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An investigation of Laser Induced Breakdown Spectroscopy for use as a control in the laser removal of rock from fossils found at the Malapa hominin site, South Africa

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ABSTRACT

Laser Induced Breakdown Spectroscopy (LIBS) was used to study the spectra from fossils and surrounding rock recovered from the Cradle of Mankind site at Malapa, South Africa. The objective was to find a suitable spectral line(s), specific to fossils, which could be used as a control signal to limit damage to fossils during high speed laser removal of the encasing rock. The calcified clastic matrix (rock) encasing the fossils was found to emit a variety of complex LIBS spectra. Nevertheless, it was found possible to distinguish fossils in a single LIBS pulse, and without significant damage to the fossil, using spectral lines of neutral phosphorus.

1. Introduction

The use of lasers to remove unwanted material from objects (laser cleaning) has been studied for many years [1–4]. These have covered such diverse subjects as statues, old buildings, artefacts, metals and paintings. The laser removal of rock from around fossils has been much less widely reported. A preliminary study of laser cleaning for various applications in natural history museums, including the removal of layers of encrustation from fossil bones, was reported by Asmus [5]. Another study which focussed on the surface cleaning of fossils, clearly demonstrated the potential for this technique by removing stone and encrustation from the surface of fossils [6]. The same authors followed this preliminary study with a study of palaeontological specimens and applied a combination of laser ablation and other removal techniques [7].

Most conventional methods of removal of fossils from rock at present use mechanical or chemical procedures or a combination of both [8]. These are not only labor-intensive and slow, but the potential for damage to the fossil is often unacceptable. The laser removal of carbonated matrix from the surface of fossils was studied in comparison with conventional techniques in some detail [9]. In this study it was found that processing quality and speed is comparable in most cases, but in some special areas the laser processing was superior in either quality or speed or both. While most studies of laser cleaning have been done with laser pulses of ≥8 ns, femtosecond lasers have recently been demonstrated to be useful for precision surface cleaning of cultural heritage artefacts [10]. A proposed femtosecond laser system for micro-surface analysis of various samples, including some samples of paleontological interest, has also been reported [11].

Many applications of LIBS for analytical spectroscopy of fossils have been reported, including LIBS of fossilized buffalo horn [12], a prehistoric animal tooth [13], and recently teeth of homo sapiens [14]. The application of LIBS to archaeology has mostly been confined to the cleaning of artefacts from more recent temporal periods [15]. The use of process control techniques to assist in laser cleaning has been discussed in [1,2]. LIBS has emerged as an online monitoring tool for this application, as described in the removal of layers from marble [16] as well as fossils from matrix [11,17,18].

As part of a general investigation of the application of lasers to palaeontology, we have studied the use of Laser Induced Breakdown Spectroscopy (LIBS) to control the laser removal of the surrounding rock from fossil remains. Our work has centred on fossil-bearing strata from sites within the Cradle of Mankind UNESCO World Heritage site, South Africa. Sites in the area have been the location of many important paleontological discoveries culminating in the finding of extremely well preserved hominin fossils at the Malapa excavation site in 2008. These have been assigned the novel species *Australopith sediba* [19,20]. It has been possible to attribute a remarkably accurate age to these remains, recently refined to 1.977 ± 0.002 million years [21]. The collection of hominin fossils from this site is among the most complete record of early hominins found to date and include a nearly complete cranium [19,22], and significant postcranial elements from at least two skeletons [23–25].

Preliminary to the present work, an investigation was carried out to see whether laser removal of rock from fossils could be performed

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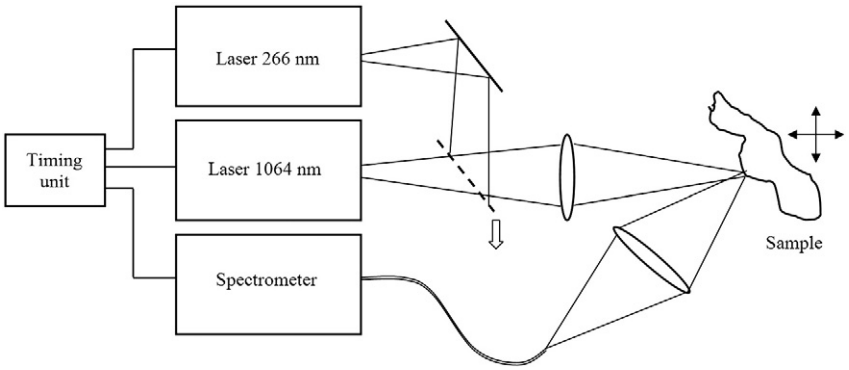

Fig. 1. LIBS experimental set-up.

