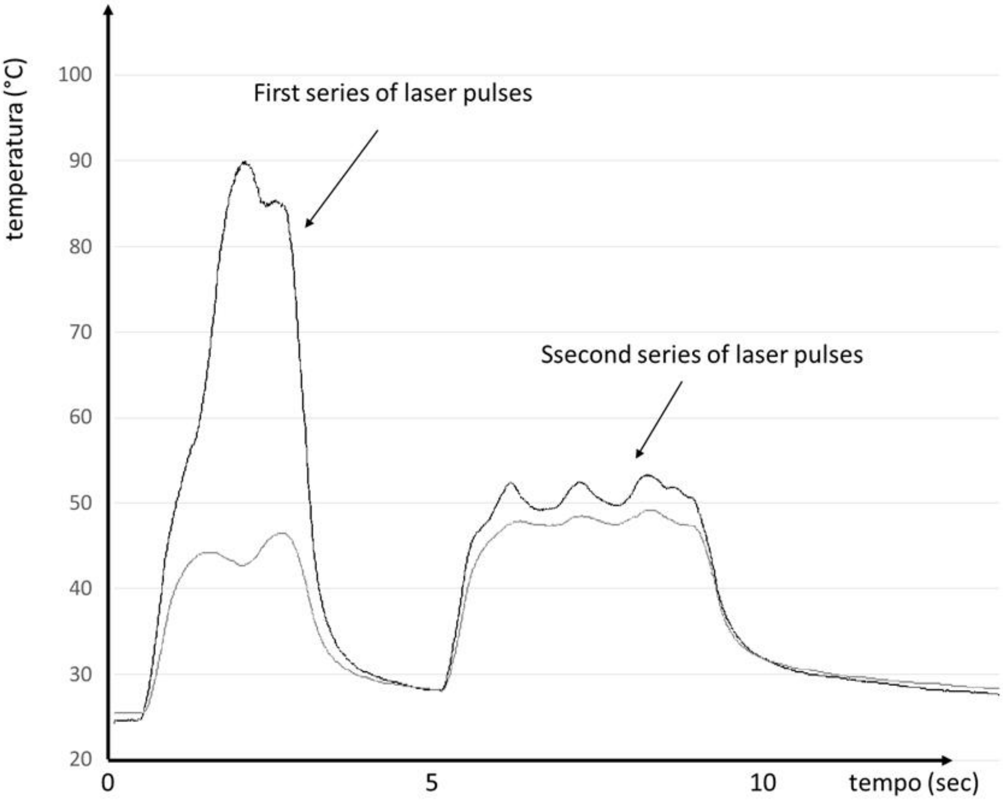

Figure 4. Laser-induced temperature increases of the specimen covered with the fossil soil and Paraloid B72, measured during about 3 seconds of continuous pulsing. Upper curve: temperature from IR sensor; lower curve: temperature from thermocouple sensor.

Temperature measurements on fossils and analytical investigation

All the fossils tested came from the Gobi Desert in Mongolia. The three fossils (shown in Fig. 5) were selected following a discussion with the archaeologists. They were chosen because they had earth deposits or encrustations with varying levels of hardness, and differently coloured, which enabled laser tests and temperature measurements to be performed on materials that exhibited the highest variability in thermal diffusivity among those available. The lizard skull (*Carusia*) from the Late Cretaceous of Mongolia was covered with sandstone (Fig. 5A), a fossil bone of the proximal tibia of *Psittacosaurus* from the Early Cretaceous Oshii was coated in a hematite matrix (Fig. 5B) and a partial skeleton of *Parmeosaurus*, an armored lizard from the Late Cretaceous from Ukhaa Tolgod was encased in a sandstone block (Fig. 5C).

