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1. Introduction

1.1.   Presentation of the project and objectives

The different conservation treatments conducted these last years at the Sculpture Department of the National Conservation Centre (National Museums Liverpool) included the laser cleaning of a few copper alloy outdoor monuments. It has been noticed that although the cleaning was carried out in a very careful way by skilled conservators, a slight discoloration of the oxidized surface of copper occurred, turning from red / brown to purple / grey. This effect having appeared systematically after laser cleaning of copper alloys, it began to preoccupy the conservators at the National Conservation Centre and English Heritage. Although the usual protective layers, such as waxes, applied on the surface of cleaned sculpture were hiding this colour change, the modification of the surface was undoubtedly present.

Compared to other materials, laser cleaning of metals has not received until now the same amount of interest. Possibly due to the high complexity of the corrosion layers, laser cleaning of metals appears non-selective or not "self-limiting". This means that in the case of e.g. copper alloys, the laser beam isn't able to discriminate between the corrosion layers to remove and the original surface to preserve. This may lead to some damage[1].

The objective of the present research is to characterize this discoloration effect occurring on the oxide level of copper alloys. Different aspects of the interactions laser/copper alloys will be investigated to reach it:

- **Study of the behaviour of different copper alloys commonly used in outdoor sculpture under laser radiations, with both corrosion-free and oxidised surfaces, as well as the impact of different fluence levels (energy density) on these surfaces.**

- **Determination of the nature of the discoloration (chemical, physical or optical change).**

- **Study of an eventual reversible effect of the discoloration**

The results obtained would determine the impact of a laser-cleaning treatment on the surface of copper alloys. It would improve the knowledge of the conservator and give him

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[1] Cooper, 2001.

useful information when dealing with such monuments, in order to minimize the risks of damaging the surface.

The study was carried out at the light of various techniques and high precision scientific tools – naked eye, optical microscopy (OM), visible spectrometry, X-Ray Diffraction (XRD), Scanning Electron Spectroscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS), X-Ray Photoelectron Spectroscopy (XPS)- and on the basis of two laser-cleaned copper alloy outdoor sculptures – The Lord Nelson Monument in Liverpool and The Queen Victoria in Southport, UK – in order to get a coherent and precise idea of what causes the discoloration of the metal surface after laser irradiation. Such optical and chemical measurements of the surface of the laser cleaned alloys were undertaken in order to characterize the nature of the discoloration on oxidized metal surface and to help finding a way to avoid or at least minimize them.

1.2. *The National Conservation Centre (National Museums Liverpool)*

This research project was proposed by the National Conservation Centre (National Museums Liverpool, UK), following a personal request and a high interest for laser cleaning of artworks and with the aim of obtaining the Diplôme des Hautes écoles spécialisées de Suisse Occidentale, in conservation of archaeological and ethnographical objects. The NCC offered a full-time placement of 5 months, with access to laser training, equipment (laser system, analytical tools) and high competence levels of supervision.

The implication of the NCC in the field of laser cleaning and technology is of great importance for the development of laser knowledge in conservation throughout the world. The first use of a laser cleaning system at the NCC dates back to 1994. This institution was the first one in England, and among the first ones in the world, to use laser technology in the field of conservation of artworks and to carry out research and development. At the beginning, the various conservation departments (metal, ceramic, organic, sculpture, laser, paper, etc.) were dispersed in different sites in Liverpool. In 1998, all departments were reunited at a unique place, in a completely renewed parking building, which sits in the heart of Liverpool City Centre, near Queen Square. At the same time, laser scanners began to be used as well for the recording and replication of artworks, leading to the creation of the Laser Technologies Department, the head of which is Dr. Martin Cooper. While laser scanning and laser research were handled by this department, practical laser cleaning of artworks was carried out at the Sculpture Department, headed by Mrs Samantha Sportun.

Although a wide knowledge and successful results of laser cleaning of stone sculpture are today well established, the use of laser to clean copper alloys monuments, and metals in general, is still a great

debate, as such materials don't benefit from the "self-limiting" effect of laser cleaning. Moreover, little research has been conducted up to now on laser interactions with copper alloy surfaces and, therefore, little information is available on the topic. Often facing copper alloys outdoor monuments and being very interested in laser cleaning development on various substrates, scientists and conservators at the NCC proposed this project in order to improve the knowledge about laser interactions with such surfaces. But a certain number of aspects still need to be investigated further and the objective of this research project is to help improving the understanding of the laser cleaning of copper-alloy outdoor statues and as a result, to allow conservators to improve the quality of cleaning and minimise the risks of damaging the surface of such sculptures.

1.3.   *Historical aspects of laser cleaning*

Laser technology has known an extremely rapid development since the 1970's, when this promising technique was first applied to the preservation of Cultural Heritage. The idea of stimulated emission of radiation originated with Albert Einstein in 1916[2], the first laser, a synthetic ruby laser, was demonstrated in 1960 by Maiman[3] and since then, it has been used in various fields, such as industry, medicine or for military applications. Cooper[4] mentions its origins as a tool for conservation purpose back to 1960s, when Schawlow used the "laser eraser" for the removal of a black pigment from white paper.

The next step in the development of laser as a cleaning tool was carried out by John Asmus and his team, from the University of California in San Diego, during the 1970's[5]. In this pioneering works carried out in Venice (Italy), Asmus proposed a pulsed ruby laser to remove black pollution crusts from crumbling sculptures made of white marble. The results of these initial tests were considered very positive and promising, as no damage to the underlying stone was observed.

At that time, the laser equipment was very heavy, slow and expensive, and more conventional cleaning techniques, such as sandblasting or chemicals, were usually preferred. But the successful results obtained by Asmus increased the interest in developing this promising tool for the cleaning of delicate surfaces. From that moment, laser cleaning has been and is still studied and developed for a large variety of materials[6], such as stone[7], glass[8], paper[9], parchment[10] and metals[11], among others.

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[2] Hecht, 1992, p.14.
[3] Dändliker, 1982, p.7.
[4] Cooper, 1998, p.7.
[5] Asmus, 1976b ; Lazzarini & Asmus, 1973 ; Asmus *et al.*, 1973.
[6] Larson *et al.*, 2000.
[7] Cooper & Loton, 1994.
[8] Asmus, 1976a.
[9] Caverhill *et al.*, 1997.
[10] Cooper & Sportun, 2000.

1.4.   *General properties and main advantages of laser cleaning*

The typical properties of the laser light gives to this technique a unique character. Laser radiation is an extremely bright, intense form of light, which properties – *monochromaticity*, *directionality* and *coherence*– allow the conservator to clean a surface in a very precise and selective way.

The principle of laser cleaning is based on the absorbtivity and reflectivity of each material, depending on parameters such as wavelength and physico-chemical properties of the layer to remove and the surface to preserve. Thus, in the case of a black pollution crust covering a surface of white marble, the black deposit will strongly absorb the laser beam, while the white marble will absorb much less. This process presents some non-negligible advantages[12] such as:

- *High selectivity* of cleaning, depending on the wavelength chosen. A dirt layer will absorb much of the energy induced by the laser beam at a specific wavelength, at which the underlying surface will be highly reflective. This means that the laser beam can "discriminate" between the layer of dirt and the material to preserve, avoiding any damage to the original substrate and sometimes revealing precious information such as traces of tools, paint or artist's patina remnants.

- *Non-contact* intervention on the objects, since the cleaning is carried out by means of a light beam. This allows very fragile or crumbling surfaces to be treated.

- *Precise, controllable and localized action* of the cleaning. As the laser emits a linear, well-collimated beam, the action of cleaning will occur only on the spot where the beam is focused, scaled from millimetres to centimetres, depending if the conservator uses the laser for extremely precise or monumental work. This also allows the preservation of fine details, relief or tool marks.

- *Immediate control*, allowing the cleaning to stop as soon as the conservator decides it.

- *Versatility*, as it is now used on a very wide range of material, which will undoubtedly increase in the future.

- *Environmental advantage*, as the laser cleaning doesn't produce large amount of waste materials and doesn't require high quantities of water. Nor is it hazardous for the health of the conservator, as no chemicals or solvents are used with this technique. The only protections

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[11] Larson, 1995.
[12] Cooper, 1998, p.7.

required are safety glasses against radiations, a good extraction system and a face mask against small particles and eventual vapours.

Today, the system which is mostly used by conservators is undoubtedly the Q-Switched Nd:YAG laser, which emits very short pulses (usually a pulse length of 10ns) at a wavelength of 1064nm (near infrared radiation) and which is absorbed by a large variety of materials. The advantage of the short pulsed laser is that the heat produced by the laser beam appears very high in the superficial layer (within a very small depth of a few nanometer) but very weak in the bulk material. This means that thanks to the short pulse mode, the temperature rise doesn't propagate in depth inside the bulk and damage can be avoided.

The measurement of the energy density, or fluence, of the laser beam, which is the measurement of the concentration of energy in the beam on the surface, is one of the most important parameters. The fluence should be high enough to remove dirt but low enough to avoid damaging the underlying surface. Pulse length of the laser, repetition rate – which is the number of pulses per second – and number of shots per surface area are important parameters as well. They'll all be presented in details later. If these different parameters are correctly adjusted, depending of the state of preservation and of the structure and composition of the material itself, cleaning is usually carried out without any damage.

1.5.   Presentation of the different chapters

The present work offers to investigate the interactions occurring between laser radiations and copper alloys during laser cleaning for conservation purposes. The focus has been applied on copper alloys used in outdoor monuments, as this kind of objects shows a typical problematic and is frequently treated with laser at the National Conservation Centre in Liverpool.

In the first part, chapter 2 presents the particularities of outdoor copper alloy monuments, regarding the technology, the various alteration factors, the typical corrosion products and the actual conservation strategies used by conservators in order to stabilize such monuments. To illustrate that, two case studies are presented in chapter 3, showing the conservation treatment and laser cleaning of two important monuments exposed outdoors in Liverpool City centre and surroundings. Such sculptures show a common problematic with most monuments exposed outdoors in the area of Liverpool and sometimes in other places in the United Kingdom.

In the second part, chapter 4 presents the basics of laser cleaning and the most important parameters and mechanisms used in order to understand it and achieve a secure cleaning. Chapter 5 discusses the typical interactions between laser radiation and metal substrate. Then, chapter 6 presents the

laser cleaning of the metal samples used in this research. The samples preparation is described, followed by the laser cleaning parameters and cleaning observations.

In the third part, chapter 7 presents the analytical techniques employed in order to characterize the laser interactions with copper alloys and identify the discoloration effect. Each technique is shortly explained and all observations and results are exposed. The corresponding graphs can be found in the appendices book (follow indication in the chapter). In the final discussion and in the light of the results obtained with the analytical techniques, the most probable interpretations are proposed in order to explain the discoloration of the surfaces covered with cuprite, as well as the impact of these results for conservators who use laser for the treatment of copper alloy monuments.

Part I: Copper alloy outdoor monuments

2. Outdoor copper alloy sculpture

Preserving and conserving outdoor monuments is often a complex operation : being artworks, they both have an artistic and historic character, but as those artefacts are also part of the public heritage, they are supposed to take part in everyone's day-life. By commemorating people, events or ideas, by decorating fountains, parks, streets or buildings, outdoor monuments are often a symbol to which people may be closely linked. They belong to the public, playing a major role in the history of the city and being an expression of art and civilization. As these monuments are dedicated to "live" along with people, they obviously degrade with time. As such, they need to be regularly maintained and cared for to remain attractive and highly visible.

Alterations to the surface are strongly dependent on the geographical environment of a sculpture. Artworks exposed to a marine atmosphere would not behave in the same way than the same sculpture exposed to a rural or an industrial environment. Humidity, sun, salts, winds, pollutants, temperature are uncontrollable external factors that strongly interact with copper alloys monuments and are responsible for the type and rate of degradation and corrosion. Direct location (for example if it is placed near the ground, part of a fountain, etc) or internal factors such as surface details, shape or metal combinations have to be considered as they can generate microclimates which can highly damage a monument.
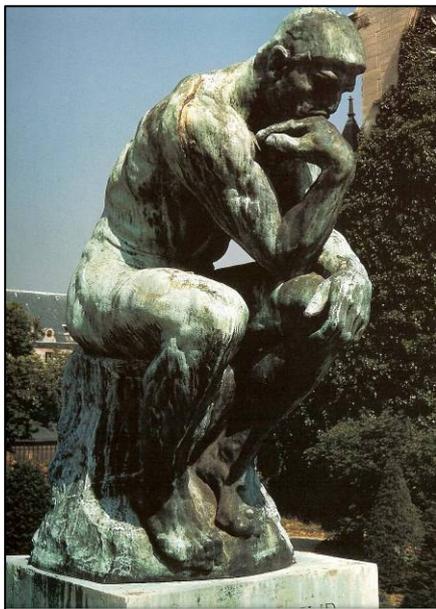
Thus, outdoor copper alloy monuments need to be understood and aesthetic considerations have to be applied in a different way than for other types of metal artefacts. Unlike archaeological objects, which original surface lies within the corrosion layers formed during burial, outdoor copper alloys monuments are slowly losing their original surface as it is dissolved and washed away by weathering. Furthermore, corrosion crusts, consisting of organic or mineral deposits mixed with diverse pollutants, as will be discussed later, have a damaging and inaesthetic effect on sculptures, making them appear streaked and disfigured. Outdoor monuments would finally become unattractive, invisible to the eye of the public and at last they would lose their symbolic force and therefore, their meaning.

Figure 1 *The Thinker* from Rodin, Musée Rodin, Paris (From Scott, 2002, p.40). The famous sculpture shows a streaked and darkened surface, typical for copper alloys corroding in an outdoor environment. Such monuments require specific conservation interventions to stabilize the surface and a maintenance plan needs to be established to ensure long-term protection.

2.1. Most common copper alloys used for outdoor monuments

Copper and its alloys have been commonly used to create sculpture since Antiquity, as craftsmen gradually became aware of the improved properties and workability provided by copper alloys. While Egyptians used to mix copper and lead to produce their sculptures, Greek and Roman civilizations preferred tin and zinc to lead. The craftsmen of the European Middle Ages usually chose tin and only a very small amount of lead and zinc. In the 19th Century, chemists considered pure tin bronze as the best choice to achieve the most aesthetically pleasing surfaces. Nevertheless, craftsmen or sculptors' individual habits often prevailed and choices were mainly dictated by aesthetic tastes or local economy.[13]

These variations in alloying metals can be explained by the fact that copper alloys show various mechanical, physical and chemical properties, depending on the alloys compositions and percentage. While the addition of tin (Sn) reduces the melting point of copper, increases hardness, resistance to corrosion and improves the polishing quality of the metal, the presence of zinc (Zn) improves the pouring properties during the casting process. Adjunction of lead (Pb) also lowers the melting point of the alloy and increases the sharpness of the figure, allowing very fine details to be designed. Depending on the provenance and the period, being natural inclusions coming from the ore or voluntary adjunctions in the alloy, copper alloys may also contain traces of nickel (Ni), silver (Ag), antimony (Sb), arsenic (As), iron (Fe), bismuth (Bi), sulphur (S) or aluminium (Al). It is commonly admitted that, compared to other metals used for outdoor exposure (iron, lead), copper alloys generally show good resistance to corrosion in outdoor environments.[14]

The distinction between the various copper alloys isn't very accurate. It has to be underlined that usually, conservators use the general term "bronze sculpture" to assemble the large group of outdoor copper alloy sculpture. As most outdoor monuments are cast in bronze, this habit is not totally wrong. It can be explained by the fact that systematic elemental analysis of the metal constituting sculptures is expensive and not always necessary to achieve good conservation interventions. Therefore, metallographic analyses are not always done. But other copper alloys can be used for casting.

Three different metals have been used within the frame of this project to carry out laser tests and surface analysis : copper, brass and bronze. Those alloys are commonly found as constituents of outdoor cast statuary. Copper and brass have been employed for the construction of two monuments exposed in Liverpool City centre (Lord Nelson's Statue) and its surroundings (Queen Victoria)[15], which

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[13] Doktor & Mach, 2000, p.34.
[14] Doktor & Mach 2000, p.35 ; Urban F., 1983-1984, p.7-11.
[15] See Chapter 3.

have been laser cleaned by the conservators at the National Conservation Centre (National Museums Liverpool). Bronze, the most common alloy for casting sculpture has also been selected in this research to study its behaviour after laser radiation and compare it to copper and brass. The type of bronze chosen here is actually named "*gunmetal bronze*".

In this chapter, the characteristics of copper and its most common type of alloys, bronze and brass, are discussed.

2.1.1. Copper

Copper is a salmon pink or reddish metal, ductile and deformable, very good at conducting thermal and electrical energy. Its crystal structure is face-centered cubic. It can be hammered, stretched or / and laminated.[16] As copper is a soft metal, it is more commonly found as copper sheet, which is a popular roofing material, especially on historic buildings. Copper sheet have also been used to make the outer shell of the Statue of Liberty in New York (USA).[17] Pure copper is not easy to cast and therefore, very few monuments are made of cast copper; it has to be alloyed to other metals like tin (Sn) and zinc (Zn) to increase its hardness and to produce good quality castings.[18]

The Nelson's Monument in Liverpool[19], actually made of copper, is an exception; the selection of such a material might have been dictated by the lack of availability of other metals in a war period. Nevertheless, 2% zinc and other elements were alloyed to copper in order to slightly increase its hardness and casting properties.

2.1.2. Brass

Brass is a yellow alloy mainly constituted of copper and zinc. It can also contain other elements like tin (Sn), lead (Pb), nickel (Ni), manganese (Mg) or iron (Fe) but in much lower proportions. Depending on its zinc content, its colour can vary ; the higher the zinc proportion, the paler the tinge, making it look like silver. Inversely, it may look like gold. Its use is usually dictated by the percentage of its constituents : the lower the copper proportion, the easier the casting. Brass can also be hammered and laminated.[20]

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[16] Arminjon & Bilimof, 1998, p.20-21.
[17] Baboian *et al.*, 1990.
[18] Arminjon & Bilimof, 1998, p.76.
[19] See Chapter 3.
[20] Arminjon & Bilimof, 1998, p.21.

The Queen Victoria's Statue in Southport (UK) was cast in a paradoxically named "commercial bronze". This is actually a brass because of its 12% zinc content.[21]

2.1.3.   Bronze

Bronze has a yellow-red colour, is highly resistant to corrosion and harder than copper. It is constituted of copper and tin (Sn) as primary components, but other metals are sometimes added, such as aluminium (Al) or zinc (Zn). Distinction is generally made between low-tin (< 17% Sn) and high-tin bronzes, as these alloys are constituted of various phases which may corrode differently.[22] Low-tin bronzes are preferably used for casting, while high-tin bronzes are usually cold-worked (hammered, stamped or stroked)[23] and annealed.[24] Bronze is harder and more fusible than copper and has been used since Antiquity for objects manufacture (containers, jewellery, mirrors) and as a casting material for statuary.

"Gunmetal" bronze[25] is a yellow low-tin copper alloy which also contains zinc. It was originally used to cast canons. It was the most common alloy in the 19th and 20th Centuries for maritime use. As this alloy is very commonly found today in castings in the UK, gunmetal bronze samples were used within the frame of this study.[26]

2.2.   *Technological aspects*

Copper alloys monuments are numerous in our European cities and landscapes. These sculptures are mostly of modern manufacture. Indeed, it appears very rare to find antique bronze sculpture in our streets, except, among a few others, the classical equestrian statue of Marcus Aurelius in Rome, which remained outdoors for 1'700 years and was recently displaced indoors[27], or the four gilded bronze horses from St. Mark Basilica in Venice : the originals where also moved indoors while replicas where placed outside.[28]

Hence, copper alloys monuments are generally contemporary artworks or date at least from the 18th or 19th Centuries.[29] As such, they show specific problems, like inherent characteristics due to the type of process they were made of and more ethical considerations like the presence of an artificial "patina" on the surface, often voluntarily created by the artist.

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[21] See Chapter 3.
[22] Scott, 2002, p.401.
[23] Arminjon & Bilimof, 1998, p.22.
[24] Scott, 2002, p.401-402.
[25] « Bronze à canon » in French.
[26] Selwyn, 2004, p.57 and 61-62.
[27] Fiorentino, 1994 ; Melucco Vaccaro, 1992.
[28] Alunno-Rossetti & Marabelli, 1976.
[29] Doktor & Mach, 2000, p.17.

2.2.1.   Casting processes

For centuries, copper alloys sculptures have mostly been built with casting techniques such as lost-wax or sand-casting processes. Some monuments are made of wrought metal but cast sculptures are more numerous, especially large statuary and even though wrought metallic structures better resist to atmospheric corrosion.[30] Sculpture manufacture is often a very complex process: the alloy composition, the percentage of various alloying metals or the surface treatments carried out on the piece can be very different from one piece to the other. Each copper alloy sculpture is characterized by such particularities, which will determine its future conservation state. The grains[31] in the metal structure can be large or small ; the metal structure can be homogeneous or not ; contain inclusions ; show various metal phases ; be more or less porous.[32]

Sand-cast sculptures are recognizable from lost-waxes sculptures as they do not show core pins, which are not used with the former as they cannot provide stability to the sand form. Lost-wax process uses numerous core pins to keep the distance between the core and the outer form and traces of these pins are often detectable on the metal surface. Furthermore, the surface of sand-cast sculptures is more granular.[33]

2.2.1.1.   Lost-wax process

The lost-wax process[34] is a very ancient method. Its use goes back to Antiquity and it is still employed today by artists and craftsmen.

It consists in fabricating a plaster negative form of the sculpture and filling the inner walls with a thin layer of wax of approximately 0.5-1cm thickness. Then, the inner space behind the wax layer is filled with clay on an armature (often iron) inserted to support and stabilize the structure. After that, the plaster negative is removed and the fine details can be added on the wax layer. Metal tubes used to cast the fused metal are also added. Then, the wax is covered with several layers of a clay-based mixture and fine metal pins are inserted to maintain the space between the clay and the core. Heat is applied to melt the wax and once it has flown out of the form, a hollow space for the metal is created. Then, the casting form is heated before casting the metal, in order to avoid cracking during the process. At last, the fused metal is poured through the tubes and fills the hollow space between the inner and the outer clay forms. Once the metal has turned cold, the clay mould can be removed and the sculpture appears.

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[30] Dent Weil, 1982, p.132.
[31] See Appendix 4.
[32] Dent Weil, 1982, p.130.
[33] Amarger, 2001a, p.213.
[34] See Appendix 7.1.

The lost-wax process is an expensive and intensive process. It is also risky as often a small defect in the construction of the form can compromise the whole procedure.[35]
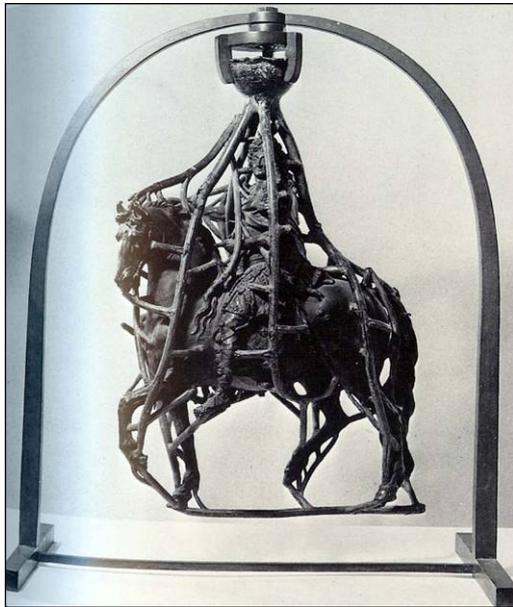
Figure 2 Bronze model for the lost-wax casting of the equestrian statue of Louis XIV, Royal Museum of Fine Arts, Copenhagen. The tubes are kept around the statue, showing the way of the fused metal during casting (From Arminjon & Bilimof, 1998, p.78).