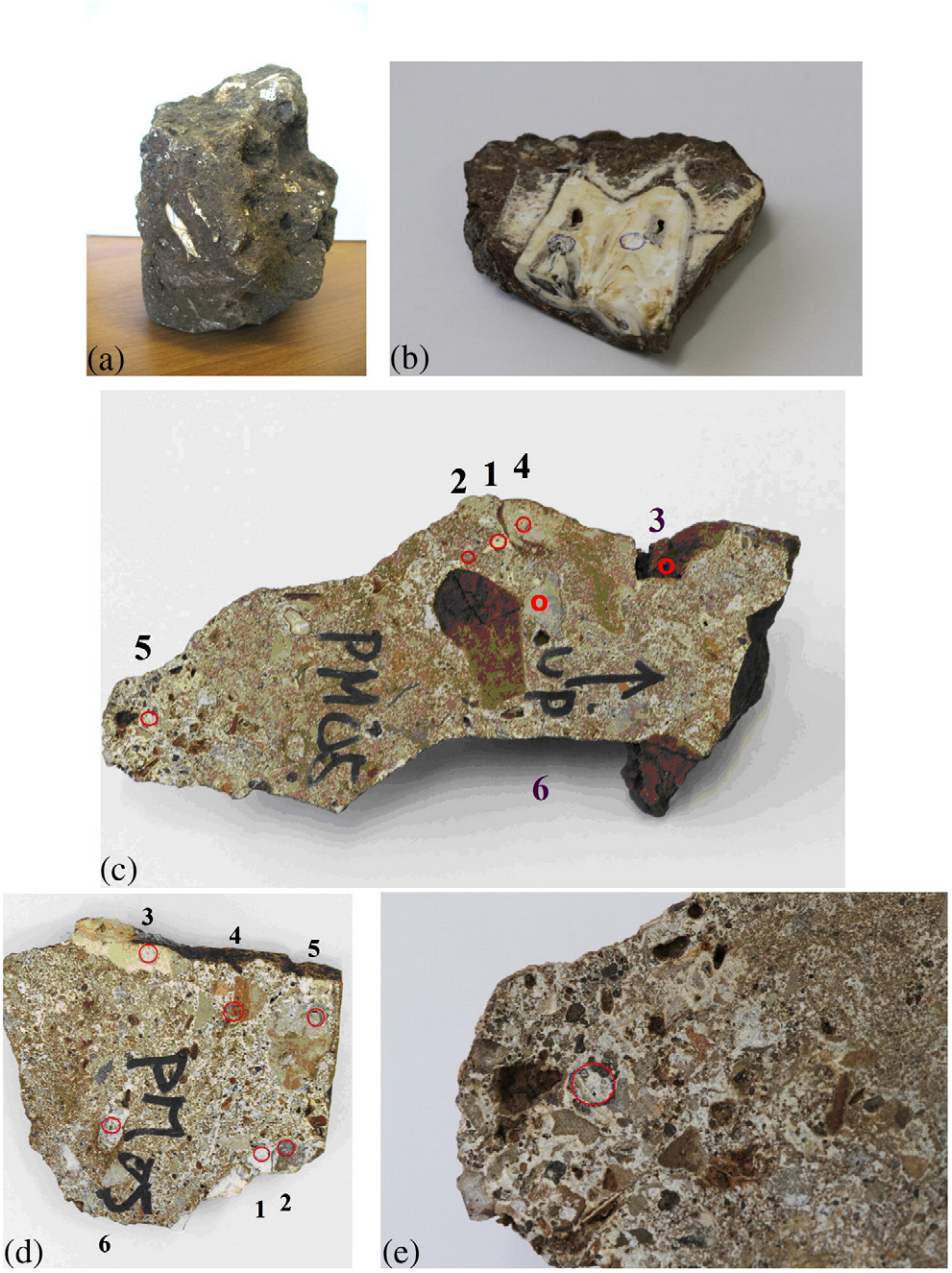

Fig. 2. Samples from the Malapa site Facies D (a) A sample 120 mm in height showing exposed fossil bone fragments (white appearance), (b) A cross-section of a fossilized bovid tooth from the same site, sample width is 49 mm. Other samples have circles indicating different regions analyzed using LIBS. (c) Sample width is 158 mm, (d) Sample width is 69 mm, and (e) is a close-up of (c) emphasizing the inhomogeneity of the rock.

