

Research Article

Laser Cleaning Tests on Archaeological Copper Alloys Using an ND:YAG Laser

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Laser cleaning tests were performed on five archaeological copper alloy objects using a Q-switched Nd:YAG laser at 1064 nm. As a comparison, a section of each object was cleaned mechanically. Prior to cleaning, cross-sections were prepared to characterise the corrosion crust and help to locate the position of the original surface. Laser cleaning was not successful at removing burial deposits on two of the objects. For the other three objects, the laser removed most of the corrosion crust. This was not always satisfactory, as cleaning was sometimes accompanied by the loss of the original surface. In addition, laser-cleaned surfaces were matt compared to mechanically cleaned surfaces. In some instances, the former had a disfiguring purple hue which was attributed to the formation of particles that could be seen when examining the surface using scanning electron microscopy. For all the objects examined here, superior results were obtained by mechanical cleaning.

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1. INTRODUCTION

The British Museum holds many archaeological metal artefacts within its collections. Most metal finds are covered by corrosion crusts that may have to be removed and the present study is focused on the cleaning of archaeological copper alloys. The formation of corrosion products on archaeological copper alloys can be complex and differ according to the burial environment and composition of the metal [1–4]. For example, in the case of bronzes, a selective copper dissolution often takes place leaving the outer corrosion layers of archaeological bronzes enriched in tin [5, 6] and brasses with substantial amounts of zinc are known to lose zinc through dezincification [2]. A detailed review of the corrosion process in copper alloys is beyond the scope of the present paper and only a schematic description of the process for pure copper is presented here. Throughout the lifetime of an object, the surface oxidises producing a very thin compact corrosion layer. During burial, the copper under the surface is further attacked and intergranular corrosion occurs. A compact layer of cuprite, Cu_2O , forms along the grain boundaries, filling the voids. This layer is called the “primary” cuprite layer. As corrosion progresses, the metal core reduces in size becoming pitted and formless. This is accompanied by the migration

of copper ions through the primary cuprite layer and the formation of secondary corrosion products such as cuprite, malachite, and basic copper chlorides [1, 2]. The outer-most layers of corrosion often incorporate minerals and quartz grains from burial deposits [2]. Variation in burial environments will produce additional areas of different compounds, including sulphides and chlorides.

In this context, cleaning is defined as the beneficial removal of altered material originating from the object or externally deposited material. Archaeological metals are usually not cleaned back to the metal surface as, in the majority of cases, the metal core will be shapeless. Instead, the “original surface” is sought. In conservation, the term original surface denotes a layer within the corrosion products where decoration, tool marks, or evidence of wear can be found. The position of the original surface in copper alloy corrosion crusts varies depending on the condition and state of mineralisation of the object and can be anywhere in the corrosion crust. Detection of the original surface in the layers of corrosion can be difficult, but it is often a more or less continuous compact layer, which differentiates it from the less dense secondary corrosion products. The original surface retained in the mineralised deposits often has a smooth, even, and lustrous surface from original finishing of the object or due to

polishing throughout its useful life. Conservation cleaning does not aim to remove every trace of corrosion overlying the surface, but to reveal and preserve the original surface. Overcleaning can lead to removal of intergranular corrosion or disruption of the original surface creating a matt appearance. The choice of cleaning method for a particular object has to be assessed by conservators in terms of risk and benefit to the object, as no method currently in use is 100% successful. Chemical cleaning methods are not easily controlled and can be unpredictable, usually resulting in the loss of the original surface. Air abrasive, whilst useful, is often difficult to control and can produce a matt surface. The most accurate and adaptable method for archaeological copper alloys is mechanical cleaning using a scalpel. However, mechanical cleaning can take a long time and damage can occur either through breakage due to pressure applied to the object or scratching of the surface.