2.2.1.2. *Sand-casting process*

The sand-casting process[36] was most generally used during the 19th Century. The basic principle is the same than previously, which means that a hollow space is created between the core and the outer form for the fused metal to be poured, but the forming material for the outer form and the core is sand.

First, sand is strongly packed in one or several horizontal frames, generally made of wrought or cast iron. The number of frames depends on the thickness and height of the pieces to be cast. The positive replicas of the artist's model are in plaster, wood, metal or synthetic materials. They are covered with a coating of talc, ashes or lacquer prior being half-buried in sand. At the end, the exposed top half of the sculpture is covered by small and carefully moulded sand pieces. The sand pieces are maintained by a coarser outer sand bed, supported in another metal frame.

Once the print is taken, frames are carefully opened and the replica is removed : the negative shape of the piece to cast is visible in the sand bed. Frames are then slightly heated to remove all humidity from the sand, as interactions between moisture and fused metal would create steam and then the burst of the form. The whole negative form is covered with a thin layer of talc or carbon to facilitate

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[35] Arminjon & Bilimof, 1998, p.76-104 ; Doktor & Mach, 2000, p.31.
[36] See Appendix 7.2.

the removal of the cast piece later on. After that, frames are replaced one on the other and strongly held in place.

Then, a core is placed in the void inside the two halves of the mould. This core is built around an iron armature and is made of porous material to allow expansion and contraction during the casting process. A hollow space is created between the core and the sand to allow the penetration of the fused metal. Channels are pierced in the mould to allow fused metal to enter the empty space (gates) and to permit gases to escape during the casting process (vents). At last, the metal is vertically poured into the mould through the gates.[37]
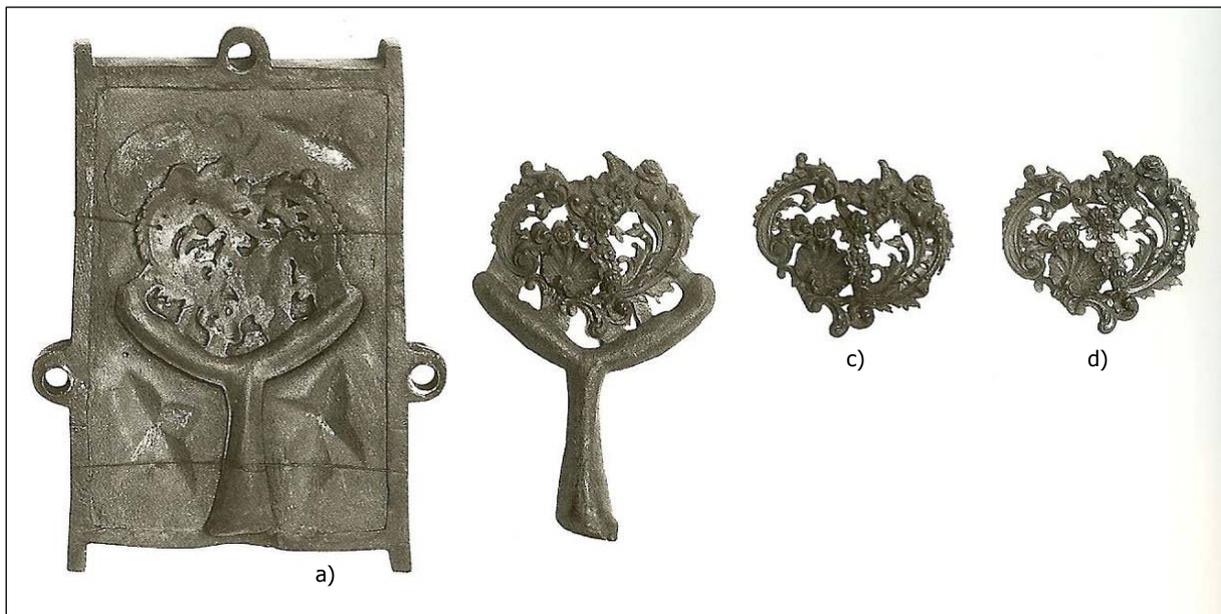
Figure 3 Various steps following the sand-casting process of a decorative element in bronze, Musée des Arts et Métiers, Paris. a) in the metal frame, after casting ; b) out of the frame, with the tubes ; c) with the tubes removed ; d) after final treatment (From Arminjon & Bilimof, 1998, p.86).

2.2.1.3. Final treatments

Larger sculptures are generally made of several pieces joined together. This is achieved by welding after the casting process. Nails and rivets, often in iron like the internal armature, can be used to fix the pieces together. The assembled parts are often recognizable as after several years of outdoor exposure, corrosion on the boundaries can develop in such a way that the surface appears patchy.[38]

Surface treatments are generally applied. Sculptures are often polished and waxed ; they can also be painted, gilded, silvered or tinned. Very often, they are artificially patinated to obtain a desired colour.

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[37] Arminjon & Bilimof, 1998, p.76-104 ; Doktor & Mach, 2000, p.33.
[38] Amarger, 2001a, p.213.

Such treatments, mainly the use of chemicals for patination which etch the metal surface, may greatly influence the final conservation state of a monument.

2.2.2.   Natural and artificial patination

In the case of outdoor copper alloy monument, the patina is the pleasant smooth and green layer naturally created by the oxidation of the metal in contact with the atmosphere. This colour, evidence of age and authenticity, has been widely reproduced by men since Antiquity by applying various substances (chemicals, paint) on the generally heated metal surface of sculpture. Such surface treatments form metal oxides, producing various tinges such as brown, green, black, blue or red. Depending on the type of chemicals used and the degree of rinsing, some of these artificial patinas are stable while others are not, which means that they can be extremely reactive and as such, do not protect and even attack the metal surface.

Hence, a patina can be natural, which means due to environmental influence only, or artificial, which means man-made. Artists and foundry-men traditionally treat newly cast bronze with chemical solutions in order to produce an intentional coloration known as *artificial patina*. Such treatments are mostly selected for aesthetic purpose, as they can produce a wide range of colours. By exposure to the outdoor polluted atmosphere, this artificial patina is gradually replaced over decades with green corrosion products which are typical for outdoor monuments. Such corrosion products still may contain traces of the artificial patina, which are testimonies of the original surface. Thus, the term *patina* may refer to the artificial layer as well as to the naturally grown corrosion products.

This is why the patina concept is so difficult to determine. The name *patina* can be considered totally differently, depending on the time period and the location. The patina can certify the value and authenticity of an artwork ; it can be an evidence for its degradation ; it can be considered as a protective layer against an aggressive environment.

In a low corrosive environment, a natural or artificial patina may first play the role of a protective layer on the metal surface, as the oxides constituting the patina may isolate the metal against corrosive agents like oxygen or humidity. Such a physically and chemically stable patina is considered "noble" and may appear thin and shiny, like cuprite, which is brown-red in colour and close to the metals surface. If the patina of an object exposed indoors, for example in a museum, cannot be really altered as the climate should be well controlled, the patina of the same object exposed outdoors in a strongly polluted atmosphere can be severely damaging and damaged. It is said to be "vile", unstable. In this case, the oxide layer formed on the metal surface will quickly be attacked by the corrosive atmospheric agents and weathering. The chemicals residues used for artificial patination may also enhance the corrosion process. The artificially patinated surface mixed in the corrosion products and

containing the original surface is very often lost after years of exposure, attacked by aggressive atmospheric corrosion due to industrial pollution.

Today, the sulphur dioxide present in the air pollution has formed light green patinas consisting of a basic copper sulphate, named brochantite, upon the copper oxide layer, cuprite. This familiar green colour is unfortunately not always stable but its cultural value is well settled, also because of the precious information it eventually still may contain, like tool traces, artificial patina, paint or gold remnants, etc.[39]

2.3. *Alterations factors*

Due to the important increase in atmospheric pollution in Europe since the 19th and all along the 20th Century, the aspect of outdoor monuments disastrously began to darken, alter and the metal surface to corrode. Even though copper alloy sculpture generally shows good resistance to corrosion, monuments began to strongly suffer from coal and SO_2 emanations during the industrial development and the reconstruction period after the two World Wars.[40] Dent Weil[41] reports the first concerns to have been expressed in London during the 1850's because of the dangers posed by "*…the conditions of the London atmosphere, especially in relation to the sulphur acids derived from coal…*". Between 1880 and 1900 a great number of investigations into the new problems of outdoor bronze conservation were carried out in Berlin. It is only in the early 1960's, with the severe threat on the bronze horses in Venice[42], that general interest and concern awoke in many parts of the world. Since that time, corrosion mechanisms and degradation causes have been studied and alteration factors are today well identified.

Alterations factors are various and can be totally different depending on the location of a monument, its direct environment and its inherent structural characteristics. Temperature and relative humidity (RH) fluctuations, freezing-melting cycles, water, wind, particulate matter (sea salt, de-icing salts, sand, dirt), pollutants (sulphur dioxide, nitrogen oxides, ozone), local conditions of acidity, surrounding vegetation, people or / and animals are general factors which may strongly influence the corrosion level of a monument. Inherent structural properties of a single sculpture can also become harmful and generate strong corrosion. Condensation and water ingress through cracks or defects, contact between dissimilar metal on the sculpture or / and a corroding inner iron structure very often lead to strong damage and severe corrosion.

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[39] Doktor & Mach, 2000, p.35-37.
[40] Graedel, 1992, p.18.
[41] Dent Weil, 1980, p.131.
[42] Alunno-Rossetti & Marabelli, 1976.

2.3.1.   Environment

General environments in which monuments are located are usually classified as follows:

- *Rural*, where the air is generally clean, with low acidity and atmospheric pollutants levels. Corrosion development may proceed very slowly in such atmospheres.

- *Urban*, with intensive road traffic and particles generated by cars, high acidity and sulphur levels. SO_2 deposition rate may be from 10 to 80mg per m^2/day in such an amosphere.[43]

- *Industrial*, with a high level of atmospheric pollutants. SO_2 deposition rate can be > 200mg per m^2/day in such an atmosphere[44], leading to highly acidic conditions.

- *Marine*, with a high concentration of chlorides (between 5 to 500mg NaCl per m^2/day with a maximum at 1500mg)[45] and strong winds containing abrading particulates. Acidity is generally low in such environments.

These four typical environments strongly influence the way a monument may corrode. The rate, depth and level of corrosion will increase in a more aggressive atmosphere and different corrosion products may develop depending on the type of pollutant contained in the air with which metal would combine.

Moreover, the direct location of the monument (exposed in parks or to heavy traffic), its position (sheltered or facing wind, sun and rain), its distance from the ground and from the pollutant sources are determining factors.[46]

2.3.2.   Water and relative humidity (RH)

For most metal surfaces exposed outdoors, the corrosion rate will be strongly influenced by the relative humidity (RH). The amount, frequency and duration of rain, fog, mist, freezing or condensation are of significant influence on the corrosion development of monuments. Obviously, moisture is always present in the air in outdoor environments, especially in our countries. A thin water layer (even from fog or mist) on a metal surface can be strong enough to highly increase the corrosion rate. Many corrosion processes occur when RH is > 65-70 %.[47]

The main problem today is that natural precipitations, like rain or snow, are slightly acidic (acid rain). Over the last decades, pH of rainwater has dramatically decreased (pH < 4) because of its SO_2 and

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[43] Strandberg *et al.*, 2000, p.39.
[44] Strandberg *et al.*, 2000, p.39.
[45] Strandberg *et al.*, 2000, p.39.
[46] Payer, 1992, p.110 ; Selwyn & Roberge, 2006, p.289.
[47] Selwyn & Roberge, 2006, p.290.

NO_2 content, leading to the formation of acidic conditions. Acidity locally dissolves the protective surface layers (stable corrosion products like cuprite and brochantite), leading to streaking and surface disfigurement. Dissolution of the patina causes the loss of the original surface and all the information it may contain, like tool marks, artificial patina or paint residues, etc.

Furthermore, surface roughness (cracks, corrosion products or casting defects), water ingress through holes or voids and the presence of hygroscopic particulate matter may trap water and generate condensation on the metal surface, leading to corrosion development.[48] The strongest increase in corrosion formation is generated by wetting – drying cycles. Freezing-melting cycles may also damage a sculpture. Especially in the northern countries or in winter, the transformation of water in ice may cause damage to the sculpture and to its marble base, like cracking and deformation due to ice expansion. The sculpture may be destabilized and special attention is required in such cases.

2.3.3. Temperature

Monuments may suffer from thermal expansions and contractions due to daily and seasonal temperature fluctuations. These can result in mechanical stress leading to failure, cracking or tearing, especially with metals containing zinc, lead and aluminium. Pure copper is less sensible to this type of alteration.[49] Temperature also affects the rate at which corrosion reactions caused by pollution may occur. The higher the temperature, the more rapid the corrosion rates.[50]

2.3.4. Pollutants

Pollutants affecting outdoor monuments are various and can be in a gaseous or in a solid form.

2.3.4.1. Gaseous pollutants

The main pollutants interacting with outdoor metals and influencing the corrosion rate are hydrogen sulphur (H_2S), sulphur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3) and halogen gases (chlorine, fluorine, bromine, iodine),[51] as they often generate acidic conditions. Low pH environment is very corrosive for metal sculpture. Sulphur and nitrogen oxides tend to attack the metal by forming acids, while ozone and halogen gases are mainly corrosion catalysts. If the air contains high sulphur dioxide chloride levels, synergistic effects may occur.[52]

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[48] Stranberg *et al.*, 2000, p.44-45 ; Selwyn & Roberge, 2006, p.289-290.
[49] Selwyn & Roberge, 2006, p.291.
[50] Lins, 1983, p.16.
[51] Stranberg *et al.*, 2000, p.43-44 ; Morissette, 1988, p.12-15 ; Selwyn & Roberge, 2006, p.290.
[52] Stranberg *et al.*, 2000, p.42.

- **Hydrogen sulphur (H_2S)** is mainly produced by paper industry. This highly toxic gas is recognizable by its rotten egg smell. Combustion of H_2S leads to the formation of sulphur dioxide (SO_2), following the equation:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$
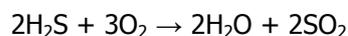
It also leads to the formation of solid sulphated deposits, combined with SO_2 (a) or O_2 (b):

$$(a)\ 2H_2S + SO_2 \rightarrow 2H_2O + 3S \downarrow$$

$$(b)\ 2H_2S + O_2 \rightarrow 2H_2O + 2S \downarrow$$
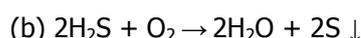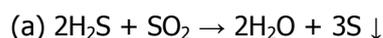
- **Sulphur dioxide (SO_2)** is the prime corrosive agent for outdoor monuments. The principal source of sulphur dioxide is the combustion of fossil fuels (particularly coal) containing sulphur, by pulp and paper mills, by smelting of ores and volcanic emanations. SO_2 level was very high in the European cities in the 1970's but has decreased during the last decades. SO_2 is an acidic gas which combines very easily with water vapour in the atmosphere to produce sulphurous acid (H_2SO_3) and then sulphuric acid (H_2SO_4), following the equations:

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$H_2SO_3 + O_2 \rightarrow 2H_2SO_4$$
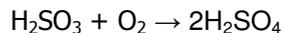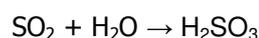
H_2SO_4 is present in acid rain as well as in atmospheric particulates. In contact with metallic copper, H_2SO_4 may form copper sulphate (the light green brochantite $CuSO_4.3Cu(OH)_2$), leading to the formation of further SO_2:

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2$$

- **Nitrogen oxides (NO_x)** are by-products of the combustion of fossil fuel, principally from road traffic. Thus, the pollutant level depends on the intensity of the traffic. Acid deposition may occur as a result of the conversion of nitrogen dioxide to nitric acid (HNO_3) in the atmosphere.

$$NO_2 + H_2O \rightarrow HNO_3 + H^+$$
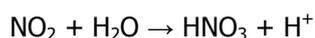
NO_2 shows a synergistic effect with SO_2 when RH is > 90%[53] and because of its role in the formation of ozone, it indirectly contributes to the effects of ozone pollution.

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[53] Strandberg, 1998, p.298; Strandberg & Johansson, 1997, p.83-85.

- **Ozone (O_3)** is a secondary pollutant which is formed in photochemical smog by the interaction of sunlight with nitrogen oxide gases and hydrocarbons from vehicles emanations. Ozone is a powerful oxidizing agent and as such, it increases metal corrosion rates. It also shows synergistic effects with SO_2 when RH is >70%.[54]

- **Halogen gases** like chlorine (Cl_2), bromine (Br_2), fluorine (F_2) and iodine (I_2) cannot be found in their pure chemical state. Their ions usually combine with other bodies to form salts and acids. In areas located near the sea, chlorine is present in the form of chloride ions Cl^-, which combine with water to form hydrochloric acid (HCl):

$$Cl^- + H_2O \rightarrow HCl + OH^-$$
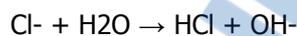
Chloride ions are commonly found in contact with outdoor monuments. They come from sea salt particles, winter de-icing salts or atmospheric hydrogen chloride gas (HCl) produced by paper industry and by the combustion of coal and waste products. Halogen gases also may be residues of chemicals used for artificial patinas.

2.3.4.2. Particulate matter

Particulate matter refers to small wet or dry particles present in the atmosphere. They provide two types of effects on metal: a chemical action, when combined to moisture or to other pollutants like sulphate and nitrate ions, and an abrasive action, by hitting and scrapping the metal surface. These often very hygroscopic materials trap moisture just next to the metal surface, sometimes for long periods of time. Such humid environments generate acidic conditions and favour electrolytic process, leading to the development of an extensive corrosion. Main sources of particulate matter in the UK and in other European countries are road traffic emissions, particularly from diesel vehicles as well as being a result of industrial processes.[55] Various particulate matters have to be considered.[56]

- **Sulphur bearing particles**[57] produce damage similar to those made by gaseous H_2S and SO_2. Except calcium sulphate $CaSO_4$, those particles are water-soluble and as such, may be mixed within the electrolyte. Furthermore, as they are composed of sulphate ions SO_4^-, they tend to form acids in presence of moisture, as demonstrated by:

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[54] Strandberg, 1998, p.299 ; Strandberg & Johansson, 1997, p.83-85.
[55] http://www.liverpool.gov.uk/Environment/Pollution/Air_quality/Air_quality_information/index.asp
[56] Stranberg *et al.*, 2000, p.43-45 ; Morissette, 1988, p.16-17 ; Selwyn, 2004, p.64 ; Selwyn & Roberge, 2006, p.290.
[57] Morissette, 1988, p.16: Sulphur bearing particles are present mainly in urban areas and may be sulphuric acid H_2SO_4, ammonium sulphate $(NH_4)_2SO_4$, magnesium sulphate $MgSO_4$, calcium sulphate $CaSO_4$, sodium sulphate Na_2SO_4, zinc sulphate $ZnSO_4$.

$$MgSO_4 + H_2O \rightarrow H_2SO_4 + MgO$$
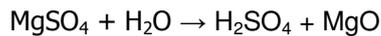
- **Chloride bearing particles** (mostly NaCl, KCl) combine with other pollutants to form salts or acids. They also interfere in the electrolyte as they are highly water-soluble and conductive.

$$2NaCl + H_2SO_4 \rightarrow 2HCl + Na_2SO_4$$
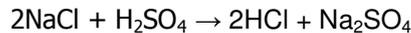
- **Bird's dejections** contain sodium nitrates $NaNO_3$ as well as other substances like ammoniac, uric acid and phosphates, which combine with water to form an acidic environment and lead to growth of micro-organisms and fungus.

- **Soot** consists mainly of carbon and is produced by incomplete fuel combustion. Like SO_2, the soot level was very high in the 1970's and drastically decreased since that time. Soot does not chemically react but it is very hygroscopic and maintains water near the metal surface, enhancing the corrosion rate. Furthermore, it is partly responsible for the disfiguring black colour of altered monuments.

- **Various particles**, like silica SiO_2 and alumina Al_2O_3, may be very hard and scratch the patina on the monument, leaving the bare metal exposed to the aggressive atmosphere. These particles, as well as quartz and soil, do not chemically react but they are highly hygroscopic. They are also mainly responsible for the inaesthetic aspect they give to monuments, disfiguring their details.

2.3.5. Vegetation

Monuments exposed to a dense vegetation environment may suffer from various alterations. Sculptures located directly on or close to the ground suffer from corrosion because of the moisture emanating from the plants and the ground itself. Hygroscopic material, like uncollected leaves filling voids, seeds, lichen, or sticky material exuded by trees, do trap water on the metal surface. Shadows provided by trees prevent the metal from drying properly in the sun and sculptures always remain damp, leading to the increase of corrosion processes.[58]

2.3.6. Animals

Animals may also affect monuments. Sitting of birds can harm the surface as they scratch it with their nails, weakening the surface and leading to corrosion. Birds, small animals or insects often settle their nests in the complex structure of a sculpture, trapping moisture close to the metal surface. Organic

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[58] Selwyn, 2004, p.69 ; Selwyn & Roberge, 2006, p.291-292.

materials deposited can contain additional salts and acidic by-products, like insects producing formic acid (ants) and bird's dejections, which contain variable quantities of ammoniac, uric acid and phosphates, combining with water to form an acidic environment and leading to growth of micro-organisms and fungus.[59]

2.3.7.   Function and use

The practical function of a monument may also influence its conservation state and be a threat for its conservation. Being part of fountains, being regularly touched by the public or being an invitation for children to climb on it are some of the various uses of monuments.

- Copper alloy fountains often aesthetically suffer from thick lime deposits coming from the water. Such crusts cover and discolour the surface but their alkaline properties may also protect the patina. Flowing water may protect the surface to some degree but it removes the patina at the same time. The strongest effect is the very high relative humidity (RH) overall the sculpture, which creates a very corrosive environment. Severe pitting corrosion is often observed on metal fountains, due to the acidic conditions of water. Algae also sometimes grow on the metal surface.