Table 1
Comparison between atomic species found in rock and human and animal teeth (in ppm).

	Rock	Tooth
Mg	14 800	6100
Al	97 500	17
Si	147 000	14
P	4400	100 000
S	<100	350
Cl	<100	790
K	<100	280
Ca	130 700	200 000
Ti	4500	8
Cr	<100	5
Mn	233 200	6
Fe	367 900	20
Ni	<100	10
Cu	<100	5
Zn	<100	100
Sr	<100	100
Ba	<100	63

without feedback control to switch off the laser when the fossil is reached. As in [26], our studies showed that the depth of removal of rock per laser pulse is a strong function of laser fluence with a fairly well defined threshold that could, in certain cases, be lower than the threshold fluence for fossil removal. In such cases the rock could be removed from the fossil simply by operating the laser between the two fluences. However, the fluence was then so low that the removal rate was very slow and only really suitable for a final fine cleaning of a fossil. Moreover, the threshold fluence was found to be very dependent on the specific type of rock and with the extremely inhomogeneous calcified clastic matrix (breccia) of interest here could vary considerably over distances of as little as a millimeter across the rock face.

For these reasons the emphasis moved to fast bulk removal of rock. It is then desirable to work at the maximum laser power available and adjust the fluence for optimum removal. For maximum *volume* removal this fluence is not critical with typical laser focus spot sizes <1 mm. The removal laser is normally operating at a repetition rate of ≥10 Hz and it is necessary to have a feedback signal to switch off the laser in the time between pulses to minimise damage to the fossil. Such a feedback signal can be obtained from LIBS with a laser that is not necessarily the same as the one used for removal.

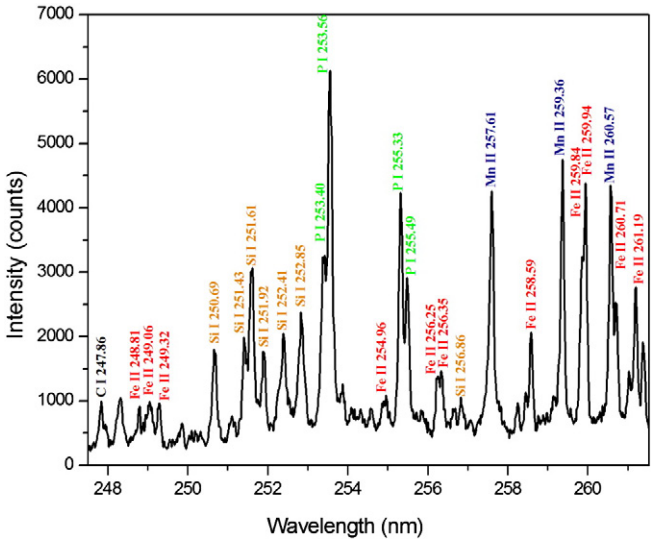

Fig. 3. Region of spectrum in the UV, from an incompletely cleaned fossil bovid tooth shown in Fig. 2, showing P I lines as well as lines of C I, Si I, Fe II and Mn II.

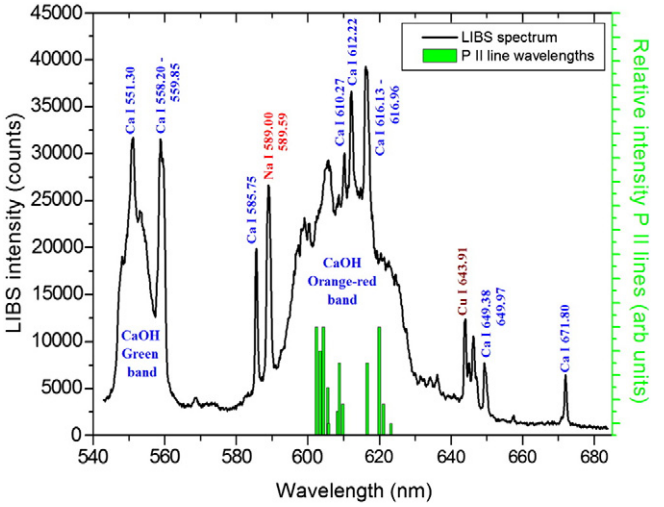

Fig. 4. Spectrum in the afterglow plasma showing strong orange-red CaOH band emission in the wavelength region embracing strong P II lines.