2. EXPERIMENT

Laser cleaning has gained considerable success as a valuable method of conservation since the 1970s and often has the advantage of being faster than conventional techniques, while producing equal or superior results on certain materials (e.g., [7]). Recently investigations of the use of the Nd:YAG laser to remove corrosion crusts on archaeological copper alloy artefacts have taken place. The results of these investigations have been varied. Pini et al. [8] laser-cleaned 16 bronze objects covered by green calcareous accretions and silicates, preserving the oxidation layer beneath. The Nd:YAG lasers used in their study had a pulse duration of either 20 μ s or 2–10 ns, and Pini et al. report that long pulses were more efficient at removing thick encrustations than short pulses. They sometimes observed discolourations on the surface of calcareous encrustations, which changed from green to grey or red. This was not considered a problem since all the objects were cleaned down to the cuprite layer, where no colour change ever took place. A comparison was done with mechanical cleaning on one of the objects and the authors report that manual cleaning was more time-consuming and did not produce the same homogeneity of cleanliness as laser cleaning. In another study, Batishche et al. [9] have performed successful removal of corrosion layers from a bronze fastener to reveal surface detail and decoration using a combination of Nd:YAG lasers with pulse durations of either 100–120 μ s or 15 ns. They did not report any side effects from laser cleaning. Drakaki et al. [10] have laser-cleaned two Roman coins using a Q-switched Nd:YAG laser operating at 532 nm and 0.4 J/cm². On the first coin, the surface obtained was rather smooth with a bright colour and, from the photograph published, surface detail was lost. For the other coin, the laser-cleaned surface was smooth but had a dark colour, which was deemed less satisfactory. Although these three studies indicate that laser cleaning is successful at removing corrosion layers, none of them clearly assessed where the original surface of the objects lay and whether it was preserved by laser cleaning. The original surface does not always lie at the primary cuprite layer and it has not been demonstrated that laser cleaning is successful at retaining surfaces above this.



FIGURE 1: Objects after cleaning; the left side of each object has been laser-cleaned and the top right has been mechanically cleaned. The bottom right side was left uncleaned.

Descriptions of success or failure can be subjective depending on expectation and cleaning requirement. Systematic comparison with mechanical methods is also required so that the results can be objectively assessed before application.

The British Museum has recently acquired an Nd:YAG laser and the present study forms part of ongoing research into its use in cleaning metal artefacts in the Museum's collection. In particular, the aims of the current work were to look in more detail at the effects of laser on archaeological copper alloy in relation to its practical use in conservation, and add to the body of work in this field. The use of the laser has interesting possibilities as an alternative low contact cleaning method and the parameters of the laser require assessment before application on registered museum objects. Laser cleaning tests were performed on several archaeological copper alloy objects using an Nd:YAG laser and whether the laser treatment preserved the original surface was carefully assessed. In addition, mechanical cleaning was conducted as a comparison.

3. MATERIALS AND METHODS

3.1. Samples

As it is not possible to produce in the laboratory corrosion crusts similar to those present on archaeological objects, tests were performed on five unregistered archaeological copper alloy objects of unknown provenance (see Figure 1). Except for Object 1, the corrosion crust on each object was relatively thin and appeared homogeneous across the surface of the object. All the objects were covered by siliceous burial deposits.

Prior to cleaning, analyses were performed to determine the composition of the alloys and the corrosion layers. Sections of each object were removed using an Isomet

saw, embedded in an epoxy resin, ground on carborundum paper and polished with diamond pastes of $6\ \mu\text{m}$ and $1\ \mu\text{m}$. X-ray fluorescence (XRF) analyses were carried out on the uncorroded metal core of the objects using an ArtTAX spectrometer (voltage 50 kV and current 0.80 mA) and the results are shown in Table 1. The corrosion layers were examined in cross-section using polarised light microscopy, Raman spectroscopy, scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX) to help in locating the position of the original surface. It should be noted that oxygen is easily detected using EDX and all the corrosion crusts were found to contain significant amounts of oxygen. However, the amount of oxygen calculated from the EDX analysis cannot be considered reliable due to inherent difficulties in calculating the background correction. Therefore, oxygen was not included in the calculations of the relative amounts of present elements. Also, it was not always possible to obtain Raman spectra of the compounds present in the corrosion crusts although most corrosion products are Raman active. This could be because corrosion products on archaeological metals are often poorly crystallised [6]. The results of the analyses are reviewed for each object in turn.

Object 1

Analysis of Object 1 indicated that this is a leaded tin bronze. The corrosion crust on this object was uneven, with areas covered by either a thin corrosion crust or warts. The section was taken on an area covered by a thin corrosion crust. Next to the metal core was a very thin layer of oxidised metal and, beyond this, a thick corrosion layer containing mostly copper and silicon with small amounts of iron and aluminium. The Raman spectrum obtained for this layer suggested the presence of chrysocolla, $(\text{Cu, Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot x\text{H}_2\text{O}$. The original surface appeared to be just above the metal oxide layer.