- Even if some artists appreciate children climbing on their sculptures or other uses, repeated contact removes the protective coatings and the stable corrosion products, leaving the bare metal exposed to the aggressive polluted atmosphere. To a certain degree, touching a sculpture polishes and greases its surface and hence can be protective by inhibiting the corrosion. But if the touching removes the copper oxide layer and exposes the bare shiny metal, damage is certain and direct contact should be prohibited.[60]

2.3.8.   Vandalism

Vandalism is of great concern mainly in the cities, as many public monuments are highly deteriorated because of people acts, like graffiti, inscriptions with sharp objects or garbage deposition. More radical vandalism may result in the use of explosive or in breakage or removal of the sculpture. But a neglected monument is an invitation to vandalism. As a result, neglecting the care of a vandalised monument has to be avoided. Paint products on copper alloy surfaces is sometimes very difficult to remove without altering the underlying patina, especially when time has passed and corrosion has

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[59] Selwyn, 2004, p.69 ; Selwyn & Roberge, 2006, p.291-292.
[60] Strandberg *et al.*, 2000, p.45.

been incorporated in the corrosion products. Rapid cleaning and removal of graffiti and garbage is often the best way to discourage repeated vandal acts.[61]

2.3.9.   Design and metal structure particularities

The specific design, shape, metallic and structural components of a sculpture may strongly influence the corrosion rate.[62]

- Alloy composition and homogeneity is of great importance in the monument's resistance to corrosion. Generally speaking, pure copper is less subject to corrosion than its alloys. A copper alloy with a high tin (Sn) content (> 20%) would better resist to corrosion than a low tin content alloy (5-10%).[63]

  Alloy homogeneity is of great influence as well. Chemical heterogeneities can result from the segregation of alloying elements, inclusions, casting defaults, porosity or cracks. This may decrease the stability of the metal. For example, lead added to the alloy is not uniformly distributed. It causes the formation of lead globules inside the metal lattice, randomly located and providing preferential sites for corrosion to initiate.[64]

  Moreover, wrought metal sheet are generally less affected by corrosion than cast sculptures.[65] This is due to the heterogeneity of a cast metal, which may show extensive dendrites formation[66], various inclusions and higher porosity, due to the expulsion of gases or water when metal solidifies.[67] A smooth and polished surface would better resist to corrosion.

- Contact between dissimilar metals leads to a galvanic corrosion process, which consists in the corrosion of the most reactive or less noble metal. The presence of an electrolyte, like water, can strongly increase this phenomenon. Such processes are quiet common as artists often use combinations of metal for aesthetic purpose, in the alloy itself or by joining different parts. With large monuments, joints, nails, internal structure are generally needed. Iron is often used and as copper is more noble than iron, it is very common to see a bronze sculpture containing an extensively corroded internal iron armature. Iron corrosion is known to expand in volume and it may cause cracks in the external envelope of the sculpture. It also produces

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[61] Selwyn & Roberge, 2006, p.292.
[62] Morissette, 1988, p.21 ; Selwyn & Roberge, 2006, p.292.
[63] Morissette, 1988, p.26.
[64] Scott, 2002, p.403.
[65] Dent Weil, 1982, p.132 ; Payer, 1992, p.111.
[66] See Appendix 4.
[67] Dent Weil, 1982, p.130.

rust staining. A stable material like stainless steel should replace iron armatures when new constructions and repairs are made.

- A piece with a shape consisting in numerous details and folds allows water to be collected, lying stagnant for long periods of time, which increases corrosion rates. Various hygroscopic deposits are also retained in the folds, trapping water and promoting acidic conditions.

- Chemicals (salts and acids) used to create artificial patinas may leave corrosive residues on the metal surface which enhance corrosion rates.

- At last, salts created by core material (clay, plaster) remaining in casts can also produce large deposits on the external surface through cracking, which then may cause subsequent corrosion.

2.4. Specific corrosion products

All metals tend to corrode. This natural process occurs as metal is obtained from ores, which have been melted or transformed and tend to go back to their original and stable state. Corrosion is an electrochemical process which takes place at the atomic level and is influenced by the metal itself and by its direct environment (mostly humidity, oxygen and other gases contained in the atmosphere). Atmospheric corrosion mechanisms are electrochemical processes, or oxidation-reduction processes, which involve interactions of the adsorbed moisture with various atmospheric gases at the metal – air interface. Gaseous pollutants present in the atmosphere combine with water vapour and oxygen to produce acids, which then decompose to form salts. If exposed to some moisture, these salts will lead to an electrochemical activity.

For a corrosion process to develop, a potential difference between two electrodes (+ and -) is needed to produce electricity, as well as an electrolyte, which is a solution containing ions. Chemical oxidation, occurs at the anode (negative - electrode), while reduction occurs at the cathode (positive + electrode). Metal surfaces are covered with numerous cathodic (black areas) and anodic (green areas) cells which, in presence of the electrolyte (humidity), induce a potential difference. Generation of this electrochemical process between the anode and the cathode leads metal to be gradually converted to corrosion products. The greater the potential difference, the greater the corrosion process.[68]

Corrosion generally occurs where the metal surface shows heterogeneities and defaults (cracks, pores, grain boundaries, inclusions combining different elements), which are preferential sites for corrosion

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[68] Strandberg *et al.*, 2000, p.39 ; Crespo *et al.*, 2004 ; Dent Weil, 1982, p.132 ; Morissette, 1982, p.18.

to develop. Various types of corrosion may occur[69], which will not be extensively discussed here, like active powdery corrosion (due to chlorides), pitting (formation of active corrosion pits due to chlorides), uniform (rare and very even, produced by acidic attack) intergranular (propagating along the grains in the crystalline lattice of the metal), galvanic (preferential corrosion of the less noble metal), generalized corrosion (complete conversion of the object to corrosion products), etc.
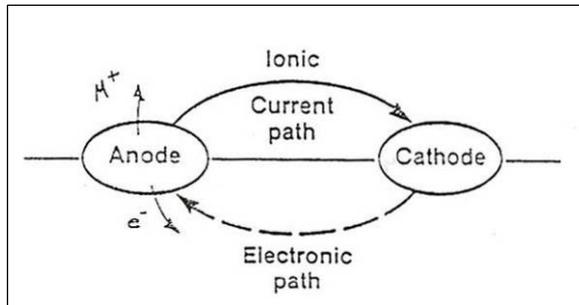
Figure 4 Schematic representation of the four requirements of an electrochemical corrosion cell (From Payer, 1992, p.118).

2.4.1. Corrosion development on outdoor copper alloy sculpture

Copper alloys exposed to the outdoor atmosphere rapidly corrode. The corrosion rate is more or less pronounced depending on the alteration factors previously discussed: environment, moisture, pollutants and so on.

Soluble corrosion products form first (copper sulphates, copper chlorides), which are washed away with rain and leave green stains on the adjacent support, usually a porous stone base. Then the surface forms an insoluble red-brown oxide layer, followed by green and blue compounds. With time, the corrosion rate decreases as further insoluble compounds form. The corrosion products formed are usually a copper oxide, which layer is adjacent to the metal and upon which green copper products form. After a few decades of exposure to weathering and pollution, the appearance of a sculpture becomes patchy and streaked with run offs and alternating black and green areas.[70]

Green areas play the role of the anode (-) in the electrolytic process of corrosion, while black areas play the role of the cathode (+).[71] The most important metallic loss occurs at the anode, where metal ions are liberated into the electrolytic liquid. Active corrosion generally develops on the green exposed areas due to the high concentration of chlorides.[72]

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[69] Urban F., 1983-1984, p.60-74.
[70] Selwyn, 2004, p.68-69.
[71] Dent Weil, 1982, p.132 ; Selwyn & Roberge, 2006, p.294 : " *A potential difference of 280mV has been measured between the anodic green areas and the cathodic black ones*".
[72] Crespo *et al.*, 2004 ; Selwyn & Roberge, 2006, p.294.

- Black areas are protected from rain and winds and may usually correspond to the original surface.[73] This black colour is mainly due to the accumulation of dirt like soot, pollutants and organic deposits. They are often composed of a complex mixture made of dark particulate matter (quartz, soot), copper oxide (cuprite), basic copper sulphates (brochantite, antlerite), and if chloride ions are also present, active corrosion products like copper chloride hydroxides (atacamite, paratacamite). When exposed for more than several decades, black crusts also form on the sheltered areas, containing basic copper sulphates (brochantite, antlerite) and gypsum in addition to the previous compounds.[74]

- Green areas are zones exposed to rain and weathering. The corrosion products are regularly dissolved and washed away by rain water and the corrosion layer generally remains very thin. These areas tend to be light green in colour and mainly consist in the basic copper sulphate named brochantite ($CuSO_4.3Cu(OH)_2$). Sometimes, the copper oxide (cuprite Cu_2O) is exposed. As a result, green areas are located on a lower level than black areas, which appears like small islands of black crusts. [75]
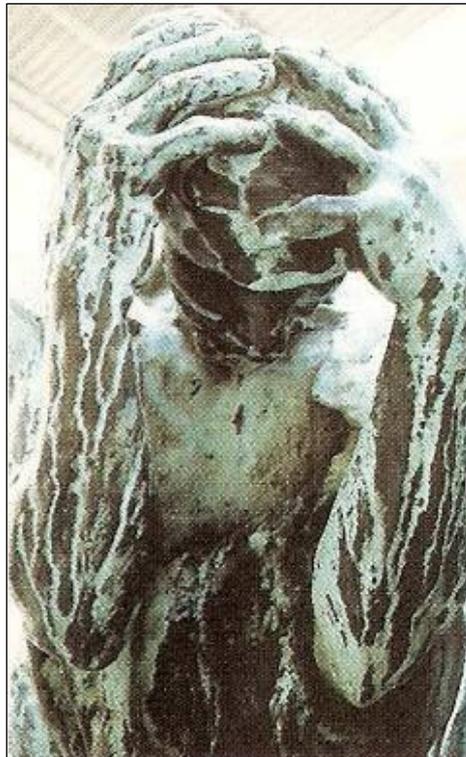
Figure 5 Corrosion details on the figures of *Les Bourgeois de Calais* from Rodin. The black deposits are visible in the areas sheltered from rain and the black and green streaks due to the flowing rainwater (From Amarger, 2001, p.215).

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[73] Dent Weil, 1982, p.132.
[74] Strandberg *et al.*, 2000, p.40 ; Selwyn & Roberge, 2006, p.294.
[75] Strandberg *et al.*, 2000, p.40 ; Selwyn & Roberge, 2006, p.294.

Table 1 Some common copper corrosion products.

MINERAL NAME	CHEMICAL NAME	FORMULA	COLOUR
Cuprite	Copper oxide	Cu_2O	Red
Tenorite	Copper oxide	CuO	Metallic grey black
Spertiniite	Copper hydroxide	$Cu(OH)_2$	Blue green
Brochantite	Basic copper sulphate	$CuSO_4.3Cu(OH)_2$	Vitreous green
Antlerite	Basic copper sulphate	$CuSO_4.2Cu(OH)_2$	Vitreous green
Posnjakite	Basic copper sulphate	$Cu_4SO_4(OH)_6.H_2O$	Vitreous green
Bonatite	Basic copper sulphate	$CuSO_4.3H_2O$	Pale blue
Calchantite	Copper sulphate pentahydrate	$CuSO_4.5H_2O$	Blue
Gerhardtite	Copper nitrate	$Cu_2(NO)_3(OH)_3$	Transparent green
Atacamite	Copper chloride hydroxide	$Cu_2(OH)_3Cl$	Vitreous green
Paratacamite	Copper chloride hydroxide	$Cu_2(OH)_3Cl$	Pale green
Nantokite	Copper chloride	$CuCl$	Pale green
Malachite	Copper basic carbonate	$CuCO_3.Cu(OH)_2$	Pale green
Azurite	Copper basic carbonate	$2CuCO_3.Cu(OH)_2$	Vitreous blue
Chalconatronite	Copper basic carbonate	$Na_2Cu(CO_3)_2.3H_2O$	Greenish blue
Chalcocite	Copper sulphide	Cu_2S	Metallic black grey
Covellite	Copper sulphide	CuS	Metallic blue

2.4.2.   Oxides

In contact with the oxygen contained in the atmosphere, a copper oxide layer naturally forms first directly on the metal surface. The most common copper oxide is the red – brown copper (I) oxide Cu_2O, named *cuprite*. The copper (II) oxide CuO named *tenorite* is more stable but rarer as it forms after exposure to higher temperatures (400 – 600°C). Its colour is grey – black.[76]

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[76] Scott, 2002, p.95.

2.4.3. Sulphates

The presence of sulphur ions coming from atmospheric gases increase water conductivity and interact with metal ions to form both soluble and insoluble corrosion products. Soluble compounds form first and some of them are then converted to insoluble compounds if they are not washed away by rain.

In the presence of sulphur ions, the oxide layer is with time followed by an adherent, insoluble and relatively stable green layer of copper (II) compounds, which tends to slow down the corrosion process.[77] This green corrosion product commonly found on the rain-washed areas is mostly the basic copper sulphate named *brochantite* ($CuSO_4.3Cu(OH)_2$) and forms just upon the oxide layer. Its green colour and relative stability are responsible for the concept of the patina on monuments.

Antlerite, another stable green copper hydroxide sulphate ($CuSO_4.2Cu(OH)_4$), is less common but it may be found in sheltered areas, where the pH is lower. Indeed, antlerite forms in more acidic conditions than brochantite and as such, is a good indicator for acidic degradation processes.[78]

Other copper sulphate products, like *chalcanthite* ($CuSO_4.5H_2O$) and *posnjakite* ($Cu_4SO_4(OH)_6.H_2O$) have occasionally been identified on copper sculpture. They are considered intermediate products and can be washed away by rain or be converted to a more stable product, like brochantite.[79]

2.4.4. Nitrates

Nitrate ions also increase water conductivity but contrarily to sulphur ions, they all quickly dissolve in water where they mostly contribute to create acidic conditions. That explains why they are more rarely found in corrosion crusts. [80] The product which is mainly formed on outdoor monuments is the copper nitrate *gerhardtite* ($Cu_2(NO_3)(OH)_3$).

2.4.5. Chlorides

Chloride ions are highly concentrated in the precipitations and in the deposits of coastal regions. They enhance the corrosion rate as they form soluble salts and complex ions with many metal ions. Moreover, they contribute to the conductivity of water and are responsible for the development of active corrosion, like localized pitting, because they interfere with the formation of protective corrosion layers. Pitting is particularly severe because once it has begun ; the metal dissolves within the pits,

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[77] Selwyn & Roberge, 2006, p.290 and 294.
[78] Scott, 2002, p.149 ; Selwyn & Roberge, 2006, p.294.
[79] Selwyn, 2004, p.70.
[80] Selwyn & Roberge, 2006, p.290.

leading to a local increase of the acidity.[81] Copper alloys exposed to Cl$^-$ can result in the development of "bronze disease", a corrosion phenomenon generally associated with archaeological objects but which has sometimes been observed on copper alloys monuments.[82] It can appear as *(par)-atacamite* (copper (II) chloride hydroxides $Cu_2(OH)_3Cl$), and occasionally *nantokite* (copper (I) chloride CuCl), the typical compound of bronze disease.

2.4.6.   Carbonates

Even if commonly found on archaeological objects, copper (II) carbonates, like the green *malachite* ($CuCO_3.Cu(OH)_2$) or the blue *azurite* ($2CuCO_3.Cu(OH)_2$), have been very rarely identified on copper outdoor sculpture. They can sometimes be found on copper corroding in solutions containing carbonate ions, for example near damp limestone (calcium carbonate $CaCO_3$). It seems that any copper (II) carbonate is then converted to copper (II) hydroxide sulphate when the surface is exposed to water containing sulphate ions.[83]

2.4.7.   Other compounds

Copper sulphides, copper oxalates and gypsum have sometimes been identified on outdoor sculpture.[84]

- Copper sulphides (*chalcocite* Cu_2S) may be produced by the alloy reacting with hydrogen sulphides. These substances may come from chemicals used for repatination (ammonium, potassium or sodium sulfides)[85] and especially if the monument is located close to pulp or paper mills.

- Copper oxalates can form after exposure to oxalic acid, which is secreted by micro-organisms like fungi and lichens and which is a component of acid rain and fog in urban areas.

- White accretions of gypsum ($CaSO_4.2H_2O$) may develop when residual casting material like plaster of Paris ($CaSO_4.1/2H_2O$) is dissolved inside and then deposited on the external envelope of the sculpture, after seeping of water through pores and cracks.

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[81] Selwyn & Roberge, 2006, p.290 ;
http://www.liverpool.gov.uk/Environment/Pollution/Air_quality/Air_quality_information/index.asp.
[82] Selwyn, 2004, p.70.
[83] Selwyn, 2004, p.70 ; Selwyn & Roberge, 2006, p.295.
[84] Selwyn & Roberge, 2006, p.295.
[85] Selwyn, 2004, p.70.

2.5.   *Current conservation strategies*

As previously discussed, the degradation rate of monuments has strongly increased since the 19th century, as a result of the higher level of pollutants present in the atmosphere. Since that time, people began to worry much more about outdoor statuary, seeing them gradually turning darker, becoming streaked and disfigured.[86] In response to the problem of the increased deterioration rate, conservation strategies, or maintenance plans need to be established. The objective of such a planning is to eliminate or at least minimize the effect of the damaging elements on and around a monument and to assure its future protection. Direct and indirect interventions need to be considered, as the former interacts on the monument and the latter, on the environment around it, without necessarily touching it.

Thus, any conservation strategies should be considered as a wider project, embedding different aspects. It is generally the responsibility of the local government, museums or private owners to take care of a monument and plan intervention strategies. A multidisciplinary approach is often needed to consider each aspect of such complex artworks, involving conservators, artists, art historians, curators, foundries, local administrators, architects and engineers.

2.5.1.   **Ethical considerations**

Indirect interventions are the first step to consider in conservation strategies. They are necessary to eliminate or at least minimize the damaging conditions around the monument, in order to prevent it from risks of corrosion, vandalism or deterioration. Often consisting of simple precautions, they help preserve the original state and stability of the monument and reduce the degree of direct interventions on it. Moreover, each monument needs a very specific conservation approach. A successful intervention on one monument could harm another one, having not been adapted to its specific condition. Thus, before taking any decision regarding a precise intervention, some ethical considerations need to be considered and kept in mind. [87]

- First, a monument needs to be *prevented* from deterioration, especially if it is newly built, by choosing an adapted location with little polluted atmosphere, isolation from the ground and appropriate artificial patination methods. In locations where regular vandalism occurs, measures must be taken to make the access less easy. *Prevention* also consists of regular maintenance of the monument by quickly indicating any undesirable change in its aspect or any vandal act, which is the first care action and is the best way to keep it in its original

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[86] Dent Weil, 1980.
[87] Strandberg, 2000, p.50.

condition. Again, regular maintenance is of great importance, by superficial cleaning of the accumulated dirt, by removing any sign of developing active corrosion.

- *Consolidation* of the sculpture may be necessary when it shows physical instability – by inserting supportive material with an adequate material, like stainless steel. *Protection* of the surface is the best barrier against the development of chemical instabilities, as a developing corrosion can be temporarily stopped by applying protective coatings, like waxes, on the metal surface. Of course, any external material needs to be chemically and physically stable, reversible and durable, to allow eventual future re-treatment.

- *Conservation* of the monument consists of totally or partially removing the active corrosion products by physical techniques (tools like scalpel or brush, abrasive particulates like nut shells, sand or glass beads, laser, high-pressure water) or chemical methods, in order to stabilize the surface. It can then be repatinated with chemicals, following traditional or the artist's recipes. This step is generally conducted by specialists (foundries, artists).

- *Reconstruction* can be necessary if a piece is broken or missing, in order to restore the visual appearance and meaning of the monument. But such interventions must always be based on an accurate documentation, allowing an exact reconstruction of the original appearance of the sculpture.

Obviously, before and during every intervention, description of the artwork, observation of its condition (signs of active corrosion), artistic and historical documentation, photographical records, drawings, analyses results must be collected. The expectations of the owner and the aesthetic and respect for the artist's original intent also have to be kept in mind.

At last, recommendations and planning for a long-term care must be considered. This is of great importance as the success of a conservation intervention can be compromised if no long-term maintenance is planned.

2.5.2. Direct interventions

Direct interventions are often of great importance in extreme cases, when a sculpture is strongly damaged and severely corroded. From a theoretic point of view, a conservation intervention should not lead to a change in the material structure or in the visual appearance of an object, if not to recover its original and well-documented appearance. If it does, the integrity of the object may be lost, as well as precious information. Regarding metals, testimonies of the technological process involved (casting material residues (sand, clay, plaster, traces of tools…) or of surface treatments (traces of paints or gilding, artificial patination residues …) could be irremediably lost.

Keeping in mind the basic principles of conservation like reversibility, minimum intervention and respect of the original design of the monument, the techniques involved should be sensitive enough to preserve the remaining original surface and details, while respecting the initial aesthetic qualities of the artwork, its historical and artistic meaning.

2.5.2.1. *Surface cleaning*

In the case of outdoor copper alloy monument, it is often complex to determine what to clean. As corrosion products are in fact altered original material, conservators must try to preserve them. Often mineral deposits or soil are mixed in the corrosion products and this increases the difficulty to remove the foreign bodies while preserving the patina. Furthermore, cleaning will not recover the sculpture's original appearance, as it has been lost through weathering.

Hence, cleaning always has to be minimal to preserve the original green or red patina and stable corrosion compounds, while effectively removing dust, soot deposits, disfiguring and active corrosion products. Depending on the conservation strategies of countries or museums, brochantite or cuprite tend to be preserved.[88] Conservators at the NCC in Liverpool tend to remove corrosion to cuprite: the particularity of Liverpool's atmosphere, as a coastal industrial city with a high chlorides and pollutants levels, leads conservators to clean to the cuprite level in order to remove all active corrosion. Furthermore, cleaning should never tend to expose the bare metal, as such a surface could become highly reactive and atmospheric corrosion would develop much more rapidly than on a stable corrosion layer.[89] After aggressive active corrosion has been removed, bare metal is sometimes exposed, as the unstable corrosion penetrates through all layers of corrosion down to the metal.

If a sculpture is well maintained from the beginning, simple mechanical cleaning with anionic or non-ionic detergent in tap water[90], soft brushes or sponges and scalpel, followed by thorough rinsing, is usually carried to remove soluble compounds, old coatings and dirt. After that, the protective coating is renewed by application of a wax or a lacquer.

When a sculpture has suffered from decades of neglect in an outdoor environment, the protective coating will be worn and generally preserved very unevenly. A non maintained sculpture would appear covered with various copper corrosion products (active or not), dirt, bird droppings, and black crusts of diverse compositions. The surface will be disfigured with patchy light green and black areas, run offs due to water flowing and thick deposits obscuring the overall figure and details. In such extreme cases, conservators may decide to employ other cleaning techniques like mechanical cleaning (air – abrasion, water under pressure), chemical cleaning and more recently, laser cleaning. These methods

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[88] Cooper, 2001, p.118.
[89] Chase & Veloz, 1985, p.29.
[90] Selwyn & Roberge, 2006, p.299.

must be carried out with great care, in order to avoid damaging surface details and minimize the cumulative loss of material due to repeated corrosion removal. They are sometimes used in combination, each technique offering its advantages to the surface to be most efficiently cleaned. Obviously, the success of cleaning largely depends on the nature and state of the surface to be treated as well as on the skill and personal judgment of the conservator.