The present investigation therefore centred on two points:

1. Can an appropriate spectral line (or lines) be found with LIBS which is a distinctive marker for the fossil but is not emitted by the rock and can therefore be used for feedback control purposes?
2. LIBS is an inherently destructive diagnostic technique insofar as ablation of the surface occurs to a certain depth (albeit small, of the order of microns). Therefore can a depth be removed that is big enough to give a LIBS signal for control purposes and yet produce minimal damage to the fossil?

2. Experimental details

2.1. Laser irradiation

A typical setup for Laser Induced Breakdown Spectroscopy was used (Fig. 1). A Continuum Powerlite Nd:YAG laser (Model 9010) supplied 10 ns duration pulses with up to 100 mJ per pulse at 1064 nm. A second laser (Spectra Physics Quanta-Ray Pro 270-10) produced 8 ns pulses of up to 3 mJ pulse energy at 266 nm, the fourth harmonic of 1064 nm. The flash lamps were run at 10 Hz but the Q-switching at 1 Hz to allow enough time for data recording between shots. The timing system allowed the possibility of dual pulse plasma heating but for simplicity only each individual laser (mainly the 1064 nm YAG) was used for plasma excitation for the results recorded here. A moveable mirror enabled the change between lasers (Fig. 1).

The pulses were focused onto the sample using a 250 mm focal length lens giving a peak fluence of 600 Jcm^{-2}. The sample was

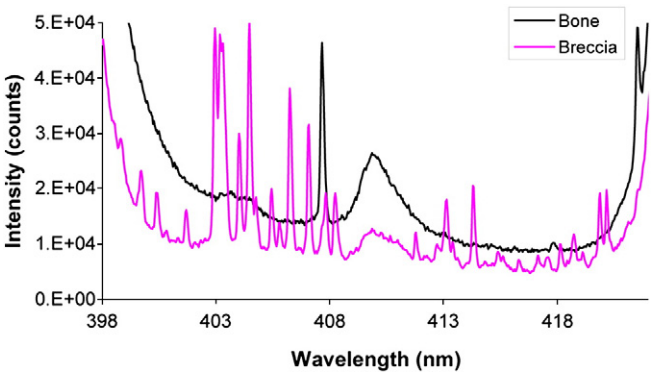

Fig. 5. LIBS spectra from fossil bone and breccia showing Sr II 407.77 nm in the wing of Ca II 396.84 nm.