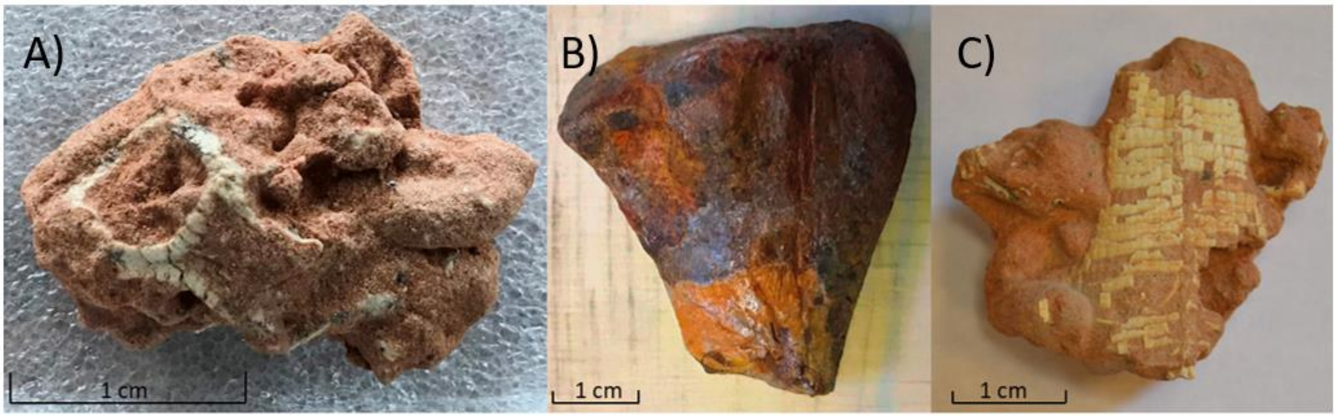

Figure 5. (A) Lizard skull (*Carusia*) from the Late Cretaceous of Mongolia (IGM 3/610). (B) Fossil bone of the proximal tibia of *Psittacosaurus* from the Early Cretaceous Oshii coated in a hematite matrix. (C) Partial skeleton of *Parmeosaurus*, an armored lizard from the Late Cretaceous from Ukhaa Tolgod (MAE 14-16).

Before starting the cleaning tests, a multi-analytical approach was undertaken to determine the composition of the superficial encrustations of the fossils, and also the synthetic resin coating the fossils.

The ATR-FTIR spectra of material scraped from the fossil surface did not show absorption attributable to any organic material. The sandstone samples only showed absorption bands attributable to the presence of silicates. Absorptions were observed at 3600 cm-1 due to the (Si)-OH stretching mode, absorptions in the spectral range of 1100-900 cm-1 were attributable to the vibrational modes of Si-O and Si-O-Si stretching and, finally, absorptions in the spectral range of 500-400 cm-1 were due to Si-O-Si deformation and Si-C stretching modes.

Characterisation of the organic component of the unwanted material on the fossil surface was performed using analytical pyrolysis (EGA-MS and Py-GC-MS).

The superficial ablated materials with the laser operating parameters reported in Table 2, were collected on a glass coverslip for chemical characterization. These materials were analysed by evolved gas analysis (EGA-MS).

A highly degraded protein was identified from all the fossils. Fig. 6C-D report the EGA curve both in total ion current (black line) and in extract ion chromatograms of the m/ z 91 (blue line) characteristic of proteinaceous compounds (Orsini, 2017). For the ablated material collected from the *Psittacosaurus* (Tibia Oshii, Fig. 5B) fossil, EGA-MS analysis revealed, together with a highly degraded protein mixture, an unidentified organic material on the surface (Fig. 5D). Unfortunately, for these materials the MS spectra did not give a clear match with known chemical compounds.

In order to check what the laser beam was able to remove, a few samples of the ablated materials were also subjected to PY-GC-MS analysis. Once again, identification of the superficial degraded proteinaceous material was not possible, however a precise characterization of the synthetic resins removed was obtained. The fossils embedded in the sandstone were consolidated with Paraloid B72, in fact the monomer methyl acrylate, methyl acrylate and ethyl methacrylate were found in all the samples. A cyanoacrylate resin was detected in the superficial thick layer of material removed from

Table 2 - Er:YAG laser operating parameters for the test performed on the *Psittacosaurus* (Tibia Oshii).