Object 2

Object 2 is a leaded brass. There was a layer of cuprite next to the metal core, followed by three homogeneous layers. The layer immediately above the cuprite contained mostly copper, but also silicon and traces of zinc. The second layer had a similar composition as the first layer, but contained slightly less silicon and also small amounts of tin and iron. The outer layer contained mostly copper and silicon, with small amounts of iron and zinc. Chrysocolla was possibly present in this layer. The original surface appeared to lie just above the cuprite layer.

Object 3

Object 3 is a bronze containing copper, lead, tin, and zinc. Adjacent to the metal core is a layer of cuprite and possibly cassiterite. As distinct from the other objects, Object 3 has a compact layer of cerrusite which is not homogeneous across the surface of the object but interrupted by discrete areas of

TABLE 1: Composition of uncorroded metal core determined using XRF. (The results should have an accuracy of $c. \pm 1\text{--}2\%$ for copper and $c. \pm 5\text{--}10\%$ (relative) for tin, zinc, and lead when present above 10% in a copper alloy, deteriorating to $c. \pm 20\text{--}30\%$ (relative) when present above 1% but below 10%.)

Object	Composition (% wt)
1	86% Cu, 13% Sn, 1% Pb
2	77% Cu, 20% Zn, 3% Pb
3	87% Cu, 5% Pb, 5% Sn, 2% Zn, traces
4	73% Cu, 20% Zn, 7% Pb
5	78% Cu, 21% Zn, 1% Sn

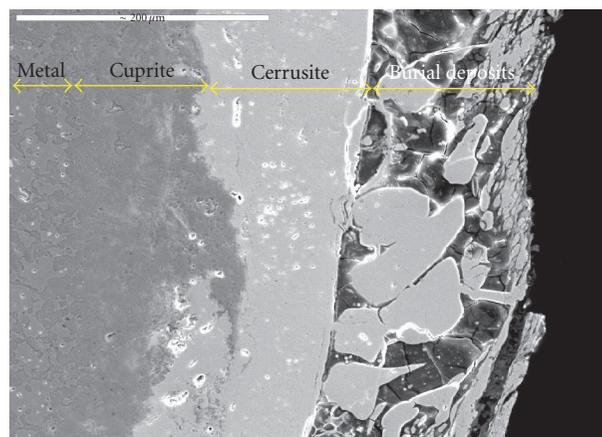


FIGURE 2: SEM picture of the cross-section of Object 3, showing the corrosion layers before cleaning. The core metal and the primary cuprite layer are located on the left of the picture. The light grey layer in the middle of the section is cerrusite and to its right is a corrosion layer containing particles of cerrusite and burial deposits. The original surface is at the top of the cerrusite layer. (Length of scale marker is $200\ \mu\text{m}$.)

cuprite and malachite. The presence of cerrusite has been reported on archaeological bronze artefacts rich in lead (e.g., [11]). The outermost layer of corrosion was complex containing large amounts of lead, oxygen, and copper, as well as particles of cerrusite and burial deposits. The original surface lies at the top of the compact cerrusite layer, see Figure 2.

Object 4

The metal core of Object 4 is leaded brass. The corrosion layer next to the core contained cuprite. Above the cuprite was a layer containing copper, silicon, phosphorous, and lead. Raman spectroscopy showed the presence of malachite and possibly chrysocolla. The outermost layer contained inclusions of silica, copper, iron, lead, and phosphorous and is probably corrosion mixed with deposits from burial. The original surface of the object was at the top of the malachite rich layer.

TABLE 2: Parameters used for the laser cleaning.

Object	Fluence	Condition
1	400 mJ/cm ²	No water
2	400 mJ/cm ²	Immersed in water prior to cleaning
3	240 mJ/cm ²	Immersed in 50/50 water/IMS* prior to cleaning
4	900 mJ/cm ²	No water
5	600 mJ/cm ²	Water applied on surface

*IMS= industrial methylated spirits.

Object 5

Object 5 is a brass containing copper, zinc, and tin. Next to the core lies a very thin layer of cuprite with traces of zinc and tin. The adjacent corrosion layer contained a large amount of copper, silicon, tin, and phosphorous. It was found to contain malachite and possibly chrysocolla. The original surface of the object appears to be contained in this layer.