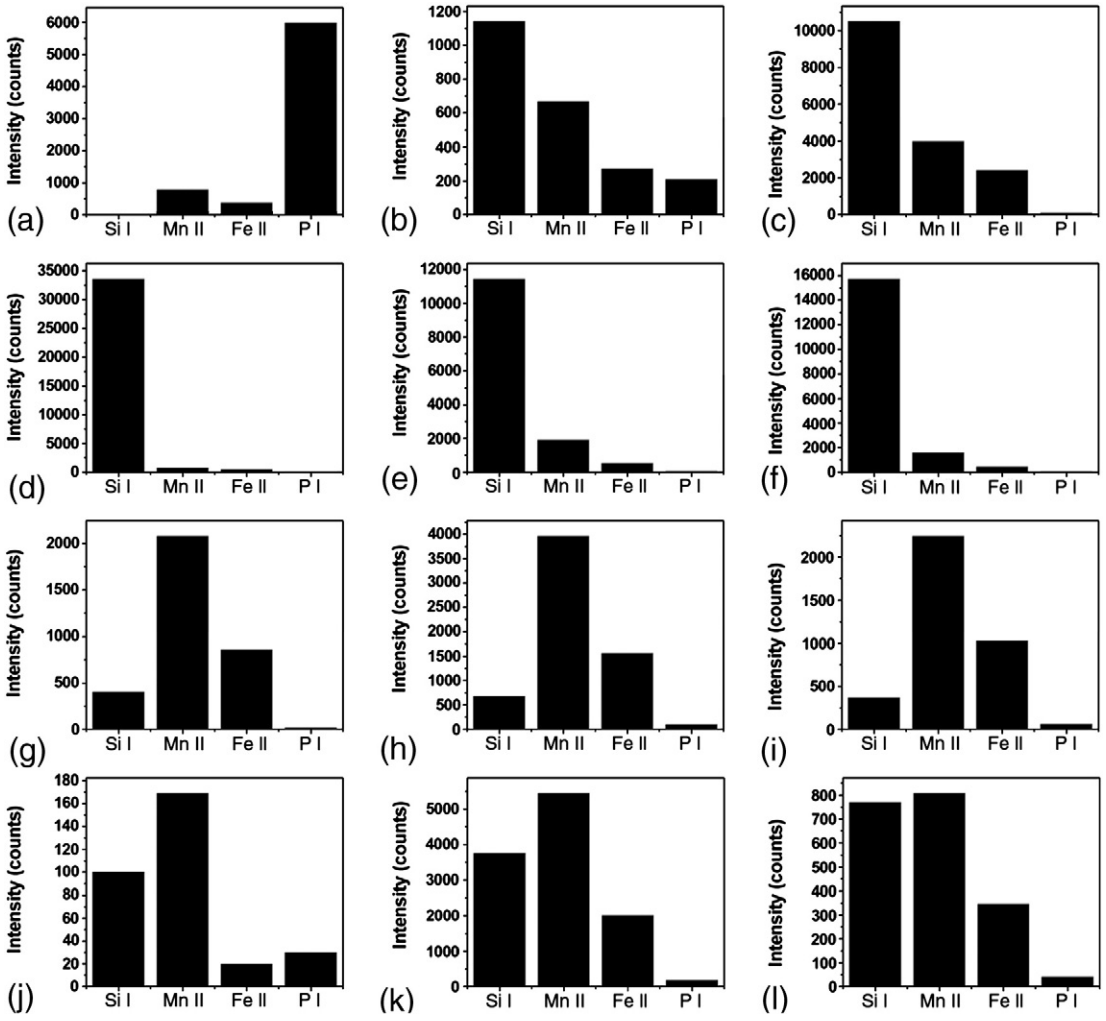

Fig. 6. Summary of LIBS spectra from different positions on the rock samples in Fig. 2. The locations on Fig. 2(c) 1 to 6 correspond to histograms (a),(b),(c),(k),(d),(f) above and on Fig. 2(d) 1 to 6 to histograms (l),(i),(e),(h),(g),(j) above. Histogram (a) is from a fossil fragment.

mounted on an x–y–z stage which allowed positioning to well within the 3.5 mm Rayleigh range about the focus. The fluence on the sample was controlled by changing the pulse energy by varying the delay between the flashlamp and Q-switch triggers. The M^2 of the beam was found to be approximately 1.5 so that the minimum diameter of the spot size on the sample ($1/e^2$ peak intensity) was 85 μm. The plasma emission was collected with a 100 mm focal length UV-quarts lens and focused into a fiber connected to an Andor Shamrock SR-303i spectrometer with an iStar DH734-18 F-03 ICCD camera. The time from the Q-switch to the gate was normally 1.5 to 2.0 μs to minimize background continuum, while the gate open time was typically ≤5 μs. Survey spectra were taken with a low resolution 300 lines/mm grating but all high resolution spectral results reported in this paper used a 2400 lines/mm grating blazed at 300 nm. The slit width used was normally 50 μm giving an instrument width of 0.10 nm. Wavelength calibration was done using a low pressure Hg-Ar lamp.

2.2. Rock samples

Various rock samples from the Malapa hominin excavation site were obtained, but only those from Facies D were used in this study. Facies D refers to a specific section of the site that is richest in hominin fossils [20]. Some of these samples were cut into flat sections for initial tests. Fig. 2(a) shows a raw rock with some fossil bone fragments exposed, while Fig. 2(b) shows a cross-section of a fossil bovid tooth cut from such a rock for tests. The "rock" or breccia from the Malapa site is actually a calcified clastic matrix which is a complex mixture of different types of rock. This is seen from the specimens in Fig. 2(c) to (e) which show clearly that the rocks are very variable in composition as well as density. The red circles show regions where detailed LIBS spectra were taken of visually different areas of the rocks.