2.5.2.1.1. Air-abrasive cleaning

The main advantage of air – abrasive cleaning consists mainly in the fact that it is a dry technique, as the use of water could theoretically increase the corrosion rate. It also allows a relative visibility and control during cleaning, at least better than when using chemical poultices or gels whose long-term effects are uncontrollable. It also quickly reveals a very uniform surface aspect after treatment. Among the disadvantages, it may sometimes cause over-cleaning of the surface (figure 6), and produce a relatively large amount of waste-products and dust, which requires collecting means, adequate ventilation and protection for the conservators. Air-abrasive techniques consist in "*accelerating abrasive particles in an air-stream through a hose to the nozzle where they are blasted at the surface to be cleaned. The particles hit the surface with a velocity determined by the accelerating conditions and by the distance from the nozzle to the work*".[91] The choice of abrasive is determined by the particle shape, mass, density and hardness. Its action depends on the characteristics of the substrate, the working distance and the angle of impact.[92] In practical applications, the best results are obtained in using large nozzles with low pressure.[93]

A large range of abrasive materials (alumina, sodium bicarbonate, pumice, talc , etc) can be used for conservation purpose.[94] The most commonly used ones for cleaning copper alloys statuary are the following.

- The use of methods like blasting with organic material such as ground walnut shells or apricot core is very efficient as this material is much softer than the corrosion products of copper alloys. Powdery active corrosion products are well removed while stable layers are preserved, but sometimes some of the light green patina may be removed and the brown cuprite revealed.[95] Furthermore, organic material is biodegradable, which makes it an ecological material, even if the waste products need to be collected and disposed of.

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[91] Chase & Veloz, 1985, p.24.
[92] Chase & Veloz, 1985, p.24.
[93] Scott, 2002, p.361.
[94] Connolly, 1986.
[95] Chase & Veloz, 1985, p.29.

- The use of sand as a blasting material is usually avoided by conservators if the green patina needs to be preserved, as even the finest and softest abrasive material may remove it while maintaining the brown cuprite.[96]

- Commonly used during the 1970's, the glass beads peening technique is now generally avoided as this material is harder and less elastic than the metal. As such, it is quite aggressive if not used at very low pressure. Surface deformation and reflectivity change due to glass beads impacts have been observed on metal surfaces by Chase & Veloz.[97]
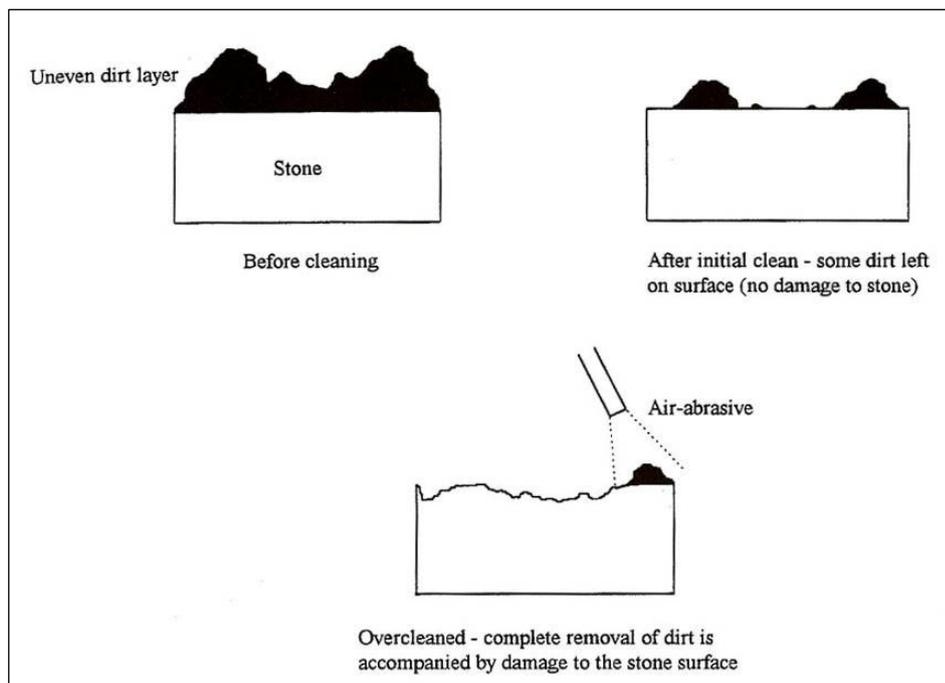
Figure 6 Schematic representation of a possible result of air-abrasive cleaning on stone (From Cooper, 1998, p. 3). The same process could happen on metal surfaces.

2.5.2.1.2. Water pressure cleaning

Water pressure cleaning is often used to clean copper alloy monuments. This technique offers the advantage of cleaning the surface mechanically but without abrasion, by removing old coatings, loose particles and soluble compounds from the surface, which are then flushed away. This method avoids abrasion of the surface like with air-abrasive techniques and deposition of abrasive debris on the monument. It is also very cheap, easily collectable and does not generate toxic or waste products. The major disadvantage is that the monument has to be perfectly dried after treatment, particularly with very detailed artworks, as water remaining in folds and passing through cracks may lead to an increased corrosion process, water playing the role of the electrolyte.

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[96] Strandberg, 2000, p.51.
[97] Chase & Veloz, 1985 ; Chase & Veloz, 1989.

Pressure and nozzle size determine the velocity of water hitting the surface. The larger the orifice size, the stronger the hydraulic force and the risk of surface deformation. It is then imperative to choose the right nozzle regarding the conservation state of the sculpture to clean. Working distance is a fundamental parameter as well and is easily controllable by the conservator.[98] Therefore, the efficacy of this technique depends mainly on the condition of the surface and the skill of the conservator.

Water pressure cleaning techniques have long been used in the conservation of metals. In the case of copper alloy monuments, low and medium pressure water have mostly been used. High pressure water was mostly employed for commercial and industrial purpose but is still sometimes used in conservation.[99] The effects of water pressure cleaning was studied by Merk-Gould et al.[100] Her researches demonstrate the effectiveness of low and medium pressure water to remove loose corrosion products while preserving the patina and the excess force of high and ultra high pressure water, leading to some material loss.

- Low pressure water (LP < 800psi) and medium pressure water (MP 1000-4000psi) allow a controllable cleaning, going through the superficial corrosion products and deposits but avoiding the exposure of bare metal and surface deformation. The use of medium pressure water may remove some of the light green patina.

- High pressure water (HP 4000-30'000psi) or ultra high pressure water (UHP 30'000 - 35'000psi) do not directly deform the metal surface but produce microscopic surface tunnels in the corrosion layer, resulting in more loss in the green sulphate corrosion crust than with air – abrasive techniques. Such high pressures should be avoided on delicate metal surfaces.

2.5.2.1.3. Chemical cleaning

Chemical cleaning was commonly used in the past as the objective was often to remove all the corrosion on a metal object to get a clean and shiny metal surface. Today the objective of cleaning has changed with the aim of preserving the original surface while removing active products and disfiguring crusts. Chemicals are sometimes used locally in poultices or gels, on active sites to remove active or insoluble corrosion products or on very thick crusts, to soften the surface and allow an easier removal with other techniques. Some of them show chelating properties[101] which allow selective removal of the metal ions. Chemicals have to be used with care and moderation as they are aggressive and not controllable. There is always a risk to damage the copper patina layer during such

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[98] Sembrat *et al.*, 2005, p.124-125.
[99] Draughon, 1989.
[100] Merk-Gould *et al.*, 1993.
[101] Volfovski, 1999, p.99. Chelating or complexing agents are molecules which fix metallic cations to form complex ions. With this technique, insoluble corrosion products are fixed to this molecule and leave the metal surface and pass in the washing solution.

operations and to leave residues which may later enhance corrosion rates if the treated area is not intensively rinsed.

The chemicals used to clean outdoor copper alloys are the same than those used to clean indoors objects, but sometimes more concentrated. The most commonly alkaline agents are[102]:

- **EDTA (ethylenediaminetetraacetic acid)** at 1% in a water solution (pH 9-11) and forms chelate complexes with a number of metal ions (Na, Ca, Cu, Fe, Pb, Zn, Ni, Mg, Mn).

- **Sodium hexametaphosphate / sodium polyphosphate (Calgon®)** at 5-15% in distilled water (pH 8.5) is used to soften calcareous crusts and to complex copper ions. It may strongly attack exposed metal and copper carbonates.

- **Sodium tripolyphosphate** is used at 0.5-5% in distilled water and is much safer than sodium hexametaphosphate while equally effective to complex copper compounds.

- **Alkaline glycerol** removes copper corrosion products like trihydroxychlorides, basic carbonates and sulphates, while leaving cuprite unaffected. It also may etch exposed metal surfaces but addition of 1% benzotriazole (a corrosion inhibitor) can reduce this effect.

- **Sodium potassium tartrate (Rochelle salts)** is more aggressive than alkaline glycerol. It complexes copper compounds but may attack cuprite very slowly. Addition of 1% benzotriazole may also reduce the etching effect on exposed metal.

- **Sodium dithiolate** is used to remove copper sulphide corrosion products.

Acids (like for example citric or formic acid) are generally avoided as they even more strongly dissolve the corrosion products and attack and etch the metal.[103]

2.5.2.1.4. Laser cleaning

Laser is a non-contact and sensitive technique allowing vaporization of various deposits and corrosion products to a precise level. As cleaning is achieved with light (a neodymium (Nd) laser at a typical wavelength of 1064 nm), no abrasive or chemical effects are produced. Although being not self-

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[102] Theopanopolou, 1995a ; Scott, 2002, p.366-267.

[103] Lins, 1992, p.210-211 ; Theopanopolou, 1995a ; Scott, 2002, p.366-267 ; Volfovski, 1999, p.99-100.

limiting[104] like in laser cleaning of stone, laser cleaning of metals provides a very careful and even cleaning.[105]

Laser cleaning for metal is still under development but it appears to be one of the most respectful current cleaning techniques for copper alloy monuments. On very fragile metal surfaces, traditional cleaning methods like air–abrasive techniques[106], water pressure and the use of chemicals may sometime become aggressive, leading to surface damage, extensive loss of material or corrosion stimulation in the case of chemicals. Laser cleaning may then be a very gentle cleaning technique for such fragile surfaces.

Laser cleaning could also be used on sculptures whose surface does not retain any artificial patina. Recent or indoor sculptures generally still show the original artist's patina, which has to be preserved and so, laser would not be a suitable tool to clean these. Outdoor monuments usually do not retain any original patina anymore and, therefore, laser can be used to clean and stabilize them. But special precautions should also be taken when original pigments or paint is still present on the surface, as such layers may more or less absorb laser radiations (especially at 1064 nm) and great damage may be irremediably done to pigments.

The only disadvantage is that corrosion products may behave differently under laser radiation, like the cuprite layer which discolours after laser radiation at 1064 nm. Originally red – brown, cuprite turns to a grey / purple tinge after exposition to a single laser pulse.[107] This discoloration effect is discussed in this paper. But in spite of the noticed colour change, laser cleaning seems to be a highly sensitive and precise technique to remove active corrosion compounds, organic deposits and old coatings, thus stabilizing the metal surface of outdoor copper alloy monuments.

Once cleaning is achieved, thorough rinsing is generally carried out to remove all debris of abrasive material, deposits and loose corrosion products, first with an non-ionic or anionic detergent in water and then with clear tap water. The sculpture should then be degreased with an organic solvent before being protected with wax, coloured or not. Repatination is sometimes achieved after cleaning, but this is not a common practice as the chemicals used may be aggressive to the metal.

2.5.2.2. *Artificial patination*

Initially, artificial patination is used by artists and foundry-men mainly when a precise surface aspect needs to be reached quickly. In the field of conservation, repatination may be achieved for aesthetic purpose to uniform the aspect of the metal after surface cleaning, following the artist's original

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[104] See Chapter 4.3.1.
[105] Cooper, 2001, p.110.
[106] Cooper, 2001, p.116-117.
[107] Cooper, 2001.

intentions. It can also happen that conservators use patina recipes to recreate a determined stable corrosion product, like cuprite.[108] But protective properties of such layers can vary and long-term behaviour of artificial patinas is often unpredictable. Artificial patination of restored artwork generally shows a few disadvantages, like insufficient adhesion to the metal substrate, partial wash-out by precipitation and undesired evolution of its appearance during ageing, as the artificial patina may gradually corrode and turn to a naturally-formed patina.

A large number of patina recipes do exist, using various components, mostly chemicals such as chelating agents or acids. Each would produce a typical colour, usually following the one initially intended by the artist or according to foundries traditional recipes. Most of them are complex procedure which should be carried out by experimented persons, like foundry-men. Furthermore, if repatination is improperly achieved, the use of chemicals may enhance corrosion and badly attack and damage the metal surface.

Repatination may involve treating the whole surface or only small damaged area. The metal surface is heated with a torch to vaporize all traces of humidity and enhance the chemical reaction. The corrosive substance is then applied in a few layers with a spray or a brush. Meanwhile, the surface is regularly rinsed to remove all residues of un-reacted chemicals.[109]

Retouches with a coloured mastic or resin (Maimeri® Restauro)[110] may be a good alternative if the colour reintegration is locally needed for aesthetic purpose. For an overall uniform aspect, pigmented wax can also be preferred to repatination, which would not only be less aggressive but offer a better protection, but needs to be renewed regularly to be efficient.[111]

2.5.2.3. Surface protection

After cleaning a monument, one of the best ways to protect the metal surface is first to apply by brush a corrosion inhibitor, generally 2-3% (w/v) benzotriazole (BTA) in ethanol[112], followed by a protective coating applied in one or various layers. This allows the surface to be isolated from the atmosphere and from the pollutants, particles and corrosive substances it may contain. By applying an additional coating and regularly renewing it, the metal can be protected from corrosion and can be preserved for future generations.

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[108] Socha *et al.*, 1980.
[109] Scott, 2002, p.374.
[110] Amarger, 2001a, p.221.
[111] Amarger, 2001a, p.221 ; Kreislova, 2007, p.267-268 ; Selwyn & Roberge, 2006, p.299.
[112] Scott, 2002, p.380.

The selected protective coating should show properties like minimal thickness, ease of application and of removal, protection against water vapour and air pollutants, adequate durability and stability. Usually, substances like wax or synthetic lacquers are used.

- Synthetic waxes are today the most popular protective coatings used on outdoor bronzes, as they are very effective in protecting the metal against corrosion in a short term. They also are insensible to micro-organisms and give the monument a pleasant aspect, reducing the colour contrast caused by corrosion and providing the surface a silky metallic shine.

  In the past, natural substances like beeswax or lanolin were used. They have been replaced today by petroleum-based (microcrystalline wax) and synthetic (polyethylene) waxes for two reasons: first they provide a better resistance to water, weathering in general and micro-organisms, while allowing oxygen to pass through the coating; second they have a higher melting point than natural wax, which avoids stickiness under sunlight whilst low enough to allow removal with steam.[113]

  Generally, a first wax layer is applied with a brush, sometimes on the heated metal surface (about 100°C), and can be toned with pigments to match the surface and provide a uniform tinge. The wax is absorbed into the surface and gives a depth to the colour which is already there. As the surface is usually quite matt after cleaning, the wax gives it some reflects. A second layer is then applied on the cold surface. The waxed surface is then polished with a soft cloth to provide a smoother, more resistant and more pleasant surface.[114]

  Due to weathering, waxes disappear with time and need to be renewed regularly to keep their complete protective effect, nearly once a year. Each four or five years, the wax coating should be totally removed in order to apply a new wax layer.[115] Dirty waxes can be removed with mineral spirits or steam before the application of fresh wax but removal may sometimes be difficult due to the wax penetration into porous metal surfaces and corrosion products.[116]

- Synthetic lacquers have also been used on outdoor sculpture, as in the case of the past treatments on Queen Victoria's Statue.[117] The most popular one is named Incralac®. This acrylic coating contains a mixture of 74% Paraloid®B44[118], 20% toluene, 5% ethanol or butyl

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[113] Strandberg, 2000, p.51. The melting point of beeswax is about 65°C while the vitreous transition temperature of microcrystalline wax is 80°C and its melting point 100°C.
[114] Amarger, 2001a, p.223-224 ; Argyropoulos *et al.*, 2000, p.59.
[115] Texier, 2001, p.211.
[116] Scott, 2002, p.289 ; Selwyn & Roberge, 2006, p.299.
[117] See Chapter 3.
[118] Paraloid®B44 is a methyl methacrylate copolymer used on outdoor monuments because of its good adhesion properties, good resistance to UV ageing and yellowing and high Tg (60°C). Tg is the Transition Glass Temperature and is the temperature above which the substance becomes sticky. (Theopanopulou, 1995b, p.8).

acetate, 0.5% Benzotriazole (BTA)[119] and 0.5% epoxidised soya bean oil. Incralac® is generally very long-lasting but tends to be replaced by wax as it does not offer any advantages compared to it: lacquers give more problems with reversibility and show bad ageing properties.[120] Incralac® is not removed by weathering and as a result, it remains in its degraded state, becoming grey and brittle with age.[121] Removal of aged Incralac® is difficult as it has a tendency to cross-link with time. Lacquers in general give the surface an unpleasant darker and plasticized aspect.[122]

The use of ORMOCER® as a synthetic coating providing good protection has been suggested by Pilz & Römich (1997, p.245-250). Developed by the Frauenhofer Institute in Munich, it is mainly an organic-inorganic copolymer (heteropolysiloxane) which most promising derived lacquers are OR1, OR15 and OR16, the last two being used as top layer coatings. ORMOCER® is reversible with organic solvents and provides good adhesion to the substrate. Applied in bilayers with OR1 and OR15 or OR16, the coating protectiveness is very effective and shows a better adhesion after weathering than Incralac®. But ORMOCER® also shows low reversibility and badly darkens the treated metal surface, providing a "wet" aspect, which explains why it is not so much employed.[123]

Sometimes wax is applied over the lacquer to increase protection, to slow lacquer ageing and to improve the appearance of the metal, darkened by a lacquer layer.[124]

Protective coatings are preferentially applied in spring or in the early summer, during the hot day, as the substance penetrates better into the metal surface as it expands at warm temperatures.[125] Sometimes the surface is heated with a torch, but this should be avoided as it can cause discoloration and alteration of the surface. Furthermore, the protective layer should not be applied inside the monument to allow natural ventilation and hydrothermal exchanges.[126]

In the case of monuments being part of fountains and constituted of dissimilar metals, further precautions than only application of a protective coating may be necessary. Besides the protective coating application, Amarger[127] did test an electrochemical system to prevent corrosion. He totally submerged soluble zinc anodes, which would preferentially corrode whilst leaving the copper alloy

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[119] A copper corrosion inhibitor used here as an anti-UV agent (Theopanopoulou, 1995b, p.8).
[120] Letardi, 2004, p.385.
[121] Selwyn & Roberge, 2006, p.300.
[122] Strandberg, 2000, p.51 ; Selwyn & Roberge, 2006, p.299.
[123] Pilz & Römich, 1997, p.245-250 ; Scott, 2002, p.387-390.
[124] Scott, 2002, p. 387 ; Selwyn & Roberge, 2006, p.300.
[125] Kipper, 1996, p.48.
[126] Amarger, 2001a, p.223.
[127] Amarger, 2001b, p.234-235.

elements unaffected. Although regular maintenance is needed too, these anodes are easily removable and replaceable and provide a good protection against algae development.

2.5.2.4. *Repair and restoration*

Even if the main purpose of conservation is to preserve the object and prevent it from further damage, structural repair of damaged parts or replacement of missing pieces needs sometimes to be considered. For example, destabilized or visually disturbing broken pieces could be repaired or recreated ; repairs to an unstable supporting base would obviously be more than necessary to secure the sculpture.

From an ethical point of view, reconstruction and restoration is acceptable if the aim is to return to the original state of the monument, as long as it is well-known. An accurate documentation must be collected to have a precise idea of its history, initial aesthetic aspect and the materials employed.

Some precautions need to be taken in order to avoid further problems due to this type of interventions:

- In the case of repairs, the same metal than the sculpture needs to be used in order to avoid galvanic corrosion generated by contact between dissimilar metals. An alternative is to use non-conductive material (Teflon®, non-conductive polymers, resins) in order to isolate the boundaries between different metals.[128]

- When the internal corroded iron structure needs to be replaced, one would prefer materials such as stainless steel or a metal as close as possible in the galvanic series to the copper alloy of the monument.[129]

2.5.3.   Indirect interventions

Once a monument has been cleaned, repaired, patinated and protected, it is often replaced outdoors, in the initial totally uncontrollable and aggressive environment. It can happen that in extreme cases, when particularly fragile, extensively corroded or if no maintenance plan can be assured, a monument may be moved indoors, where climatic conditions are much more controllable. Such a decision was taken for example with the four gilded bronze horses from St. Mark Basilica in Venice: the originals where moved indoors while replicas where placed outside.[130] But as outdoor statuary is made to "live" outdoors, its removal indoors would lead to the loss of its symbolic, historic and artistic meaning and should be avoided if not in extreme cases.

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[128] Selwyn & Roberge, 2006, p.298 ; Texier, 2001, p.209.
[129] Selwyn & Roberge, 2006, p.298.
[130] Alunno-Rossetti & Marabelli, 1976.

For outdoor monuments, as damages are especially caused by a bad environmental situation and a lack of care, an ongoing program must be established to preserve the newly acquired stability after cleaning and minimize the amount of further heavy interventions on the artwork due to neglect. Regular maintenance and inspections are of great importance to rapidly identify eventual problems and select the adequate intervention needed. A solid financial and administrative support is obviously required, which needs to be considered and planned from the beginning of the conservation.

2.5.3.1. *Regular maintenance plan*

Regular care is the basic of a maintenance program and may consist in simply removing accumulated garbage, leaves and nests, cutting back trees and local vegetation to allow a good air circulation, in checking the spraying by water sprinklers and the accumulation of de-icing salts. The monument should be regularly washed with mild soap, water and soft brushes to remove soluble compounds, dirt, salts, pollution and bird droppings. Graffiti should be removed as soon as possible to avoid further vandal acts and irreversible penetration of residues. Partial or total renewal of a protective coating is necessary to isolate the metal surface from the aggressive atmosphere, usually nearly once a year, more often with fountains.[131]

People in charge of such tasks should systematically inspect the sculpture, check and report any damage or corrosion developed since the conservation treatment.

Making the public sensitive and interested in the monument may help keeping the monument in a good conservation state. People have to feel concerned by public heritage and its conservation programs. Maintenance may then also consist in elaborating an educational program for the public and especially for children, in order to inform them and make them more responsible and sensible about what a monument represents for a city, the risks it incurs by pollution, neglect, vandalism or inappropriate behaviours and how important it is to take care of it in order to preserve it for future generations.

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[131] Amarger, 2001a, p.223-224.

3. Two case studies: the conservation of the monuments to Lord Nelson and Queen Victoria in the UK

All the information regarding the alterations and the conservation treatments on Monument to Lord Nelson and the Queen Victoria Statue comes from the treatment reports of both sculptures, kindly shared by Samantha Sportun, conservator in charge of those works and Head of Sculpture Department.

3.1. General aspects

As was previously explained, the atmospheric conditions of a specific location strongly influence the corrosion rate and the corrosion species developing on one particular monument. Thus, each site generates a specific microclimate depending of its direct environment (rural, urban, industrial or marine).

The city of Liverpool lies in the Northwest of England, more precisely in the County of Merseyside. Southport is a small town located up North Liverpool. They both sit on the coast of the Mersey River, which opens on the Irish Sea, a few kilometres from Liverpool. The weather in Northwest England is very humid, with lots of rainfall (1.050 mm/year) [132]. The average January temperature is 4°C and the average July temperature is 16°C[133]. Being not far from the sea, strong winds sweep across this region, which obviously carry a lot of chlorides and particulate matter that may be highly aggressive for the monuments.