3.2. Methods

For the cleaning tests, the top surface of each object was divided into three areas: half of the surface was treated by laser, a quarter was left untreated, and the remaining quarter was cleaned mechanically. The laser used was a Lynton Phoenix Athena laser (wavelengths: 532 and 1064 nm, pulse duration: 5–10 ns). Only the 1064 nm wavelength was used in the present work as preliminary tests at 532 nm indicated that the cleaning process was extremely slow, making the use of laser at this wavelength impractical. The fluence used varies considerably, as each laser cleaning test was performed at the minimum fluence at which the overlying soil deposits could be removed on each sample object. Once the working energy levels had been established, the laser spot area was estimated by taking a burn pattern on a photographic paper and the average fluence was calculated by dividing the energy per pulse by the laser spot area. To achieve an even clean, the pulses were overlapped slightly, therefore only a few pulses per area were applied to the surface. A liquid was applied to the surface of some of the objects while using the laser, as this has been reported to improve the laser cleaning of metals (see, e.g., [10, 12–14]). Some objects were immersed in a liquid prior to testing to increase penetration into the corrosion crust. The parameters used for the laser cleaning of each object are summarised in Table 2. Mechanical cleaning was performed with a scalpel fitted with a Swann-Morton No.15 stainless-steel blade under $\times 40$ magnification. All the objects were more time consuming to clean mechanically compared to the laser treatment.

After the cleaning tests, the treated surfaces were examined using an optical microscope (up to $\times 60$ magnification). The corrosion crusts and the cleaned surfaces were examined using SEM-EDX and Raman spectroscopy. EDX spectra were measured using a JEOL JSM840 scanning electron microscope with an Oxford Instruments ISIS EDX analyser. Raman spectroscopy was carried out using a Jobin Yvon LabRam

Infinity spectrometer with a green laser with a wavelength of 532 nm. Spectra were measured in the 100–1600 cm⁻¹ region with a resolution of 2 cm⁻¹. Each spectrum was collected for between 10 and 60 seconds and at least five repetitions were used to produce a spectrum.

4. RESULTS AND DISCUSSION

4.1. Results of cleaning tests

Where the laser cleaning had been successful at removing burial deposits, the laser-cleaned surface was analysed using SEM-EDX and Raman spectroscopy (see Table 3 for the results of the SEM-EDX analyses). The results are reviewed for each object in turn.

Object 1

It could be observed with the naked eye that, unlike mechanical cleaning, the laser treatment had not removed the burial deposits from Object 1 completely. Due to the uneven thickness of the corrosion crust on this object, it was not possible to remove the warts during the laser cleaning tests without exposing the core metal in adjacent areas covered by thinner corrosion layers. The dendrite structure of the metal was also exposed as the laser had removed the intergranular corrosion. Slight discolouration to the cuprite layer was also noted under high magnification. As no liquid was used during laser cleaning on Object 1, it was investigated whether using a liquid would improve the cleaning process. Laser cleaning tests were done on the back of the object using water, but it was still not possible to remove the burial deposits. This is in agreement with the work of Degriigny et al. [15] who reported that using a liquid did not have any effect when laser cleaning tarnished silver threads.

Object 2

When the cross-section of Object 2 was examined using SEM-EDX prior to cleaning, it was found that the metal core was covered by several layers of corrosion, with the outermost layers containing small amounts of iron. It appeared that the original surface lies just above the primary cuprite layer. The laser treatment removed the burial deposits from Object 2, but the laser-cleaned surface had a matt appearance, which was very different from the lustrous surface obtained by mechanical cleaning, suggesting that the original surface had been removed. This can be seen in Figure 3 where original tool marks on the surface are less visible in the laser-cleaned areas. In addition, it was observed using an optical microscope that the laser had uncovered the core metal in a few very small areas (approximately 1 mm in size). This could be due to the hot spots in the laser beam or heterogeneities in the corrosion products. When analysing the laser-cleaned surface using SEM-EDX, the copper content was high and no iron was detected (see Table 3). In contrast, the presence of iron on the mechanically cleaned surface and relatively low copper content suggest that not all the outer-most corrosion

TABLE 3: SEM-EDX analyses for the mechanically cleaned surface and laser-cleaned surface for the objects, on which laser cleaning was successful at removing burial deposits.