3. Results and discussion

In order to obtain a preliminary overview of the differences between the atomic constituents of rock and bone, a series of X-ray fluorescence spectra were taken of different areas in a rock sample. A comparison with some representative figures from (modern) human teeth [27–30] is given in Table 1. It is clear that both the rock and the tooth composition are very complex with many atomic species present. The dominant species in the tooth is calcium, but this is also present in large concentrations in the rock analyzed (as is expected in such calcified clastic matrix). There are many constituents of the teeth that are not clearly seen in the X-ray rock spectra. However, these are all in concentrations of less than 0.1% and often even less than 10 ppm. The only substantial constituent of the teeth which is present in only small quantities in the rock (and not seen at all in some samples) is phosphorus. This indicates the possibility of using this species as a unique identifier of fossil material.

In order to investigate in detail the extent to which LIBS spectra of fossil bone and rock differ, a series of spectra were first taken concentrating on identifying well isolated lines of neutral and ionised phosphorus. Subsequently spectra were taken over a wide spectral range from 230 nm to 750 nm to identify significant differences in trace element spectra.

A high resolution LIBS spectrum from an incompletely cleaned fossil covering a wavelength region around the resonance lines of neutral phosphorus is shown in Fig. 3. This shows reasonably well isolated P I lines at 253.40 nm/253.56 nm and 255.33 nm/ 255.49 nm as well as lines of C I, Fe II, Si I and Mn II. Attempts to find suitable lines of ionised phosphorus were not successful for the nanosecond laser plasmas studied here. In spite of varying the delay and gating times, the background continuum radiation was always dominant making a reliable estimate of P II line intensities very susceptible to errors. This was partly due to the strong molecular emission from the orange-red band of CaOH [31,32] in the region of the strongest lines of P II at 604 nm. This was emitted from the cool outer regions of the plasma from both bone and rock even for delays as small as 0.5 μs, but due to the broadness of the features not easy to identify until the afterglow of the plasma. Fig. 4 shows such a measurement for a very long delay of 25 μs and gate of 2 μs showing the strong CaOH orange-red band emission and indicating the overlapping with wavelengths of all the strong P II lines.

Attempts to find a trace element line more suitable than the P I resonance lines for control were also not successful. One of the strongest trace element lines seen in fossils compared with breccia was Sr II 407.77 nm (Fig. 5). However there is a breccia line of Fe I which, though weaker, is very close at 407.83 nm. Also there is a strong background, in this case from the wing of the intense Ca II line at 396.84 nm.

The above results highlighted one of the phosphorus resonance doublets as the best marker for fossils but given the complexity of the rock, as emphasised by Fig. 1(e), a series of spectra, for the same wavelength interval shown in Fig. 3, were taken at different positions to see whether this was always the case. Not surprisingly, the spectra from different locations were very variable, not only in the lines that were emitted but also the absolute intensity of these lines. A summary of the spectra, from rock locations indicated on Fig. 2, is given in Fig. 6. This shows for each area studied, the intensities of the strongest lines of four main atomic species seen in Fig. 3, ie. Si I 251.61 nm, Mn II 259.36 nm, Fe II 259.94 nm and P I 253.56 nm. Note that the intensity scales are quite different for the different areas in Fig. 6. Only Fig. 6(a) corresponded to a fossil fragment.

In spite of the complexity shown in Fig. 6, the spectra could be divided into four broad groups as illustrated by results in Fig. 7. These groups where the dominant lines were either from Mn II, Si I or a combination of these as well as Fe II. Examples of such spectra are shown in Fig. 7(a), (b) and (c) respectively. In contrast, the spectra from fossils for which the covering rock had been completely removed, were totally dominated by the two P I doublets (Fig. 7(d)). These studies show clearly that the P I doublet at 255 nm in particular is sufficiently well isolated from rock lines to be useful for process control.

The use of phosphorus detection with the LIBS technique has been used in other applications. Online LIBS monitoring of neutral phosphorus lines allowed the improved determination of phosphate rich slurry for improved phosphate mining [33]. In another application, phosphate rich ore was identified using a LIBS technique with neutral phosphorus lines as well as phosphorus to silicon line ratios [34]. The use of P II lines as an indicator for fossil bone with femtosecond LIBS has also been suggested [17,18]. Besides demonstrating the applicability of phosphorus as a control for fossil processing, the results also indicate the potential of the technique for identification of fossil material. This is particularly so with the advent of portable pulsed lasers which open up the possibility of on-site identification of fossils.