Liverpool is an industrial city of about 800'000 inhabitants. A large amount of urban works are being carried out and a high number of cars are running each day through the City Centre. The main pollutants listed by the Liverpool City Council[134] are sulphur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3) and particulate matter.

Southport is a smaller city of about 100'000 inhabitants. Both cities present a high level of chlorides, as they are located right in front of the sea.

The impact of such an environment on copper alloy monuments is considerable. It is very humid and corrosive because of the high chloride level vehicled by strong winds coming from the sea. Pollution from the heavy traffic and industry, resulting in acid rain, highly enhances the velocity and extent of corrosion processes on outdoor sculptures. It is marked by evident colour contrasts between dark and light green areas, as well as distinct vertical streaks.

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[132] http://www.iexplore.com/cityguides/England/Liverpool/The+Essentials
[133] http://www.iexplore.com/cityguides/England/Liverpool/The+Essentials
[134] http://www.liverpool.gov.uk/Environment/Pollution/Air_quality/Air_quality_information/index.asp

Between 20 and 30 years ago in Liverpool, teams of council workers used to coat outdoor sculpture with what seemed to be black epoxy paint or lacquer,[135] in order to reduce the maintenance work on these highly corroded monuments.[136] This initially very resistant coating did obviously alter with time and unfortunately corrosion developed below that "protective" layer. As moisture penetrated behind the coating, corrosion was developing even more severely. The black layer also presented the inconvenience of obscuring the figures, whose details had become hardly legible.

The following case studies, the Monument to Lord Nelson and Queen Victoria Statue, have suffered such a treatment in the past. As the black paint or lacquer is extremely difficult to remove with traditional methods such as mechanical removal with scalpel or chemical pads, even more on a delicate copper alloy surface, laser cleaning was used in order to stabilize the surface of the sculpture by removing paint and corrosion products as well as improving the visual appearance of those public monuments. Laser cleaning techniques are generally employed on statues which do not retain any original patination. For example, recent or indoor artificially patinated sculptures would not be laser cleaned, as this would remove the artist's patina. In the case of Queen Victoria' Statue and Lord Nelson's Monument, the black paint and lacquer were not considered patina. These were coatings applied in the past, which disfigured the monument and enhanced corrosion. Therefore, such coatings had to be removed to stabilize the monument, by removing the underlying active corrosion species, in order to preserve it for further generations.

3.2.   Monument to Lord Nelson

The conservation treatment on the Monument to Lord Nelson (figures 7 -8) has been carried out by the Department of Sculpture Conservation of the National Conservation Centre (National Museums Liverpool) between 2003 and October 2005.

This memorial, which is owned by Walton International Group Inc, is located in Exchange Flags Square, behind the Liverpool Town Hall. Initially, the building was placed in front of the original exchange building, but it had to be moved near the Town Hall as an extension was built.[137]

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[135] It has very often been mentioned as epoxy paint, although it had never been analysed with scientific tools. Analysis carried out by the Northumbria University (PLM, FTIR, GC-MS) on paint samples taken from a typical copper alloy outdoor monument from Liverpool City Centre (King Edward's Monument) have shown that the black paint consisted in an acrylic/styrene copolymer as medium, mixed with pigments such as charcoal (animal charcoal, possibly bone black) and extended with dolomite and clay. An upper layer of uncoloured acrylic/styrene copolymer was applied on top as a varnish.
Even if King Edward's sculpture is maybe not representative of all monuments in Liverpool, this analysis shows that the acrylic/styrene polymer could have been used possibly on a few other sculptures and that the epoxy hypothesis needs to be considered with care or even verified.
[136] Cooper, 2001, p.117-118.
[137] Cavanagh, 1997, p.55.

Figure 7 - 8 Full views of the Monument to Lord Nelson before treatment.

3.2.1.   Historical aspects

Designed by Matthew Cotes Wyatt (1777-1862) and sculpted by Sir Richard Westmacott (1799-1872), the monument was unveiled on 21st October 1813, the anniversary date of the victory of Trafalgar. The memorial was financed by public funding and private donations. It was the symbol of the Liverpool citizen's gratitude to the King for the English naval victory against French Napoleonic fleet, at Trafalgar Cape, Spain, on 21st October 1805. At the same time it paid homage to the dead national hero, Admiral Horacio Nelson (1758-1805), whose clever strategy reversed the issue of the battle to the English's decisive advantage.[138]

3.2.2.   Description and technological aspects

This 8,84m high complex is constituted of granite, Westmorland marble, iron, cast copper alloy and lead. The granite basement supports a drum-shaped Westmorland marble pedestal, around which 4 chained prisoners are seated, positioned at the cardinal points. Between each prisoner are inserted four copper alloy bas-reliefs, presenting Nelson in different naval battles. Swags of laurel and heads of lions are encircling the pedestal. The chains to which the prisoners are attached are linked to rings in the mouths of the lions. Above the swags, one can twice read the following sentence, in capital letters: "ENGLAND EXPECTS EVERY MAN TO DO HIS DUTY".

Above these elements is the *Apotheosis* group, a pyramidal group of five figures: an idealised naked Lord Nelson, the allegories of *Victory*, *Death,* represented by a skeleton and touching Lord Nelson,

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[138] Cavanagh, 1997, p.51.

and finally *Britannia*, crying his lost hero. An iron armature is present in the copper alloy complex, as well as in other modern replacements (crown, nails). The figures sit on a layer of lead and lead joints are present to separate the different elements.[139]

3.2.3. Alloy composition and corrosion products

The composition of the alloys constituting the Monument to Lord Nelson has been characterized, as well as the nature of the corrosion products present on its surface.

An Electron Probe Micro-Analysis (EPMA) of samples has been carried out prior to this research by Oxford Materials Characterization Service[140] in order to determine the exact composition of the alloy constituting the sculpture. Three types of samples have been chosen (Apotheosis group, swag decoration and proper left foot of a Prisoner). The EPMA determined the alloy to be copper rather than brass, as the zinc content was low. Thus, the main component was copper (94.6-96.8%), with 2.2-2.9% zinc, 0.4-0.9% lead, impurities such as Fe, Ni, As, Ag, Bi and S and possibly traces of Sn and Cd. The metal has been found to be very uniform with limited variations in composition between the samples. This choice of alloy is surprising in the sense that copper alloys with low zinc content are not generally used for casting, as they are not ideal for this kind of metal treatments.[141] They are more commonly used for wrought products. The choice of such an alloy for casting must have been dictated by the kind of metal available at that time, that means in a war economy period.

Powder X-Ray Diffraction (XRD) has been used to identify the corrosion products found on the metal surface. This analysis was conducted by the LGC[142] Company. Powder scraped from the corroded surface was compared to their database for identification. The main crystalline elements identified in the samples were: Atacamite $Cu_2Cl(OH)_3$, Brochantite $Cu_4(OH)_6SO_4$ and Gypsum $CaSO_4.2H_2O$. No proportions could be given. Depending on the samples, smaller quantities of Nantokite CuCl, Gypsum $CaSO_4.2H_2O$, Quartz, as well as an unidentified crystalline material were evidenced.

3.2.4. Conservation state before laser cleaning

Past interventions have been carried out on the Monument to Lord Nelson.

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[139] Cavanagh, 1997, p.52-53.
[140] Informations coming from Oxford Materials Characterization Service, Oxford University Begbroke Science Park, Sandy Lane, Yarnton, Oxford, OX5 1PF, UK, Tel: 0044 1865 283777, Fax: 0044 1865 848790, omcs.manager@materials.ox.ac.uk.
[141] See Chapter 2.1.1.
[142] http://www.lgc.co.uk/

- In the past, the prisoners had been coated with a black paint, which still remained at some places, particularly in the sheltered areas. The corrosion products were developing through that coating (figure 9).

- At the time of the manufacture, plates of copper alloy had been inserted in the surface, maybe in order to disguise the casting defaults. Since the alloy composition of the added material was different from the one constituting the sculpture, an inhomogeneous patchy effect was clearly visible all over the sculpture (figure 10).

Figure 9 Left: View on a prisoner. One sees clearly the black paint appearing through the green corrosion products.

Figure 10 Right: Patchy surface due to the addition of different copper alloys plate in order to mask defects.

Various alterations were observed:

- All the elements were heavily corroded. Green run offs from rainwater disfigured the sculpture while some points presented bronze disease with severe pitting of the surface (figure 11).

- Iron corrosion and salts, coming from the internal iron structure and others external elements, were punctually observed, with some cracks of the bronze envelope resulting from the expansion of the iron corrosion (figure 12).

Figure 11 Left: Active corrosion on a bas-relief.

Figure 12 Right: Iron corrosion from the internal structure.

- Those cracks, as well as the separation of the leaded joints, had allowed water to ingress the structure, thus creating condensation on the inner walls. Water was filling voids and relieves inside the sculpture as well (figure 13).

- Erosion, staining and fragmentation were noticed on the stonework, which was badly damaged by the corrosion products and the water ingress as well.

Figure 13 Lead joint clearly visible. Water filling relieves and increasing the corrosion rate.

3.3. Statue of Queen Victoria

The conservation treatment on the Statue of Queen Victoria has been carried out by the Department of Sculpture Conservation of the National Conservation Centre (National Museums Liverpool) from January 2006 to April 2006.

The sculpture of Queen Victoria is located in Southport (North Liverpool). Owned by the Sefton Council, it was initially located in the municipal Gardens, Lord Street. It was moved in December 1912 to its present position, facing the sea on the junction of Nevill Street and the Promenade.

Figure 14 - 15 Queen Victoria before conservation treatment: front and back.

3.3.1. Historical aspects

The Statue to Queen Victoria was sculpted by Sir George Frampton (1860-1928) and was unveiled in 1912. The Queen is represented in her middle life, wearing the robes of the Order of the Garter, a chivalry order dating from the medieval times.

3.3.2. Description and technological aspects

The monument represents an over-life sized Queen Victoria standing and wearing a richly embroidered dress, a veil and a cloak which falls to her feet with heavy falls. She holds the orb in her left hand and the Sceptre of State in her right hand. Her head is covered by a crown.

This cast copper alloy sculpture is around 18.3 m high. The pedestal on which it stands is made of Aberdeen silver granite and is 3.5m high. A lead joint has been inserted between the stone and the metal. The sculpture has been cast in few sections, which can be observed at the back of the cloak.

3.3.3. Alloy composition and corrosion products

The composition of the alloys constituting the Statue of Queen Victoria has been determined, as well as the nature of the corrosion products present on its surface.

An Electron Probe Micro-Analysis (EPMA) of samples has been carried out prior to this research by Oxford Materials Characterization Service[143] in order to determine the exact composition of the alloy constituting the sculpture. For this purpose, a metal sample has been taken from the bottom of the drapery. Paradoxically, this alloy is named today as "commercial bronze", but it is actually a brass, which means a copper alloy with 10% zinc. The exact composition is 86.8% Cu, 11.9% Zn, 0.8% Sn, 0.2% Pb, while the principal impurities are Fe, Ni and As. Small traces of Co, Ag, Bi and possibly Cd have been evidenced. Having been mainly employed for decorative and architectural features, this alloy has been traditionally used in British craftsmanship and industry during centuries (15th -19th Century). Its only limitation is that it had to be carefully handled during casting as it has freezes very quickly and thus, air bubbles and casting defaults could easily happen.

Powder X-Ray Diffraction (XRD) has been used to identify the corrosion products found on the metal surface. This analysis was conducted by the LGC[144] Company. Powder taken from the surface was compared to their database for identification. The main crystalline elements identified in the samples were: Brochantite $Cu_4(OH)_6SO_4$, Cuprite Cu_2O and Atacamite $Cu_2Cl(OH)_3$. No proportions were given. Other unidentified elements were also present.

3.3.4. Conservation state before laser cleaning

The main problems encountered on the Statue of Queen Victoria were due to past interventions on the monument.

First, abrasive techniques had been used to clean the surface, as the overall matt quality of the surface suggested.

Then, the surface had been coated with a black lacquer (figures 16-17). This coating had been applied directly on the bare sandblasted metal, isolating it from any corrosion progress. Corrosion had developed only in the areas were the lacquer had been removed by winds and particles. Partial black residues remained, especially in the protected zones, such as folds and relieves of the figure.

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[143] Informations coming from Oxford Materials Characterization Service, Oxford University Begbroke Science Park, Sandy Lane, Yarnton, Oxford, OX5 1PF, UK, Tel: 0044 1865 283777, Fax: 0044 1865 848790, omcs.manager@materials.ox.ac.uk

[144] http://www.lgc.co.uk/
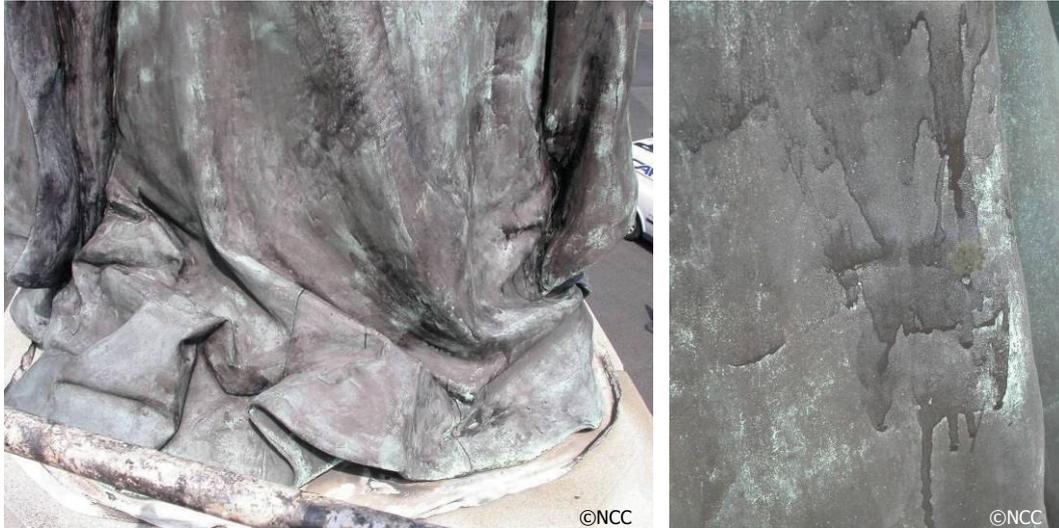
Figure 16 **-** 17 Traces of black lacquer on the metal surface**.**

The sculpture was extensively corroded, with punctual green active corrosion spots.

Iron corrosion coming from the internal armature of the monument had formed cracks, which allowed rainwater to enter the structure, creating condensation on the inner walls of the figure.

Figure 18 - 19 Left: Un-cleaned face; Right : Un-cleaned front bottom.

3.4. Conservation treatments of the Monuments to Lord Nelson and Queen Victoria

For the conservation treatment, both sculptures had to be dismounted and were brought to the Sculpture Conservation studio at the National Conservation Centre, except the *Apotheosis* group of Nelson's monument, which couldn't be removed and was treated *in situ* under protective scaffolding.

3.4.1. Laser cleaning

Different interventions have been carried out on those sculptures. The main and most interesting one within the frame of this work is the laser cleaning treatment.

Both monuments were cleaned with a Nd:YAG laser system to remove the black coating on Nelson and the black lacquer on Queen Victoria. Conservators determined laser cleaning to be the most appropriate cleaning method to be used on those strongly altered surfaces, covered with irreversible coatings. Indeed, laser is a non-contact cleaning method which can remove corrosion from a surface in a very sensitive way while preserving the underlying surface of the metal. Thus, laser cleaning offered some advantages on other more traditional techniques, like abrasive or mechanical techniques which too often remove or scratch the metal surface to be preserved or like chemical methods that, once removed and rinsed, can leave undesired salts and by-products inside the material. Furthermore, laser cleaning offered the advantage of being a dry technique, which is not to neglect in the cleaning of metals, as water is a catalyser for further corrosion to develop.

3.4.1.1. System employed

The conservators used a Q-Switched Nd:YAG laser system (Phoenix™Classic, Phoenix™2(+) and Phoenix™Zenith by Lynton Lasers[145]) to clean the corrosion and the black coatings on the copper alloy surfaces of both monuments. Emitting at 1064 nm (near Infrared wavelength), it was employed at fluence levels between 0.5 and 1.2 J/cm^2. The repetition rate was 30 Hz and the pulse length 10 ns. The beam was delivered through an articulated arm.

Prior to laser cleaning, the copper alloy surfaces were brushed with glass bristle brush to soften the corrosion products. A solvent-free paint and a varnish remover were applied on the black coating to reduce its thickness. During the laser treatment, deionised water was applied on surfaces to improve the cleaning. As will be discussed later (See 4.3.3 *Steam laser cleaning*), application of water on the surface during laser cleaning improves the removal of undesirable products.

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[145] Lynton Laser Ltd. For details, see Appendix 17.

Figure 20 - 21 A half-laser cleaned prisoner.

Figure 22 Left: Laser half-cleaned head and shoulders.
Figure 23 Right: Laser half-cleaned face.

3.4.1.2.   Results and observations

Laser cleaning successfully removed the powdery active corrosion (atacamite, paratacamite), some of the sulphate layer (brochantite) and the black coatings on both sculptures. Stains and run offs were removed, while preserving the oxide layer surface upon the metal. The sculptures recovered a more uniform aspect and details of the figures became legible again.

But an unexpected phenomenon appeared on the cuprite layer after being exposed to laser radiation: the cuprite layer appeared in a slight grey / violet tinge instead of its usual brown / red colour. Strangely, this discoloration process did not happen on the brochantite layers as the colour only turned slightly darker. Furthermore, the discoloration effect seemed to reverse with time, as was

noticed by conservators a few weeks later. This change in colour had to be considered as it obviously translated a chemical or physical change in the corrosion layer or in the metal itself.

3.4.2.   Other conservation treatments

Where copper corrosion was thicker, the surface was mechanically cleaned with a scalpel. Iron salts were treated in the same way.

Glass bristle brush was used to remove any remaining undesired material.

Iron armatures were partly replaced with stainless steel and open cracks were filled with resin.

At last, a corrosion inhibitor (BTA) was applied on the surfaces, followed by two coats of Soter® microcrystalline wax mixed with BTA in order to protect the monuments against further degradation (weathering, graffiti). Pigments were added in order to tone the monument near the original colour of the copper oxide (cuprite).

3.4.3.   Actual conservation state

Figure 24 - 25 Full view of Lord Nelson's Monument and detail of a prisoner after conservation treatment.

Figure 26 **-** 27 Full view of Queen Victoria Statue and detail of bottom of the dress after conservation treatment**.**

Both sculptures are now back to their respective locations, exposed again to weathering and vandalism. Even if their protective coatings preserve them from degradation for a certain time, they are checked and renewed every 12-24 months and the surface is regularly inspected for any signs of corrosion. But even the best treatment and protective layers cannot infinitely preserve an outdoor monument against further corrosion. Accumulation of rainwater, dust, pollutants and winds finally break through the protective layer and corrosion spots begin to develop again. The following pictures (28-29) show active corrosion spots developing again at some weaker points of the monuments. But with a regular maintenance, the monuments can be rapidly treated and so, further progress of the corrosion can be slowed down.

Figure 28 Active corrosion on the drapery of Queen Victoria - June 2006.

Figure 29 Active corrosion on the face of a prisoner on Lord Nelson's Monument – November 2006.

Part II: Laser cleaning

4. Basics of laser cleaning technique

4.1. Properties of laser radiation

Laser light is usually defined through its three main characteristics: *monochromaticity*, *directionality* and *coherence*.[146] These properties of laser light depend on the specific parameters of the laser system.

- *Monochromaticity*: Laser radiation is a form of light and, therefore, can be characterized by the electromagnetic spectrum. Laser radiation is said to be *monochromatic* as it emits light at a single wavelength in the visible, infrared or ultraviolet part of the electromagnetic spectrum (figure 30).
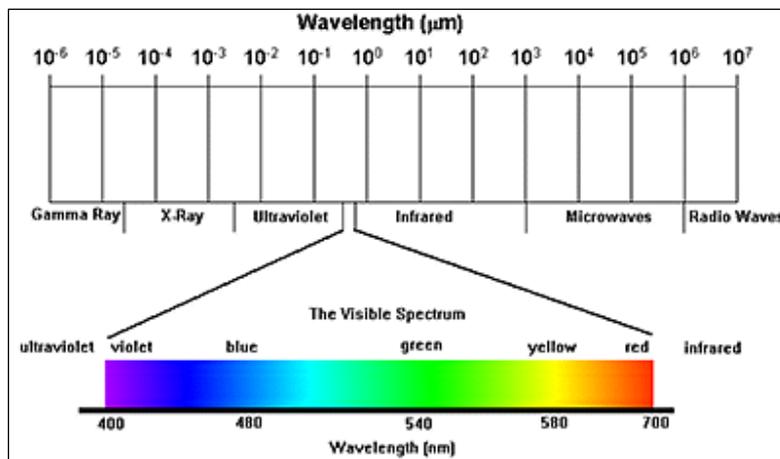
Figure 30 The electromagnetic spectrum (From http://www.crisp.nus.edu.sg/~research/tutorial/emsp1.gif).

Depending on the nature of the irradiated material, the surface will be very absorbing or strongly reflecting at a certain wavelength. Near infrared radiation of 1064 nm is currently very often used in conservation. At this wavelength, the difference in absorptivity between the material to remove and the material to preserve should be the largest.

- The *directionality* of the laser beam means that it is much collimated. The light concentrated in the laser beam delivers energy only where it is focused. In this way, the cleaning process can be very precise.

- *Coherence*: Laser radiation is a form of light, and as such, light particles, or *photons*, are transmitted under the form of waves. A wave is defined by its amplitude *a*, its wavelength λ and its frequency *f* (figure 31).

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[146] Hecht, 1992, p.2-5.

Figure 31 Amplitude a and wavelength λ of a wave in water (From Cooper, 1998, p.22).
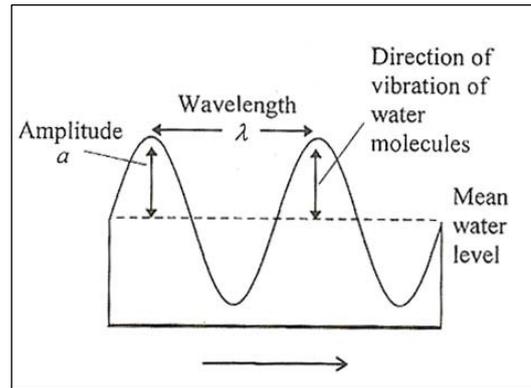
Frequency f, wavelength λ and velocity υ of a wave are linked in the following equation:

$$\upsilon = \lambda f$$

Coherence is achieved when two wave amplitudes are perfectly superposed one to the other: if the amplitudes of two waves are added, a bigger wave is formed. They are said to be in phase.