Object	Mechanical cleaning (% wt)	Laser cleaning (% wt)
2	53% Cu, 19% Si, 16% Zn, 5% Pb, 3% Fe	88% Cu, 3% Si, 4% Zn, 5% Pb
3	7% Cu, 93% Pb	52% Cu, 38% Pb, 10% Sn
5	64% Cu, 28% Si, 3% Ca, 3% Fe, 2% P	92% Cu, 2% Si, 6% Zn



(a)



(b)

FIGURE 3: Cleaning results for Object 2: (a) laser-cleaned surface, (b) mechanically cleaned surface. (Horizontal field of view is 9 mm.)

layers have been removed. This indicates that, unlike mechanical cleaning, the laser has removed the outer-most corrosion layers and possibly some of the original surface. Some areas cleaned by the laser had become very dark compared to the mechanically cleaned surface, while others had a slightly purple hue. This is illustrated in Figure 3. Purple/blue tinges on oxidised copper plates irradiated by a Q-switched Nd:YAG laser have been reported by Kearns et al. [16]. Peaks at 301 and 624 cm^{-1} in the Raman spectrum on some areas of the laser-cleaned surface suggest the presence of tenorite, CuO . Tenorite forms at temperatures between 400 and 600°C and laser irradiation has been reported to cause the oxidation of cuprite to tenorite [16].

Object 3

The corrosion crust on Object 3 was different from that on the other objects as it contained cerrusite. When analysing

the cleaned surfaces, the amount of lead was much lower on the laser-cleaned surface than on the mechanically cleaned surface (see Table 3). In addition, cuprite and cerrusite were detected by Raman spectroscopy on most of the laser-cleaned surface, whereas only cerrusite was detected on the mechanically cleaned surface. This indicates that, although a thin layer of cerrusite has been left by the laser treatment, most of the compact cerrusite layer, and therefore the original surface, have been removed. Also, the laser-cleaned surface was matt compared to the lustrous surface uncovered by mechanical cleaning further suggesting overcleaning and damage to the surface.

Object 4

The malachite rich layer on this object should be retained during cleaning as it is where the original surface lies. During mechanical cleaning, it was observed that the fragile original surface had been destroyed in many places by the corrosion process, but it was still possible to uncover the green corrosion layer on most of the surface. In contrast, the laser-cleaning tests were not successful as the burial deposits could not be removed completely. In the areas where the burial deposits had been removed, most of the green corrosion layer was removed by the laser and the original surface was lost in some areas down to the metal core. Cottam et al. [17] who laser cleaned a Roman bronze coin with a transverse excited atmospheric CO_2 laser emitting at 10.6 μm also reported the removal of a green corrosion layer and loss of surface details. The laser-cleaned surface of Object 4 was matt and had a distinct purple hue. The difference between the surfaces uncovered by mechanical cleaning and laser treatment is illustrated in Figure 4. As no liquid had been used while laser cleaning, a test was made on the back of the object using water. As with Object 1, the results were not significantly different from those obtained when no liquid was used.

Object 5

The green corrosion layer, which contained the original surface of Object 5, was retained during mechanical cleaning. In comparison, it was not possible to remove the burial deposits using the laser without removing the green corrosion layer, and therefore the original surface was lost. The laser-cleaned surface was mostly covered by cuprite, as identified using Raman spectroscopy and SEM-EDX. The laser-cleaned surface had a matt and slightly purple appearance.



(a)



(b)

FIGURE 4: Cleaning results for Object 4: (a) laser-cleaned surface, (b) mechanically cleaned surface. (Horizontal field of view is 5 mm.) Note that the purple hue of the laser-cleaned surface on Object 4 is not apparent using the microscope.

5. DISCOLOURATION

As reported earlier, there was a slightly purple discolouration to the laser-cleaned surfaces of Objects 1, 2, 4, and 5. For Objects 1 and 2, this was only on some areas, whereas on Objects 4 and 5, this was all over the laser-cleaned surface. When the green corrosion layer on the mechanically cleaned surface of Object 5 was lifted using a scalpel, it was noticed that the layer underneath the green corrosion layer had a brown colour. This shows that the unusual colour of the laser-cleaned surface has been caused by laser irradiation and was a surface effect. The discoloured areas on Objects 2, 4, and 5 were examined using SEM at a high magnification and it was observed that the purple hue was associated with the presence of particles, many of which were spherical. These are shown in Figures 5 and 6. Three spherical particles on Object 4 were analysed using SEM-EDX and found to contain copper and oxygen. The formation of particles on metals has been reported in the literature when laser cleaning tarnished copper coins [13], tarnished silver threads [15] and archaeological iron [14]. It has been suggested that this is due to the metal vaporising and being redeposited. The absence of discolouration on Object 3 is possibly due to it being the only object with a cerussite corrosion layer, or due to the significantly lower fluence at which it was laser cleaned (240 mJ/cm^2 compared to $400\text{--}900 \text{ mJ/cm}^2$ of the other objects). Pini et al. [8] and Batishche et al. [9] did not report any surface alterations at a microscopic level when cleaning archaeological copper alloys using an Nd:YAG laser at 1064 nm