In addition to the studies described above, some measurements were made of bone sections that were cut through exposing the expected soft tissue ("marrow") region of the bone, as shown in Fig. 8. Typical LIBS spectra of the material in the "marrow" region compared to the rock material on the outside of the bone where indistinguishable as shown in

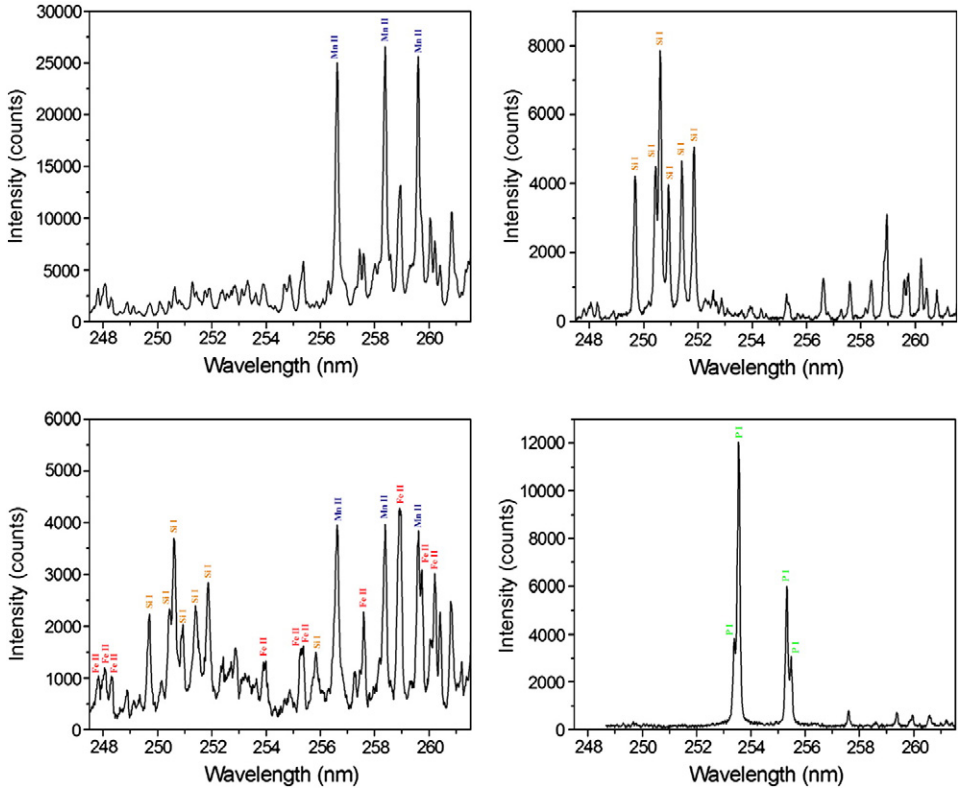

Fig. 7. Examples of LIBS spectra from different rock locations showing mainly Mn II lines (a), mainly Si I lines (b) or lines of Mn II, Si I and Fe II (c) compared with a fossil spectrum (d).

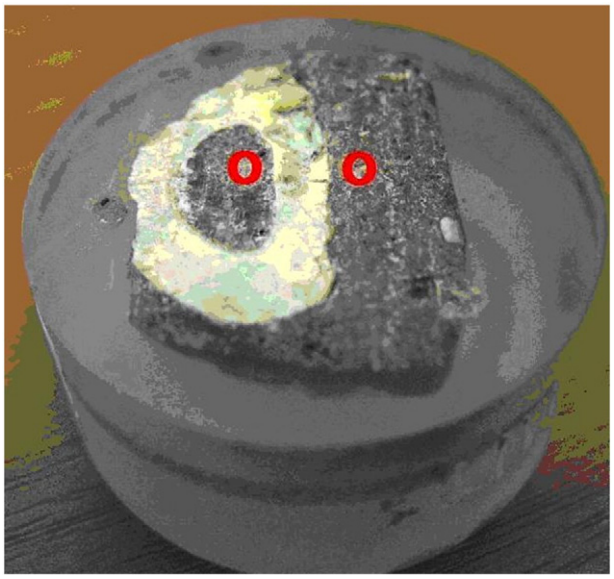

Fig. 8. Fossil bone cross-section of width 10.5 mm in a metallurgical sample holder showing soft tissue replaced by rock and areas (red) used to compare spectra (Fig. 9).

Fig. 9. This indicates that soft tissue regions have been essentially completely replaced by rock.