Frequency	9 Hz
Energy/pulse	20-45 mJ
Spot diameter	1.5 mm
Fluence	1.1-2.5 J/cm^2

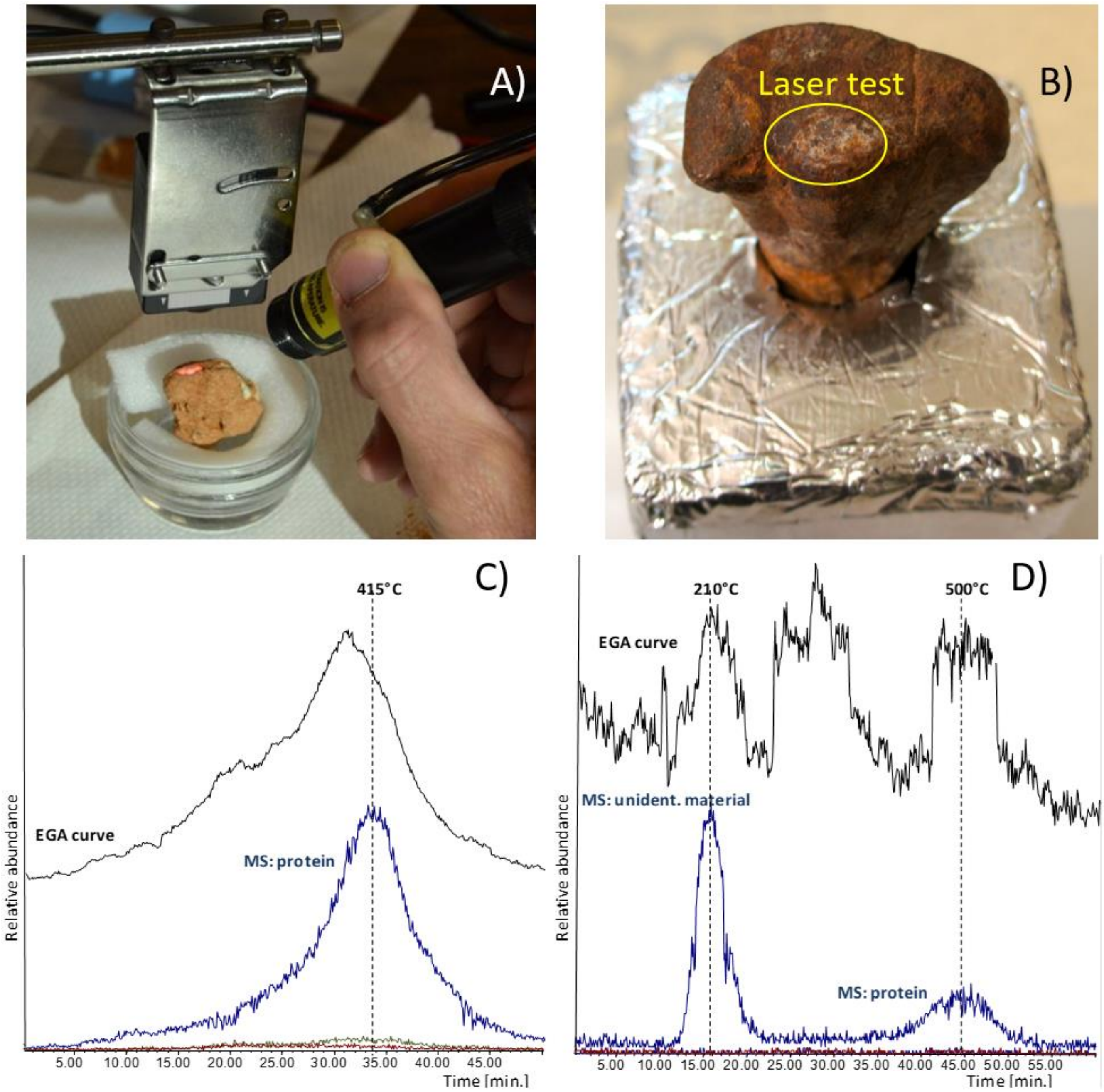

Figure 6. (A) FT-H10 Sensor Head (by Keyence, U.S.A) and laser manifold over one of the fossils, (B) *Psittacosaurus* (Tibia Oshii) with the laser ablated area for the test and EGA-MS analysis of the Lizard fossil (C) and *Psittacosaurus* (D) (black line: EGA curve; blue line: extract ion of m/z 91).

the *Psittacosaurus* fossil. The detection of the marker 2-cyanoethyl acrylate and pyrolysis product of hydroquinone, led to the identification of Aron Alpha 201 resin. This is a superior wicking and penetration synthetic glue to most other adhesive, which was used for micro consolidation during the preparation of small specimens from Gobi fossils, as recorded in the excavation diaries by archaeologists. The thick layer composed of hematite, an unidentified protein material, and the cyanoacrylate and acrylic glue, was removed from the original surface of the fossils.