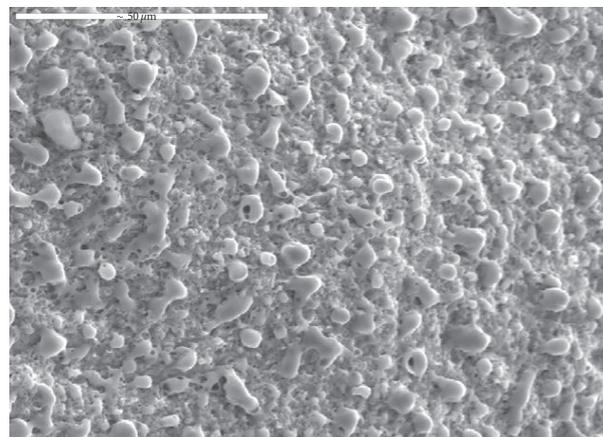


FIGURE 5: SEM photograph showing the presence of particles on the laser-cleaned surface of Object 5. (Length of scale marker is $50 \mu\text{m}$.)

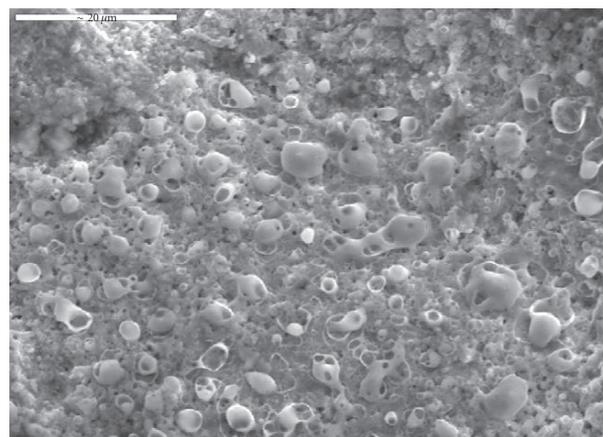


FIGURE 6: SEM photograph showing the laser-cleaned surface of Object 2. (Length of scale marker is $20 \mu\text{m}$.)

and μs pulses. The use of longer pulse durations is expected to increase heat conduction to the bulk material compared to ns pulses and, as the laser-cleaned surfaces were not examined at high magnification in these studies, surface alterations may not have been detected. Alternatively, it is possible that the burial deposits on the objects cleaned in [8, 9] were very different from those examined here and could be removed at fluences that did not affect the oxidation layer.

6. CONCLUSIONS

From the results of the tests conducted, it can be concluded that the use of a Q-switched Nd:YAG laser at 1064 nm is not a suitable method of cleaning archaeological copper alloy objects. The burial deposits were hard to remove from the surface of the objects and the fluences used were different for each object probably because of the difference in

composition of burial deposits. On two of the five samples, laser cleaning was not successful at removing these incrustations. With a single laser pulse, it was not possible to control which corrosion layers were removed and which retained. The green corrosion layers containing malachite on Objects 4 and 5 were easily removed at the fluences required to clean off the burial deposits, exposing the cuprite layer, and on several objects the metal core was revealed in small areas. This resulted in uneven cleaning and loss of detail with the total removal of the original surface on those objects where it was contained within the carbonate corrosion layer. Some of the laser-cleaned sections had a disfiguring purple hue attributed to the formation of particles that could be seen when examining the surface using SEM. In all examples, the section of each object cleaned mechanically using a scalpel-produced superior cleaning results and greater retention of surface detail. Further work will be conducted to explore whether better results can be obtained using lasers with different wavelengths and pulse durations, as these parameters have been shown to affect the laser cleaning of metals (e.g., [10, 18]).

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