In a recent study of a 150 million year old fossil, it was shown that phosphorus is retained in soft tissue [35]. Although the fossilization process and bone chemistry is not the topic of the current study, this could indicate why we have found such strong phosphorus signals from the fossil bone and much less phosphorus in the surrounding rock. Attempts were made to compare P/Ca ratios in the fossils with those in modern bones but the accuracy of the absolute ratio from LIBS is too low for quantitative comparisons at present. It does, however, point towards the possibility of using LIBS to study the migration of different elements during the fossilisation process (diagenesis).

In order to quantify the damage to the fossils during laser removal of rock, the depth of fossil removal was measured as a function of laser fluence. The threshold fluence for removal was found to be $F_{th} \approx 1.2$ Jcm^{-2}, and the depth of removal per pulse, d, up to a fluence of F = 20 Jcm^{-2}, given by $d \approx 2.8 \ln(F/F_{th})$. At higher fluences the ablation rate was faster giving d = 40 μm at 600 Jcm^{-2}. At this fluence, corresponding to maximum rock removal, the signal to background intensity for the strongest phosphorus line is greater than 20 and process control could easily be done on the basis of a single laser pulse. However, the best scenario would probably be to use different lasers for removal and control. The control laser could be run at a higher repetition rate to probe ahead of the removal laser in time. For example at 20 Jcm^{-2} the fossil removal is reduced to 8 μm per pulse. At this fluence the 255 nm phosphorus line pair to background intensity ratio is still ≈10 with an adequate enough signal to noise ratio to stop the lasers within one control pulse. In fact it would probably be better to not use a YAG laser for bulk removal since inhomogeneous material such as rock is much more efficiently removed by fragmentation or spallation rather than vaporization as in LIBS. This implies a laser with much longer pulse lengths and lower peak intensities than with LIBS.

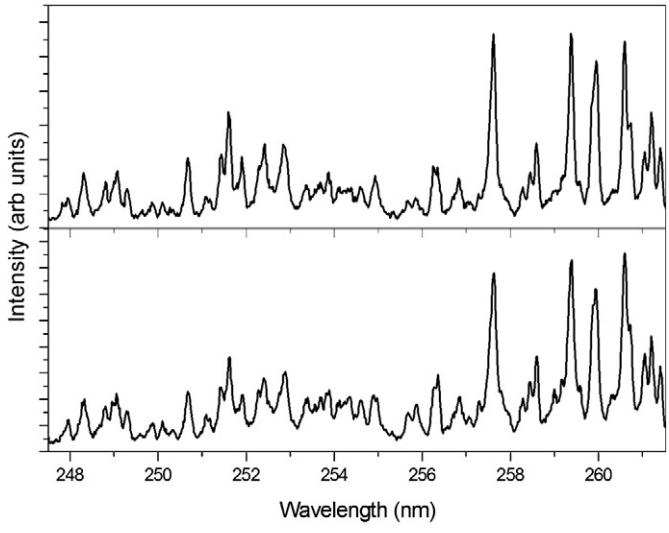

Fig. 9. Comparison of LIBS spectra from rock and bone "marrow" regions in Fig. 8 showing almost identical spectra dominated by Mn II lines (c.f. Fig. 7(a)).

Further measurements were done at a laser wavelength of 266 nm in an attempt to achieve increased absorption and a decrease in optical penetration depth for the fossils. It was found that more clearly defined smoother ablated regions with a depth of ≤5 μm could be attained while still retaining sufficient signal to background intensity to distinguish bone from rock in a single shot. However, no striking advantages were found compared with using the first YAG harmonic at 1064 nm.

4. Conclusions

We have found that the phosphorus content of 2 million year old fossils from the Malapa hominin site is significant enough to discriminate fossil bones with relative ease from the surrounding rock. The rock lines in the same spectral region were shown to be mainly from silicon, iron and manganese. Various sections of rock were tested and none had significant phosphorus content. In addition, the damage to the fossil was quantified for single pulse detection. When using high enough pulse energy corresponding to good signal to background ratios for phosphorus line detection, damage to unprepared fossil is ≤40 μm depth. In practice, the spectral acquisition for process control could be considerably simplified by using a specialized spectrometer covering only a small spectral range or by using narrow-band filters to cover the P I line and a nearby line for reference purposes. The use of this technique holds great promise for process control in laser preparation of fossils, as well as for accurate identification of fossils at excavation sites using a portable system.

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