If they are of opposite phase, the waves cancel each other (figure 32).[147]

Figure 32 Constructive and destructive interference of waves. a) In phase waves; b) In opposite phase waves (From Cooper, 1998, p.23).
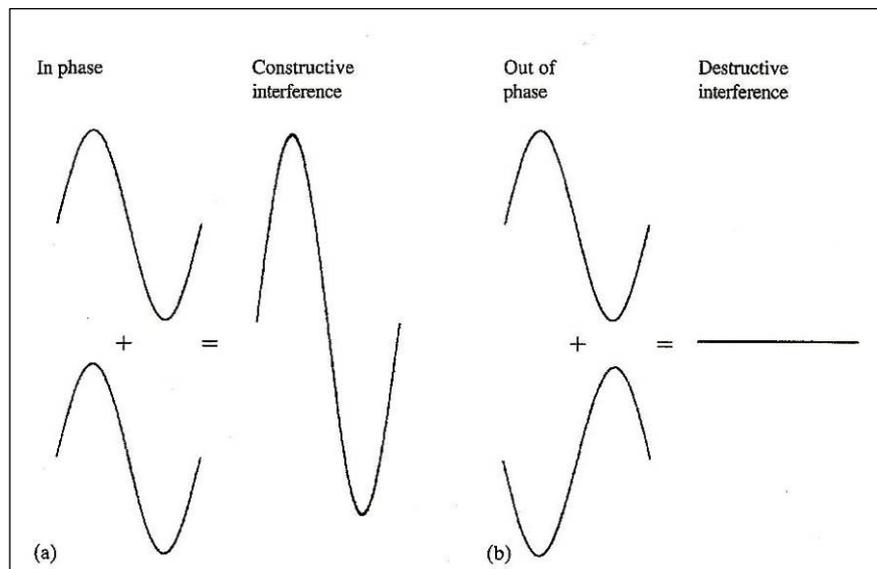
Coherence and *directionality* explain the high intensity of the laser beam, which appears to be several orders of magnitudes brighter than the sun.[148]

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[147] Cooper, 1998, p.33 : this property appears to be most important in applications such as holography and interferometry, where the laser beam is split into two or more beams and travels along to each other before recombining.
[148] Cooper, 1998, p.22-24, 33.

4.2.   *Laser system parameters*

Basically, *wavelength*, *mean power*, *peak pulse power* and *beam quality* are parameters inherent to the laser system. On the other hand, parameters like *pulse energy*, *pulse power*, *pulse duration*, *repetition rate*, *intensity* and *fluence* can be variable and selected by the operator according to the task requirements. The most important parameters are:

- *Wavelength:* While conventional light sources emit in a large spectrum in the visible and/or infrared, each laser system can produce a light source at a typical wavelength, for example in the near-infrared[149] wavelength (1064 nm) for the Nd:YAG laser or in the ultra-violet wavelength (193, 248, 308nm) for the Excimer laser[150]. A specific wavelength can be chosen depending on the absorption properties of the material that has to be removed from a substrate.

- *Pulse power* and *pulse length* τ_l determine the energy released to the material. Pulse duration, together with the *optical penetration depth* l_α and *heat diffusion length* l_τ (which depends on the pulse length, see 7.2) determine the interaction volume within the material. Lasers are mainly used in conservation in *short pulses* which system is called Q-Switched mode[151]. This system provides high peaks of power in a very short time (typically 5-30 ns)[152]. In this way, heat from the laser beam is highly absorbed on the very superficial layer of the irradiated surface. The residual heat transmitted to the bulk material is negligible[153].

- The *repetition rate* is the number of pulses per second and it is measured in Hertz. On the *Phoenix®2(+)* by Lynton Lasers for example, which was used in that project, repetition rate can be selected from 0.63 to 10 Hz. It determines the speed of cleaning. The lower the repetition rate the more precise and controllable the cleaning, as the conservator can check the exact position of the beam before firing and has more time to react if needed.

- *Intensity* and *fluence*: *intensity* is the power per unit area ($W\!/cm^2$) and *fluence* is the energy per unit area ($J\!/cm^2$). For a laser of wavelength and pulse length which interaction volume is short (which means short heat penetration by conduction, short light penetration

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[149] Hecht, 1992, p.70-72. 1-2µm region is considered near-infrared, 3-5µm is mid-infrared and 8-12µm is thermal- or far-infrared.
[150] COST Action G7, p.20 ; Hecht, 1992, p.211.
[151] See Appendix 1.
[152] Watkins *et al.*, 1994, p.909.
[153] Cooper, 1998, p.42-43.

due to high absorptivity), like in this research, *fluence* is the parameter to be considered. For longer pulses ($\tau_l \geq \mu s$), *intensity* is generally the adequate parameter.

Fluence, or *energy density*, is the measure of the concentration of energy in the beam per unit area. It is the most important parameter as it determines the ablation rate per pulse and so, the level of the cleaning. It is obtained by dividing energy in Joules by beam size in cm^2 and is measured in J/cm^2 as:

$$\frac{Energy \left[J \right]}{Beam\ size \left[cm^2 \right]} = Fluence \left[J/cm^2 \right]$$

Therefore, assuming that the energy is constant, fluence levels can be modified by playing with the working distance and so, the beam size. The smaller the spot size, the higher the fluence, and vice versa. Most of the time, laser cleaning of artworks is carried out at the lowest possible fluence to minimise the risk of damage.

- The *beam size* is the area of the beam at the interaction point and it depends on the optics. The laser beam is delivered through an articulated arm at the extremity of which is a pen-like hand-piece. Inside the hand-piece is located a focusing lens, which produces a beam converging to the focal point of the lens and diverging from it. At its focusing point, the beam is very narrow, which means that the energy is much concentrated. Where the beam becomes wider, the energy is more dispersed. By playing with the working distance[154] (figure 33), one can change the beam size and so, the energy density (fluence) of the laser beam at the surface of the object.

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[154] The working distance is the distance between the material surface and the focusing lens at the extremity of the articulated arm.
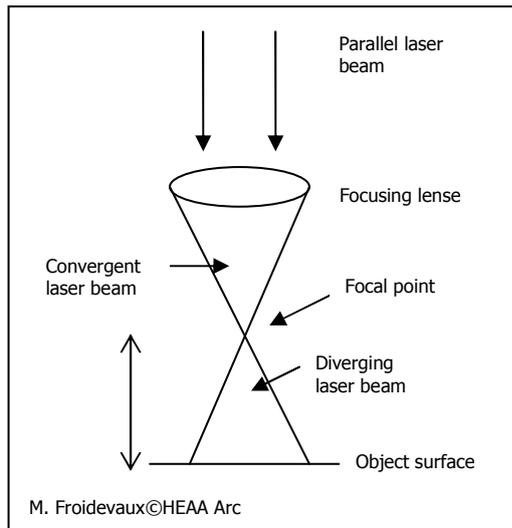
Figure 33 Schematic representation of the laser beam profile.

4.3.   *Laser cleaning mechanisms*

Laser cleaning is the result of interactions between laser light and the material to be cleaned, which shows its own chemical and physical properties. Each dirt layer or corrosion product has its own characteristic absorption spectrum which would make it react differently depending on the wavelength to which it is exposed. Each laser provides a different type of interaction determined by its wavelength. Wavelength influences the optical penetration depth, while pulse length determines the heat penetration depth.

As discussed earlier, laser cleaning of a dirty surface is effective if the dirt highly absorbs the laser energy while the underlying surface, the object, reflects most of it. For example, when a piece of white marble, covered with a thick black pollution crust, is laser cleaned at 1064 nm, the black deposit will absorb most of the energy from the beam while the marble will absorb much less.[155]

This effect is important in that the photons, or light particles in the laser beam, can distinguish through the different layers much better than more conventional techniques, like abrasive methods or chemicals, whose effects are less controllable and can lead to over-cleaning and damage to the object. The infrared Nd:YAG laser (1064 nm) is used all along this chapter as it is the most used type of laser in conservation and because laser cleaning at infrared wavelength was used during this research.

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[155] Cooper *et al.*, 1993.

4.3.1.   Self-limiting process

This property can lead us to the *self-limiting* effect of laser cleaning. This effect allows the conservator to clean a surface without causing any damage to the object (figure 34). Cleaning is said to be *self-limiting* when the cleaning effect stops once the dirt layer has been removed, as further pulses are reflected away from the surface. It means that once a black layer of dirt is removed, further pulses hitting a white underlying marble will be mainly diffusely[156] reflected from the surface and so, the energy would be insufficiently absorbed to cause damage.[157]

The *self-limiting* process cannot be achieved if the material shows different layers absorbing at the same wavelength, as is it the case of corrosion products of metal, which often show complex layers. In that case, often no *self-limiting* effect occurs and laser cleaning has to be carried out very carefully. Mostly on metal surfaces, short pulse laser is also of fundamental importance, as it would avoid heat propagation in the bulk material that could cause damage to the metal microstructure or surface melting.[158]
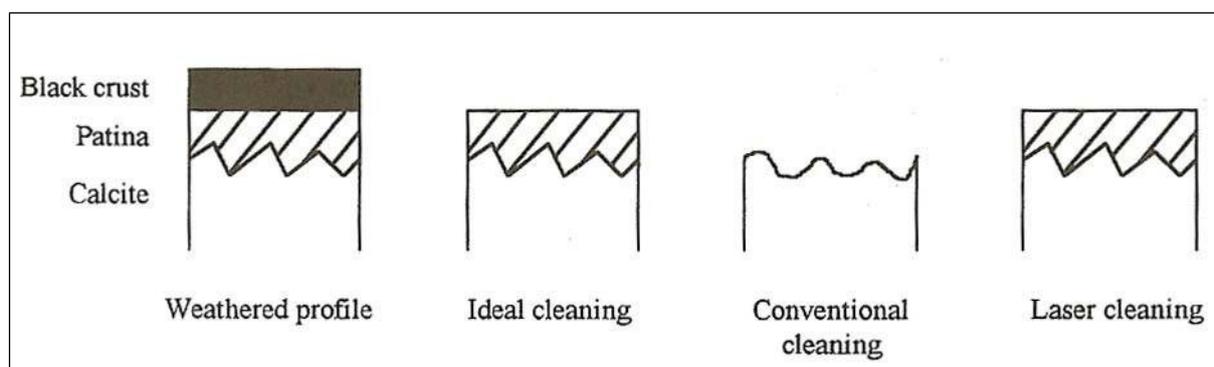
Figure 34 Schematic representation of the preservation of the patina on marble by the self-limiting effect of laser cleaning (From Cooper, 1998, p.16).

4.3.2.   Ablation and damage thresholds

Each material which has to be removed from a surface (dirt, paint, corrosion products) shows a threshold fluence above which cleaning, or *ablation* occurs. The underlying surface, which has to be preserved, also shows a threshold fluence above which damage occurs.[159]

As discussed previously and in normal cleaning use, the laser beam converges to a focus point, after which it diverges. This allows the conservator to vary the fluence level by playing with the working distance in order to modify the spot size on the surface of the object.

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[156] See Appendix 3.
[157] Cooper, 1998, p.8.
[158] Coll., *Introduction to Laser Cleaning...*, p.9-13.
[159] Cooper *et al.*, 1993, p.262-263.

Hence, during laser cleaning, if the conservator works far from the surface of the object, the beam size will be spread out and thus fluence will be too low to interact with the surface. The fluence level above which the laser begins to clean or ablate the dirt layer is called ablation threshold.

If the conservator works near the surface, the spot size will be smaller and the fluence much higher. This can cause damage to the surface to be preserved if cleaning is achieved beyond the damage threshold, which is the fluence level above which the laser beam's intensity is so high that it harms the object itself.

The difference between the ablation threshold of the material to remove and the damage threshold of the surface to be preserved should be the largest possible to achieve a safe cleaning.

At a given wavelength and pulse length, the ablation and damage thresholds depend strongly on the optical and thermal properties of the irradiated material: absorptivity, heat conductivity, specific heat capacity and density.[160] Laser cleaning should then be carried out between these two points, called "safe working window"[161], to be achieved safely, if possible in a self-limiting way.

4.3.3.   Laser cleaning mechanisms

Laser ablation is the term used to describe *"a process in which material is ejected from a solid surface as a result of irradiation by a laser beam"*.[162] Depending on the intensity of the laser beam, and thus the level of fluence, different effects can be produced. As the most common laser used today in conservation for cleaning is the infrared Q-Switched Nd:YAG laser,[163] its cleaning mechanisms are described as follows:

- *Rapid thermal expansion* is a process appearing at relatively low fluence. The dirt particles and/or the substrate strongly absorb the energy which leads to a rapid temperature rise. This is due to the short pulse mode, which allows the temperature to rise only for the duration of the pulse and to fall once the pulse has finished. A short pulse produces a maximum temperature rise at the surface and so, minimal heat propagates into the bulk material.[164] Once the temperature rise has occurred, an expansion of the heated zone takes place. The resultant forces overcome the adhesion forces of the particles to the substrate and, therefore, are sufficient to eject material from the substrate. The rapid ejection of the material can cause a shock wave in the air which is perceptible as a snapping sound[165]. This sound

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[160] Cooper, 2002, p.35.
[161] Cooper & Larson, 1996, p.32.
[162] Copper, 1998, p.39.
[163] Cooper, 1998, p.39.
[164] Cooper, 2002, p.35.
[165] Cooper *et al.*, 1993, p.263-264.

decreases as more material is removed and thus, its loudness can be used as an indicator of the effectiveness of the cleaning[166].

Removal of particles through *rapid thermal expansion* is very selective and avoids causing damage to the object (figure 35). Laser parameters should be set up in order that this process would predominate[167].
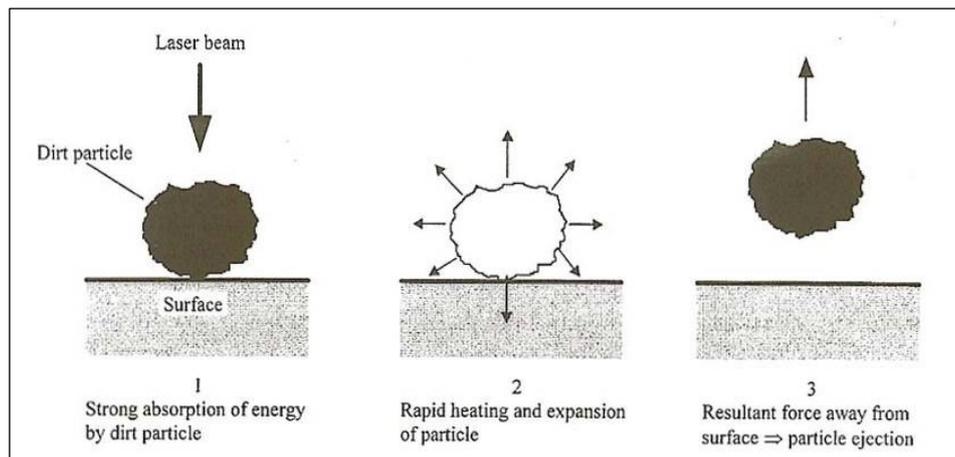
Figure 35 Schematic representation of removal of dirt particles by rapid thermal expansion (From Cooper, 1998, p.52).

- *Explosive vaporisation* happens at a slightly higher fluence. The temperature in the material to remove is raised beyond its boiling point and this leads to its vaporisation. The heating is very fast and thus, vaporization is explosive. This process can be difficult to control and as such, should be avoided[168].

- *Plasma* formation, linked to surface relaxation, happens when the fluence level is even higher (figure 36). In this process, the absorbing layer is turned to a partially ionized vapour which absorbs the laser energy very strongly. This very hot *plasma*[169] plume, just above the surface, acts as a shield against the laser beam and so, the initial vaporisation is stopped. As the pulse goes on, the vapour is heated more and this leads to a very high pressure, which results in a shock wave visible as a very bright spark, producing microscopic compression of the surface of the material. Once the pulse stops, the plasma dissipates, the material surface relaxes and a thin layer (1-100µm) is removed. This very fast compression/relaxation process allows a rapid removal of dirt from the surface but often causes damage to the underlying material.[170]

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[166] Cooper, 1998, p.14 and 46.
[167] Cooper, 1998, p.52 ; Fernandes & Kane, 2006, p.31.
[168] Cooper, 1998, p.54.
[169] A plasma is an ionised gas that is considered as the fourth state of the material (liquid, solid, gas and plasma). See http://fr.wikipedia.org/wiki/Physique_des_plasmas.
[170] Cooper, 1998, p.8, 46 and 54 ; Cooper & Larson, 1996, p.32 ; Watkins *et al.*, 1994, p.911-912.
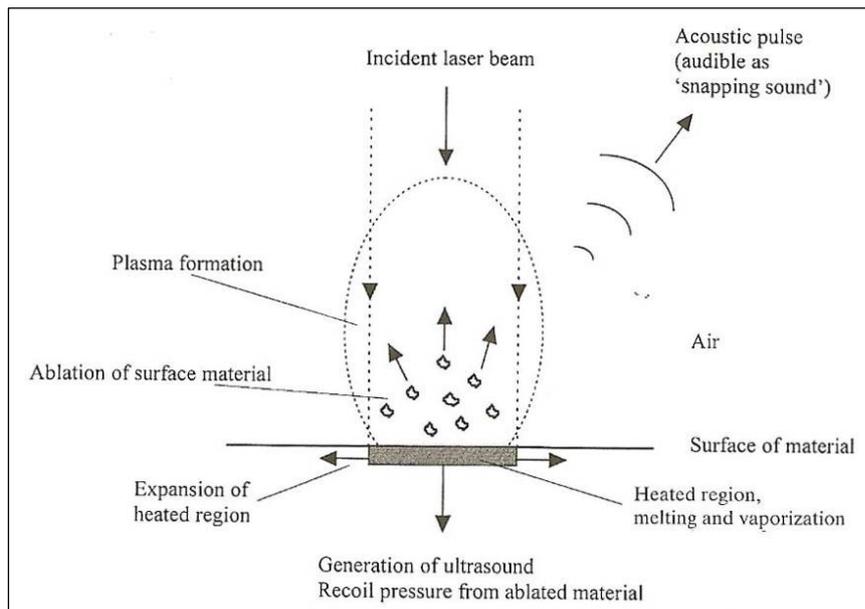
Figure 36 Schematic representation of the effects of absorption of a high power laser beam (From Cooper, 1998, p.47).

The type or combination of process induced in the laser cleaning of a surface depends on the incident fluence level, the type of contaminant, and the strength of its bonds with the substrate. According to this, laser cleaning should be carried out at the lowest possible fluence in order to minimize the risks of damaging the object.

In order to improve the cleaning efficiency without having to increase the fluence, a thin layer of water can be brushed onto the dirt crust just before laser irradiation. This technique is sometimes called *steam laser cleaning* (figure 37). Water is a liquid transparent to IR wavelengths. The water molecules cover the dirt particles and penetrate the cracks in the layer. Rapid heating of the dirt/water interface occurs which leads to explosive vaporisation of the water molecules. The resulting forces are sufficient to eject the particles from the surface.[171] This technique is used especially when the dirt is so strongly attached to the substrate that it cannot be cleaned with *dry laser cleaning*, or when the surface is so fragile that it has to be cleaned at very low fluence. In any case, the use of water has to be considered only if needed and must be avoided when dealing with water-sensitive materials.

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[171] Fernandes & Kane, 2006, p.31 ; Cooper & Larson, 1996, p.32.
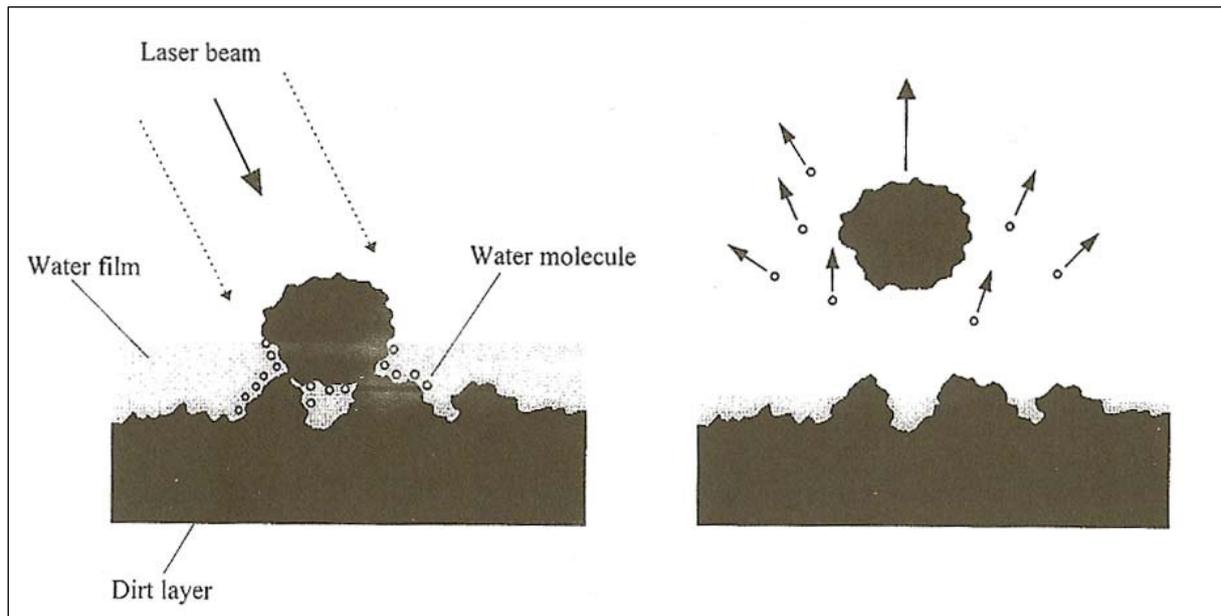
Figure 37 Schematic representation of steam laser cleaning (From Cooper, 1998, p.53).

5. Laser interactions with metal

While laser cleaning is now widely used on a large range of materials[172], its interactions with metals still have not received the same amount of attention[173], probably because of the complex nature of the corrosion products of metals. For example, copper and copper alloys, constituting outdoor sculpture as well as archaeological objects, show a layered corrosion system which is often very intricate and unevenly superposed, more or less thick depending on the zones. The original surface has often disappeared and has been replaced by corrosion products, making it difficult to distinguish. Furthermore, the difficulty lies in the fact that some corrosion products have to be preserved while others have to be removed.

Because of that surface complexity, laser cleaning of metals is not *self-limiting*.[174] Once the dirt / paint / corrosion layer is removed from the surface, any further pulse would induce further cleaning and so, modifications of the corrosion layer or of the metal structure. If cleaning is not carried out carefully, over-cleaning may occur, leading to the removal of corrosion layers that should have to be preserved. To minimise this effect, the properties of the laser as well as those of the material to be cleaned have to be considered carefully.

As was previously exposed, infrared laser radiation can be considered as a localised heat source. By fitting the appropriate laser parameters with the optical and thermal properties of a surface, the amount of heat can be controlled within *"time and space"*[175]. The temperature rise induced in a given material depends on the intensity of the laser beam, the wavelength, the pulse length, the absorptivity of the material and its thermal properties: thermal conductivity, specific heat capacity and density.[176]

5.1.   Temperature rise

It is of great importance to determine the maximum temperature rise induced by the laser on and just below the surface, both for cleaning control and optimization. A calculation can be done for that purpose. The example of copper is taken, because it was used in this research among others and mostly because it is a metal which physico-chemical values are well known, compared to brass and bronze. Furthermore, copper is the best thermal conductor after silver[177] and knowing that, this calculation with copper could help understanding better the surface transformations induced by laser cleaning.