Finally, for the *Psittacosaurus* samples in which the organic material was clearly detected, the analysis was also performed after the laser cleaning to see what was left on the fossil surface. The PY-GC-MS showed that the degraded organic material and the resin had been removed, while a lipid-proteinaceous layer covering the fossils had been preserved.

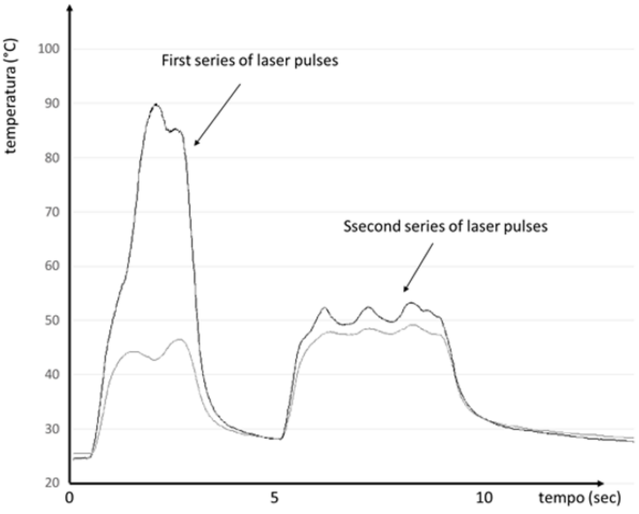

Figure 7. Temperature increase measurement during surface laser irradiation of *Psittacosaurus* (Tibia Oshii).

The temperature of all the three fossils was monitored during the laser treatment. The unwanted matrix encasing the fossil was removed using the Er:YAG laser operating according to the parameters reported in Table 2. The laser treatment was performed by applying at least five consecutive passages on the same area and wetting the surface with ethanol. It is also advisable to use a maximum frequency of 10 Hz in order to carry out the most controlled cleaning possible.

For all the tests performed on the fossils, the surface temperature increase remained below 45°C, as shown in the temperature record reported in Fig. 7.

CONCLUSION

Our results demonstrate that the Er:YAG laser safely and selectively removes undesired material from the surface of paleontological findings. Interestingly, for the investigated cases the experimental set-up demonstrated that the thermal effect during the laser irradiation was limited to a difference from room temperature of about 30-40°C. The thermal heating was not significantly high to induce any chemical/physical alterations on the fossil substrate using a common working set-up of the Er:YAG laser with a pulse duration of 300 μs (Colombini et. al, 2003:355).

Nevertheless, the temperature monitoring clearly shows the efficacy of the Er:YAG laser cleaning of synthetic polymers from the surface. The laser radiation absorption from the synthetic organic layer, which is necessary for their selective ablation, increases the surface temperature by about 50°C. The heating is confined to the surface and just to a depth of a few microns, the bulk temperature remains about 30°C above the ambient temperature (Andreotti et al., 239:2007).

Er:YAG laser is thus a promising tool for safely removing difficult matrices from fragile and delicate fossil specimens. Fig. 8 clearly shows how effective laser cleaning is. Laser treatment is particularly efficient in the case of a superficial degraded organic layer, which is not easily removable by traditional methods.

Undoubtedly this is a valuable technique in removing matrix in terms of revealing the fine details of fossil surfaces. However, the set-up parameters of the laser need to be well controlled. With a threshold fluence under 2.5 J/cm^2, and with ethanol as the wetting agent during the irradiation, the unwanted material was completely removed and without the risk of reducing or even completely losing the surface detail. The pyrolysis analysis of the fossils after laser cleaning demonstrated that the layer of organic material under the unwanted material had been preserved.

This work demonstrates that the IR sensor is particularly accurate in real time monitoring of the surface temperature and can be easily and successfully used by conservators during routine activities.

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