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[172] Cooper, 1998, p.15-18.
[173] Cooper, 2002, p.34-38.
[174] Cooper, 2001, p.109-119.
[175] Cooper, 2002, p.35.
[176] Cooper, 2002, p.35. See Appendix 3 & 6.
[177] http://fr.wikipedia.org/wiki/Conductivit%C3%A9_thermique.

The temperature rise ΔT on a copper surface at time t, under a laser irradiation at 1064nm, with a pulse length of 10ns and a beam size of 0.28cm^2, can be calculated[178] with the following equation[179]:

$$\Delta T(t) = \frac{2AI}{K}\sqrt{\frac{Dt}{}}$$

Where   A = Absorption of the surface at a given wavelength[180] = 0.1-0.3 (without dimension)

K = Thermal conductivity = 4 $\left[W/cmK \right]$

c_p = Specific heat capacity (at 25°C) = 0.39 $\left[J/gK \right]$

ρ = Density = 8,94 $\left[g/cm^3 \right]$

I = Incident laser beam power density = $\left(\dfrac{\text{pulse energy}}{\text{pulse length} \cdot \text{beam size}} \right) \left[W/cm^2 \right]$ = 217;

303; 412 $\left[MW/cm^2 \right]$ for fluence respectively = 0.61; 0.85; 1.12 J/cm^2

D = Thermal diffusivity[181] = $\dfrac{K}{c_p \cdot \rho}$ $\left[cm^2/sec \right]$ = 1,14 $\left[cm^2/sec \right]$

t = Pulse length = 10ns = $10 \cdot 10^{-9}$sec

For a copper[182] sample laser cleaned under the exposed conditions, the calculated temperature rise ΔT at three different fluence levels (0.61, 0.85 and 1.12 J/cm^2) is:

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[178] This calculation is valid for the duration of one laser pulse.
[179] Cooper, 1998, p.43.
[180] Absorptivity of a material is comprised between 0 and 1, with 0 meaning no absorptivity and 1 complete absorptivity. For rough copper, A = 0.1-0.3 ; for polished copper, A = 0.04. The value for rough copper is considered here.
[181] Cooper, 1998, p.43: "Thermal diffusivity determines how rapidly a material will accept and conduct thermal energy".
[182] See Appendix 6.

	A = 0.1	A = 0.3
0.61 J/cm^2	**653 K** **380°C**	**1196 K** **923°C**
0.85 J/cm^2	**912 K** **639°C**	**2737 K** **2464°C**
1.12 J/cm^2	**1240 K** **967°C**	**3722 K** **3449°C**

Table 2 Temperature rise at the surface of copper, with a surface absorption of 0.1 and 0.3, after laser irradiation at 0.61, 0.85 and 1.12 J/cm^2, wavelength 1064nm and pulse length 10ns.

Even if the absorptivity of metals to laser light is usually low, the results of table 2 indicate that the absorptivity value of a material is fundamental, as the temperature rise of **rough** copper is largely increased depending if A = 0.1 or A = 0.3. Hence, for a given metal, these temperature rise values would vary depending on the surface preparation (polished, rough[183] or oxidized), on laser parameters such as wavelength, pulse length and beam size and on laser beam heterogeneities.[184]

Furthermore, this calculation is valuable only for the duration of one single pulse and some of those values are already above the melting point of copper, which is of 1084°C. The obtained results would also be different in the case of irradiated brass and bronze, but consulted reference tables did not give all the values necessary to perform the calculation.

5.2. *Heat diffusion length and optical penetration depth*

Two other very important calculations that help us understand the behaviour of copper under pulsed laser radiation are: [185]

- The *heat diffusion length* l_τ, which is constituted of the thermal diffusivity D $\left[cm^2/s \right]$ and

  the interaction time with the laser beam τ_l. l_τ can be obtained with the following equation:

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[183] Surface reflectivity is also an important parameter. Bare metal surfaces are highly reflective by definition and this allows the laser radiation to be mainly reflected from the surface. With an ideal highly polished metal surface, specular reflection of the laser beam would be mainly involved, while a matt or rough surface would mostly involve diffuse reflection. See Appendix 3 Optical interactions of light waves with material.
[184] Watkins *et al.*, 1994, p.913-914. See Appendix 1.
[185] Bäuerle, 2000, p.20-21.

$$2\sqrt{\tau_l \cdot D} \ = \ 2\,\mu m$$

Where $\qquad \tau_l$ = laser pulse duration = $10\,ns = 10 \cdot 10^{-9}\,s$

$$D \ = \ \text{Thermal diffusivity} \ = \ \frac{K}{c_p \cdot \rho} \ \left[\frac{cm^2}{sec} \right] \ = \ 1{,}14 \left[\frac{cm^2}{sec} \right]$$

- The *optical penetration depth* l_α, which is the depth to which photons penetrate a material, can be obtained with the following equation:

$$\alpha^{-1} \ = \ \frac{1}{\alpha} \ = \ \frac{1}{7{,}7} \ = \ 0{,}129\,\mu m$$

Where $\qquad \alpha$ = absorptivity = $7{,}7 \left[cm^{-1} \right]$ at λ = 1064 nm[186]

The thickness of the ablated layer per pulse depends on which one of these parameters is larger.[187] In the case of copper, the *heat diffusion length* l_τ is the largest. **This means that the depth of the thermal effect induced by a single laser pulse is 2 µm.**

Of course the optical and thermal characteristics of a solid also depend on its surface morphology, crystallinity (amorphous, crystalline), surface contaminants (oxide layers, pollutants), physical (cracks, flakes) and chemical (impurities, aggregates) defects.[188] The obtained results would also be different in the case of irradiated brass and bronze.

Moreover, thermal conductivity K, and then D, thermal diffusivity, as well as α, absorptivity, strongly depend on the ambient temperature. In the case of copper, the absorptivity of laser radiations at room temperature is quite low compared to other metals. It increases at higher temperatures but still being comparatively low.[189] Some absorptivity variations may also occur with copper alloys like brass and bronze.

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[186] Bäuerle, 2000, p.701.
[187] Bäuerle, 2000, p.221.
[188] Bäuerle, 2000, p.23.
[189] Amorosi, 2004, p.43-44. Stainless steel was used to compare copper absorptivity.

6. Laser cleaning of the copper alloy samples

6.1.   Samples preparation

Metallic plates were prepared in order to have a material available on which to test the laser cleaning effect. The choice of a new material, instead of an original one such as samples from copper roofing or a sculpture, offered a few advantages.

First, the samples could be chosen as similar as those constituting the two laser-cleaned monument of Queen Victoria and Lord Nelson. Mainly, this avoided taking any material from the original monuments. But as the discoloration of oxidized copper had been observed by conservators on those two sculptures after laser cleaning, finding similar alloys could induce more realistic results after the same treatment. Moreover, it was interesting to study the particular behaviour of the different copper alloys after laser irradiation.

Queen Victoria being made of copper and Lord Nelson of brass, industrial alloys have been chosen, the most similar possible to those of the sculptures. Unfortunately, it has been extremely difficult to find alloys of the same exact composition. As the quantities requested for this research were very tiny, it has not been possible to have it cast by a foundry for that precise purpose. Hence, industrial wrought brass and copper were selected[190]. Moreover, a bronze cast ingot from an English foundry[191] was used to complete the selection. This modern bronze is named *gunmetal*[192], which characteristic is the presence of some zinc in the copper-tin alloy. It was frequently used during the 19th and 20th centuries for maritime use and sculpture casting and hence, could bring complementary results.[193] In Appendix 5, the compositions of Queen Victoria and Lord Nelsons' Monuments are given, as well as the composition of the copper alloys used for the laser cleaning tests.

The second advantage of using new metal samples was the possibility they offered to create artificial corrosion layers. It could appear strange not to have chosen authentic pieces, with thick layers of corrosion products and natural concretions resulting from outdoor exposition. But the idea was to create individual and "pure" surface layers: non-corroded metal samples, cuprite (Cu_2O) and brochantite ($CuSO_4.3Cu(OH)_2$) layers of corrosion. Cuprite and brochantite are commonly found on copper alloys having been exposed outdoors for a few decades. These separately corroded samples would allow us to study the effects of laser cleaning on both corrosion products, independently from

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[190] From *Kaufmann & Fils SA*. For details, see Appendix 17.
[191] Castle Fine Arts Foundry. For details, see Appendix 17.
[192] Which is translated "*Bronze à canon*" in French.
[193] Selwyn, 2004, p.57 and 61-62.

one another and without the interferences brought by the usual pollutants coming from outdoor exposure, such as soot, salts, sand, organic deposits, grease, etc.

To form these artificial corrosion layers, traditional recipes were selected, used by artists, foundries or even conservators. The safest and more efficient recipes were tested on the metal plates. In the following lines, the patina recipes used to create artificial cuprite and brochantite are presented.

6.1.1. Artificial corrosion of the copper alloys samples

An extensive amount of large copper and brass plates (150x50x3mm) were available. But as the bronze ingot was small, only 9 small pieces could be cut (50x25x5mm approximately).

Once cut, the surface of the samples was prepared in order to make them more reactive and as such, more sensitive to the development of the artificial corrosion.

- On one side, the samples were manually abraded with sandpaper, working the surface in the direction of the length.

- On the other side, the samples were sandblasted with glass beads (pressure 2bar). After the formation of the patina on the plates, the sandblasted surfaces appeared less reactive than the ones stripped with sandpaper.

Then, the samples were cleaned during 4 minutes in an ultrasonic bath in order to remove all traces of abrasive material. They were rinsed with water, degreased with acetone and allowed to dry in air. After that, they were ready to be corroded. A few samples were maintained corrosion-free, in order to study the behaviour of raw metals exposed to laser irradiation.

Other techniques could have been used to reactivate the metal samples, which have been later kindly proposed by Mrs Lucy Branch, from Antique Bronze in London[194], specialized in artificial patination and foundry techniques for sculpture conservation purpose. One very common technique would be to apply oxalic acid on the metal surface, which is a good mordant agent, allowing to bound atoms very strongly between themselves and the metal substrate; another would be to abrade the surfaces with pumice powder, previously mixed with water to produce a coarse paste.

6.1.1.1. Artificial cuprite

After having carried out a few tests, part of the copper, brass and bronze samples were immerged in a copper nitrate hydrate solution in order to develop a cuprite layer. The recipe was proposed by

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[194] www.antiquebronze.co.uk

Cottam[195] and consisted in dissolving 5g of $Cu(NO_3)_2.xH_2O$ in 25ml of distilled water and then to bring the solution to boil. The samples have to stay in the boiling solution during 20 minutes. Then, they have to be rinsed first in hot water and then in distilled water.

The preliminary tests carried out on copper foil samples determined the duration of the immersion of 5 minutes instead of 20. After this shorter time, the desired even red cuprite layer formed on the surface, and after 20 minutes, a purple / greyish layer had appeared on the samples, probably due to the nitrate salts deposition.

Hence, the copper, brass and bronze samples were immerged under such conditions during 5 minutes. The oxide layer developed in 5 minutes on copper samples. But for brass and bronze, it appeared that this immersion time was too short for the layer to develop evenly. It could be explained by the increased resistance of copper to corrosion when alloyed to metals such as zinc and tin, becoming less reactive to oxidation than pure copper.[196] As a result, the time had to be extended to 30 minutes to obtain an even layer on brass and bronze. For every alloy, a second immersion was necessary to form a more regular layer on the surface: 5 minutes for copper, 30 minutes for brass and 15 minutes for bronze.

But even if the oxide layer formed was nicely even, the colour of the cuprite wasn't the one expected. Samples developed a purple / greyish oxide layer but not the expected red-brown. As cuprite is generally recognizable from its red-brown colour, this purple / greyish surface was unexpected. Moreover, the risk of getting some incorrect results after laser cleaning was increased, as the reaction of laser light depends on the colour (thus the wavelength) of the treated surface. A grey surface would not maybe react in the same way than a red surface under laser radiation.

In order to understand the apparition of that unexpected colour, the samples were observed under the optical microscope. Small white-bluish crystals were detectable, which could be explained by a deposition of nitrate crystals on the surface. As the solution in which samples were immersed was boiling, its concentration increased after a few minutes, leading to the saturation point. This led to the precipitation of nitrate crystals. The precipitate was clearly visible once the solution had turned cold.

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[195] Cottam, 1998, p.113. Another recipe is presented by Socha et al, 1980, but the chemicals used in the solution were highly toxic and thus, Cottam's recipe was chosen.
[196] Doktor & Mach, 2000, p.35.
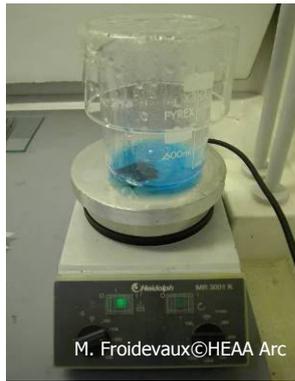
Figure 38 Copper samples boiling in copper nitrate solution.

Figure 39 Grey colour on a copper sample after 5 minutes immersion in copper nitrate solution.

A way to dissolve the nitrate crystals was to immerse the samples in stirred hot water, slightly acidified with nitric acid. A level of pH 3-4 was determined as the ideal pH, as no crystals were dissolved at pH 5 after 30 minutes and the oxide layer was badly attacked at pH 1-2 after only 2 minutes. Nevertheless, it was necessary to observe carefully the reaction of the sample in the acidified water and to remove it before it would attack the oxide layer. Then, they were rinsed in deionised water and left to dry in air.

The immersion time necessary to effectively remove crystals without attacking the oxide layer was 5-10 minutes for copper, about 20-25 minutes for brass and 5 minutes for bronze. After this treatment, all samples had recovered a reddish colour. Some crystals still remained but in a much more acceptable amount than previously.
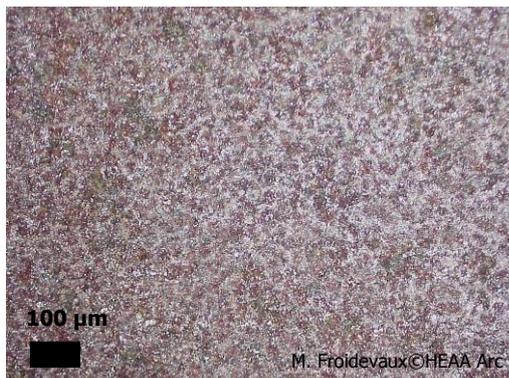
Figure 40 Visible crystals at the surface of a cuprite brass sample (100x magn.).
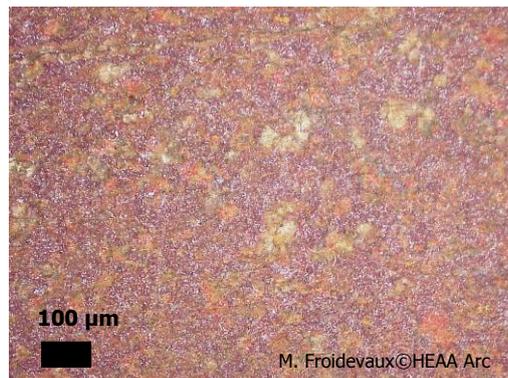
Figure 41 A cuprite brass sample after dissolution of part of the crystals (100x magn.).

Figure 42 - 43 -44 Final results for copper (left), brass (centre) and bronze (right).

Finally, a laser cleaning test was carried out with a Nd:YAG Q-Switched laser (for details see 6.2 - wavelength 1064 nm; pulse duration 10ns; repetition rate 0.63 Hz, fluence 0.8 J/cm^2), in order to determine if the artificial surface would react as natural cuprite would, hence showing a colour change. The result was positive as the laser irradiated surface appeared clearly grey, similarly to the discoloration process happening on real cuprite.

Figure 45 Laser cleaning test on a cuprite copper sample at low fluence (0.44J/cm^2).

6.1.1.2. *Artificial brochantite*

The growth of artificial brochantite (copper sulphate $Cu_4(OH)_6SO_4$) on the metal samples has been tested trying various methods. Unfortunately, the right way to achieve it was discovered too late during the course of this study and therefore there was not enough time to carry out the laser tests and various analyses on the brochantite surfaces. The different trials are exposed in the following lines.

A few recipes do exist, which were used to create the green corrosion product. But as artificial patination was mostly used for aesthetic purposes, artists, craftsmen or even conservators[197] often

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[197] Ashurst & Ashurst, 1988. The produced green corrosion layer appears to be copper chlorides instead of copper sulphates.

have not tried to determine with precision the exact nature of the green corrosion product that was produced. Furthermore, artificial brochantite is not commonly formed artificially as it seems to be difficult to create. Scott[198] proposes a wide range of green patina recipes, but none seems to produce exactly brochantite.

The more successful way of getting it would have been to expose the samples to high SO_2-bearing atmospheres, for example in hermetic climatic chambers[199]. As we know, SO_2 is the atmospheric pollutant responsible for the development of natural brochantite after long years of outdoor exposure. A dry-wet cyclic exposition of the metal plates to such an atmosphere would certainly have been successful to get the desired brochantite. Unfortunately, the lack of laser facilities in the Swiss and English museums, as well as the heavy costs of private companies owning such equipment have not allowed us to experiment this method.

Therefore, the creation of artificial brochantite had to be carried out through another method, like immersion into chemical solutions.

The most promising method[200] was proposed by Hayez et al.[201] and was successfully tested by other researchers[202]. The green surface obtained was analysed with scientific tools such as X-Ray Photoelectron Spectroscopy (XPS) and Synchrotron X-Ray Diffraction (SR-XRD). The presence of brochantite was identified, as well as some underlying cuprite[203]. The method consists of immersing the samples during three weeks at room temperature in a solution of 6g $KClO_3$, 3g $CuSO_4.5H_2O$ and 4g $Na_2SO_4.10H_2O$ in 1L of deionised water adjusted to pH 3 with H_2SO_4. The metal plates were sorted by type of alloy (copper, brass and bronze) and vertically immersed in this solution during the three weeks time. Unfortunately, the brochantite layer did not develop successfully.

- Compared to brass and bronze samples, copper plates appeared to be more reactive, as a green and relatively uniform product formed on the lower part of the plate. The upper part was only covered with red cuprite. This difference in colour is certainly due to a difference in the salt concentration inside the bath, which led the metal to react differently. This could maybe have been avoided by stirring the solution, but it was not possible to insert a stirrer in the bath as there were too many samples and they wouldn't have remained in position.

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[198] Scott, 2002, p.404-417.
[199] Schlesinger *et al.*, 2000 ; Squarcialupi *et al.*, 1998, p.271-274 ; Hayez *et al.*, 2004, p.876.
[200] Another method was tried by Von Denk & Leschhorn, 1965, p.58-65. The synthesis of brochantite based on the reaction between of copper sulphate ($CUSO_4$) and copper hydroxide ($3Cu(OH)_2$) seemed successful, but only powder was produced. This method could have been interesting but it had to be tested because the brochantite produced was not adhering to copper. Unfortunately, the lack of time during this study has not allowed this method to be experimented.
[201] Hayez *et al.*, 2005.
[202] Leyssens, 2006 (see Chapter Brochantite).
[203] Hayez *et al.*, 2005 ; Leyssens, 2006 (see Chapter Brochantite).

- The brass and bronze plates showed an equal low reactivity with the solution. Some cuprite had punctually developed on a few samples but not on others. Small brochantite crystals had formed on the surface but they were powdery and absolutely non-adherent, as they could be easily removed with the fingers. Furthermore, the brochantite crystals weren't covering the metal at all.

Obviously, the brochantite crystals formed during the three weeks immersion were not adherent, covering and uniform enough to be suitable for laser cleaning tests.

M. Froidevaux©HEAA Arc

5 cm
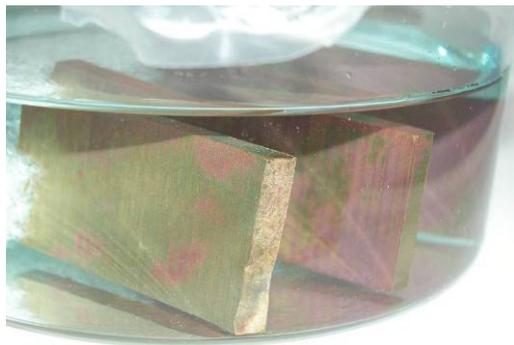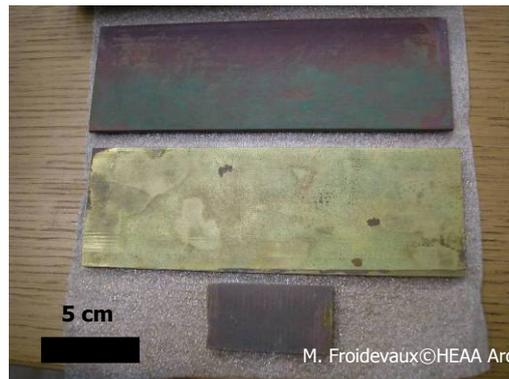
M. Froidevaux©HEAA Arc

Figure 46 Bronze plates after the first two weeks in brochantite solution.

Figure 47 From top to down: Copper, Brass and Bronze after a 3 weeks immersion in the $KClO_3$, $CuSO_4.5H_2O$ and $Na_2SO_4.10H_2O$ solution.

After that, another attempt was made by immersing only one sample per bath, as was later suggested by Valerie Hayez, who noticed that several samples in one solution lead to some difficulties for the brochantite to be formed. Hemming[204] reports a similar method and notices that a higher temperature of the solution will decrease the immersion time and increase the development of brochantite. Knowing that, the second attempt was performed immersing only one metal samples in the same solution and heating it up to 70°C on a hot plate. A few brochantite crystals initially developed more rapidly than the first time, but after a few days the process seemed to slow down. The surface appeared whitish and the crystals were not more adhering than in the first tests.

A last attempt was carried out by immersing the isolated samples in the same solution and heating it in the oven at 60°C. This method appeared successful on copper and bronze, as a nice adherent layer of bright brochantite had formed on the samples after only ten days (figures 48-51). [205] It must have been the constant and uniform heat that allowed the corrosion product to grow.

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[204] Hemming, 1977, p.95.

[205] Some cuprite was visible under the brochantite layer, as it seems that $KClO_3$ reacts at first with copper to form a cuprite layer, on which does the brochantite grow (Hemming, 1977, p.95). This affirmation seems to be confirmed as after the first immersion, some of the non-reacted samples showed some cuprite development prior to the brochantite formation. It would be interesting to confirm if the underlying red oxide is covering the entire
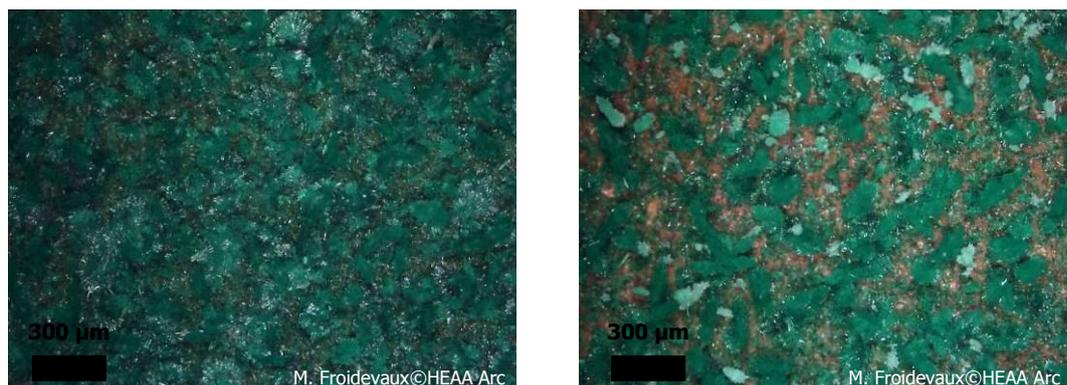
Figure 48 - 49 Microphotographs of artificially grown brochantite on bronze (left) and on copper (right) (50x magn.).
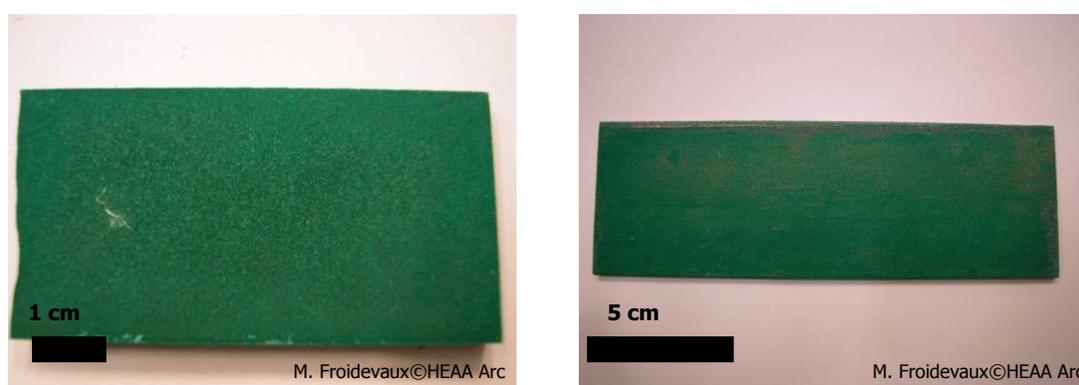
Figure 50 - 51 Brochantite formed on bronze (left) and copper (right).

The development of brochantite on brass was less effective than on copper and bronze. An inhomogeneous green product formed after 25 days in the same conditions, but the green layer was powdery, poorly adhering to the surface and could easily be removed with the fingers. The crystals had not grown as well as on copper and bronze. A cuprite layer was visible under the green product.

Unfortunately, this successful result on copper and bronze took place only after a few months, when not enough time remained to carry out new laser cleaning tests and further analysis. Moreover, the poor results obtained with the previous immersion methods were not suitable for laser tests. The scarce and low-adherent crystals under laser radiation would not have given any realistic results and were not thick enough for scientific characterization.

For all those reasons, the created brochantite samples were left on the side and the focus was put on the bare metal and cuprite samples, as the discoloration effect noticed after laser cleaning appeared only on surfaces covered with cuprite.

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surface. If it is the case, this could be problematic when identifying false objects because this recipe for artificial brochantite mimics the natural grow of a corroded layer (the oxide layer covering the bare metal and the brochantite on the oxide). But because of the limited time, this study cannot take place within that work.

6.2.   Laser settings

The bare metal and the cuprite samples were exposed to laser radiation in order to observe and analyse the behaviour of each metal (copper, brass or bronze, with and without oxide layer) before and after exposure to three different fluence levels.

The laser-cleaning system used was a pulsed Nd:YAG *Phoenix®2(+)* manufactured by Lynton Lasers, operating in **Q-Switched mode** and providing a wavelength of **1064 nm** (near infrared region of the spectrum). The pulse length was **10 ns** at the lowest repetition rate of **0.63 Hz**[206]. Energy levels could be increased or decreased in steps from **100 to 440mJ**. The beam was delivered through an articulated arm at the end of which is a pen-like handpiece. The arm is constituted of mirrors mounted in the movable arm with 7 flexible joints and a focusing lens at the extremity of the arm (20cm Focal Length, 25mm diameter).

The handpiece was removed in order to keep only the lens end. The articulated arm was fixed vertically using a clamp-stand. The distance from the laser output to the surface to be cleaned was 42cm.

Figure 52 *Phoenix®2(+)* system by Lynton Lasers (left).

Figure 53 Laser output vertically fixed with clamps for laser cleaning of metal samples (middle) ; handpiece has been removed.
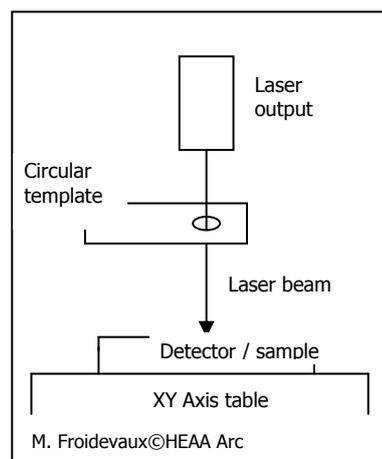
Figure 54 Schematic representation of the laser cleaning system (right).

The fluence levels values were proposed by Mrs Samantha Sportun, head of Sculpture Department, in order to match with the usual levels used by the conservators at NCC for laser-cleaning of copper alloy sculpture. The fluence levels were chosen in order to see the effects of laser cleaning on the widest range of values: **0.61, 0.85 and 1.12 J/cm^2.**

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[206] The maximum repetition rate on that system is 10 Hz.

To measure the beam area, the laser beam was targeted on photographic paper through a perfectly circular template. The same distance was kept each time (42cm), in order to always have the same beam area. First, the beam diameter was measured with the white mark left on the burnt paper. The spot diameter was 6mm and after that, it was easy to calculate the beam area following the equation:

$$\text{Area} = \pi r^2 = \mathbf{0.28\ cm^2}$$

Then, the average energy per pulse was measured with an instrument called an *energymeter*. A single pulse was fired through the same circular template, hitting a detector which gives the exact energy per pulse in mJ. This operation was repeated 10 times in order to get a mean value. It is important to note that the distance between the laser output and the detector should be the same than while firing the samples ; otherwise the fluence level would change.

Figure 55 (left) Energymeter and detector.

Figure 56 (right) Template positioned on the detector for energy measurements.

It has to be noticed that such fluence calculations are only estimates:

- First, the Nd:YAG laser delivers a beam which is not homogeneous[207] and presents more or less intense areas, like hot spots in the beam. This can easily be seen on burnt paper and means that the energy, and thus the fluence, is not equally distributed everywhere on the laser spot.[208]

- Second, the spot size measurement has been estimated with a conventional ruler, which obviously is not more precise than on the millimetre range (error ±10%).

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[207] See Appendix 1.
[208] See Appendix 1.

- Third, energy is measured via mean values. Each pulse can be slightly different from the others even if the working distance and the energy level on the machine are kept unchanged. This can be due to the beam interaction with air particles or to variations in the laser rod itself, which is in use since a few years and could have suffered from slight damage due to heat (error ±5%).

6.2.1. XY-axis table technique

The laser cleaning system was combined to a computer controlled ISEL XY table, using an ISEL C116-4 step motor controller[209]. This cleaning method was very convenient because it allowed obtaining a very evenly and regularly cleaned surface, with each point being fired by an identical number of pulse, beam size and fluence level. It was designed to reflect practical laser cleaning, in a systematic way, whilst being repeatable under laboratory conditions.

This method is different from laser cleaning on artworks in that each parameter has to be the same for every sample. In the reality, conservators have to use their sensitivity and skill while working on real objects, playing with the working distance and thus, adapting the fluence level to the surface quality of the artwork. But within the frame of this study, the most important was to have a very systematic and regular cleaning in order to get comparable results after observation and analysis of the laser-cleaned samples.

The metal samples were placed on the table which moved during the cleaning process of 2 mm/step, at speed of 1 mm/sec, pausing after each step with 1 laser pulse/step. These settings were determined in order to have a more even, regular laser-cleaned area. The laser beam was fired on the surface from the bottom left of a predetermined area and stopped at the top right (figure 57), regarding the movement of the XY axis table (figure 58). The final irradiated area was 25 x 25mm for the copper and brass samples and 20 x 20mm for the bronze samples, which were smaller.

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[209] See Appendix 17.
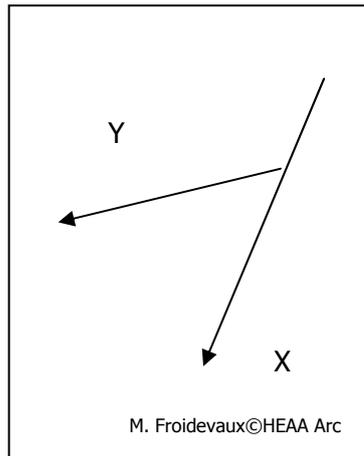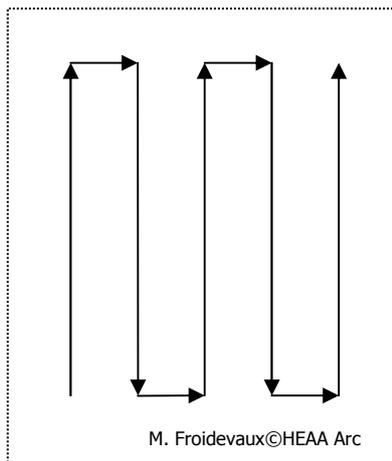
Figure 57 (left) Schematic representation of the beam movement provided by the XY axis table.

Figure 58 (right) schematic representation of the movement of the XY axis table.

6.2.2.   Number of pulses per unit area calculation

In order to determine how many pulses were fired on the surface of the samples during cleaning on the xy-axis table, the number of pulses n per unit area $\left(A_t / A_b \right)$ was calculated as follows:

$$n \cdot \frac{1}{2} \left(A_t \cdot A_b \right)$$

Where n = Repetition Rate · Irradiation time for the total area (25x25cm) = 0.63 HZ · 437 sec.

A_t = Area of the total irradiated surface = 6.25 cm^2

A_b = Beam area = 0.28 cm^2

$$n \cdot \frac{1}{2} \left(A_t \cdot A_b \right) \cong 12 \, \text{Pulses/Unit area}$$

6.3.   *Laser-cleaned samples: some remarks*

Copper, brass and bronze plates, both corrosion-free and with artificial cuprite layer, were laser-cleaned using the system described above. Three fluence levels were used: 0.61, 0.85 and 1.12 J/cm^2.

As slight variations in the energy contained in the laser beam were noticed when measuring with the energymeter, the fluence level had to be measured before cleaning each sample in order to be sure to

have always the same fluence. Sometimes the energy level had to be increased or decreased on the laser system to keep it right.

It is also important to note that, with the XY-axis table technique, the boundaries of a laser-cleaned area receive less pulse than the centre of the area. As the laser goes firing, obviously the external zones are not covered by the same number of pulses than in the middle (12 pulses as it was previously measured). On the cuprite samples for example, this can be seen as a dark grey or a yellow line all around the square area.

Therefore, the boundaries are not representative and thus cannot be taken into account for the analysis of the effect of laser radiation on the samples.

Part III : Characterization of laser radiation interactions with copper alloys

7. Surface analyses

This chapter presents all the results of the analytical methods which were used within the frame of this project to attempt characterizing the discoloration of the samples covered with cuprite (Cu_2O). The optical means included naked eye observations, optical microscopy and visible spectrophotometry. Chemical analyses included XRD, SEM, EDS and XPS techniques. The different objectives were to:

1. Characterize the discoloration of various metal surfaces (copper, brass and bronze) covered with cuprite under laser radiation, by observing their behaviour under various laser cleaning conditions (various fluence levels). The idea was to observe if each alloy behaves in the same way under laser irradiation and if they discolour to the same extent (*OM, spectrophotometry*).

2. Establish the effect of laser radiations on the bare metal surface and on the samples covered with artificial cuprite (Cu_2O). Verify if the surface is chemically, physically or optically modified and if the oxide layer has been totally or partially affected by the discoloration.

   • Chemical changes may include changes in the composition of the cuprite layer (modification of the bonding structure), as the exposure to large quantities of laser energy could eventually cause a rearrangement of the atoms (*EDS*). It may also modify the crystalline structure into an amorphous body (*XRD*); chemical changes could also include formation of new products, like for example tenorite, a grey-black and very stable copper oxide forming at high temperatures.

   • Physical changes (*SEM*) may appear as a modification in the metal phases; traces of melting on the cuprite or / and bare metal surfaces, as Nd:YAG radiations produce high levels of heat and may overpass the melting point of cuprite and copper and its alloys. Melting does not induce a chemical change, as similar atomic structure and bonds may still be present in the melted material.

   • Optical change may be due to a topographical modification of the surface covered with cuprite, which may reflect light differently than an identical non laser cleaned surface (*SEM, spectrometry*). Such a change could mean that only some wavelengths of light are reflected back and as such, the perception of the surface colour would be modified.

3. Identify an eventual effect of laser radiation on the underlying metal (*OM, SEM*).

4. Determine an eventual reversibility effect of the discoloured layer with time (*spectrophotometry*).

5. Evaluate the amount of ablated material after laser cleaning at various fluence levels (*OM, SEM*).

7.1.   *Optical analyses*

Optical analysis is usually the first step to observe a surface and become more familiar with it. It generally allows finding out which further analytical methods would be more suitable. Naked eye observations followed by optical microscope analysis were done to observe the bare metal and the cuprite surfaces, as well as cross-sections. Spectrophotometric measurements were also done to characterize the discoloration extent and an eventual reversibility process.

7.1.1.   Naked eye observations

Naked eye observation was the first type of analysis carried out, because it is the most readily and quickest method available. It sometimes allows the observer to evidence details that would not be seen under higher magnification and to get familiar with the surface of the objects, in order to point out wat has to be studied with further analytical methods. Bare metal samples as well as those covered with artificial cuprite have been studied after having been laser cleaned.

7.1.1.1.   *Bare metal samples*

The bare metal samples showed differentiated results, depending on the alloy:

- Bare copper and bronze samples showed very little reactivity under laser radiation (figures 59 and 60). No marks due to laser were visible at the lowest fluence and only very slight marks of laser cleaning became visible at the medium fluence. Tiny dark marks on copper and white marks on bronze appeared at the highest fluence, were the energy contained in the laser pulse was more intense. Such a low reactivity may be due to the high reflectivity of these alloys which only absorb a very small amount of the laser light and mainly reflect it. Even though the surfaces were not highly polished, as they had previously been abraded with abrasive paper, they were less reactive than brass.

- The reaction of brass (figure 61) under laser radiation was much more pronounced, with clearly visible marks left by the laser beam at each fluence level. This may be explained by the lower reflectivity of brass compared to copper and bronze. The beam track and the boundaries of the irradiated zone were easily detectable at all fluence levels. At the highest fluence, the laser spots appeared lighter where the beam was more energetic and brown

where it was less energetic. Variations in the beam itself are due to a heterogeneous distribution of the energy inside the beam and depend on the laser system.[210]

Figure 59 - 60 - 61 Laser cleaned bare copper (left), bronze (centre) and brass (right) at increasing fluence levels. Copper and bronze definitely show less reactivity under laser radiation than brass, which clearly shows extensive marks left by the laser beam.

7.1.1.2. Cuprite samples

All cuprite samples showed a high reactivity under laser irradiation, as the surface turned from a red / brown to a blue / purple colour at all fluence levels. The discoloration effect was more or less pronounced depending on the type of alloy.

- Copper (figures 62-63) was the metal showing the strongest discoloration, as the appearance of the red cuprite turned completely grey and shiny. The grey surface appeared lighter and shinier with increasing fluence. The beam spots were precisely marked with increasing fluence.
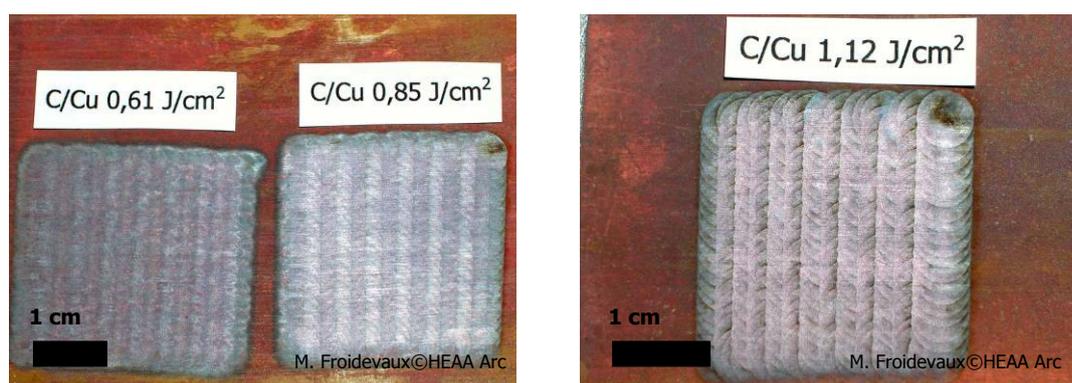
Figure 62 - 63 Photos of laser cleaned cuprite on copper at each fluence levels 0.61 and 0.85 J/cm^2 (left) and 1.12 J/cm^2 (right), showing copper turning to a greyish colour.

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[210] See Appendix 1.

- Brass (figures 64-65) showed a slight discoloration at the lowest fluence, with the red copper oxide turning to a grey / purple tinge and the surface turning slightly shiny. Bright blue marks appeared at the medium fluence, looking like burnt metal (figure 64, right). At the highest fluence level, the bright blue spots turned to a dark purple-brown colour. The laser spots were clearly detectable and the surface became more matte with increasing fluence. At all fluence, some yellow metal was apparent at the boundaries of the irradiated zone.
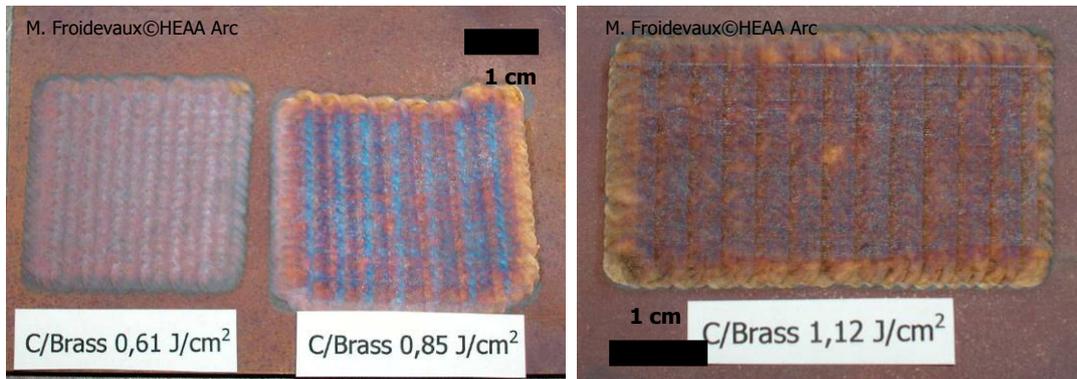
Figure 64 - 65 Photos of laser cleaned cuprite on brass at each fluence levels 0.61 and 0.85 J/cm^2 (left) and 1.12 J/cm^2 (right). Cuprite turned grey at the lowest fluence while blue spots appeared at the medium fluence, which turned purple-brown at the highest.

- Bronze was the alloy showing the less extensive discoloration of the surface, keeping a reddish colour. The colour didn't seem to change with increasing fluence (figures 66-67-68), like if no longer material was removed above the lowest fluence (0.61 J/cm^2). The surface turned shinier at each fluence level. Yellow metal areas were apparent at all fluence at the boundaries of the irradiated zone.

Figure 66 - 67 - 68 Photos of laser cleaned cuprite on bronze at each fluence level 0.61 (left) and 0.85 J/cm^2 (centre) and 1.12 J/cm^2 (right), showing a very low discoloration level to grey.

7.1.2.   Optical microscopy

Optical microscopy is a complementary tool which allows seeing details at higher magnifications, which could not be detected with the naked eye. There were two microscopes available at the

National Conservation Centre, a LEICA LEITZ®DMR, allowing magnifications of 50x, 100x, 200x and 500x, which was used for the observation of all the bare metal and cuprite samples. A smaller microscope from Optivision Ltd., allowing a lower magnification from 7x to 45x and combined with a SCHOTT® KL1500 LCD fibre optic light was used for the "spot by spot" observation of the samples (see 7.1.2.4). It was used at 15x magnification to allow the complete laser spot to fit in the picture. All the microphotographs were taken with a JVC KY-F®1030 camera. A microscope LEICA® for metallography was used by Dr. Peter Northover from Department of Materials of the University of Oxford (UK) for the study of the cuprite cross-sections.

7.1.2.1.   Bare metal samples

Copper and brass samples before laser cleaning showed flat surfaces with longitudinal streaks due to the abrasion with sandpaper. The bronze surface appeared like bubbled, which was due to the previous sand-blasting treatment.[211]

All bare metal samples showed a slightly grainy aspect under the optical microscope, which might be due to a surface change after exposure to laser radiation. This grainy texture appeared more uniform with increasing fluence, which could mean that stronger interactions between metal and laser occurred at higher fluence levels. This grainy aspect was the only microscopically detectable change on copper and bronze (figures 69-70). Further investigations with help of the SEM revealed that they were microscopic traces of melting (see chapter 7.2.1).
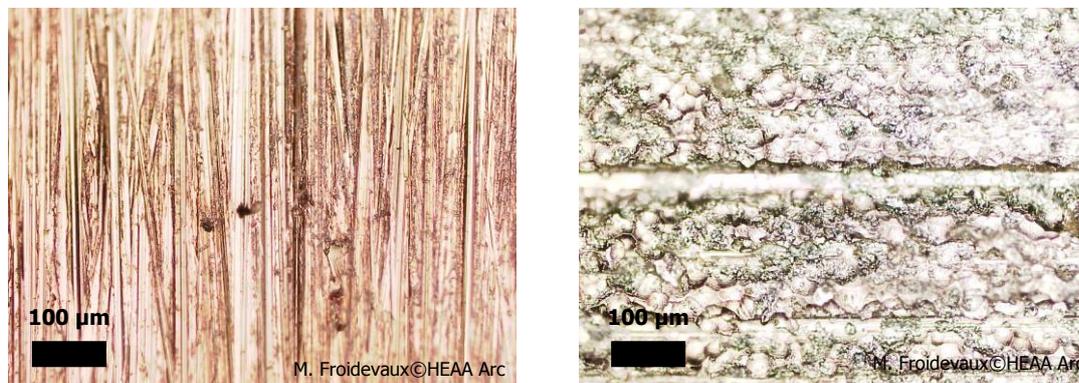
Figure 69 - 70 Microphotographs (200x magn.) of laser cleaned (highest fluence 1.12 J/cm^2) bare copper (left) and bronze (right). These two metals only show a slightly grainy aspect due to laser irradiation.

As already observed with the naked eye (see 7.1.1.1), brass reacted more strongly under laser radiation compared to copper and bronze. The surface showed light and dark areas (figures 71-72) depending on the intensity variations inside the laser beam.[212] The lighter areas were produced by a

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[211] See the un-cleaned samples in Appendix 8.1.
[212] See Appendix 1.

higher intensity in the laser beam; the darker areas by a lower intensity. Brass showed the same grainy aspect as found on copper and bronze at all fluence levels.
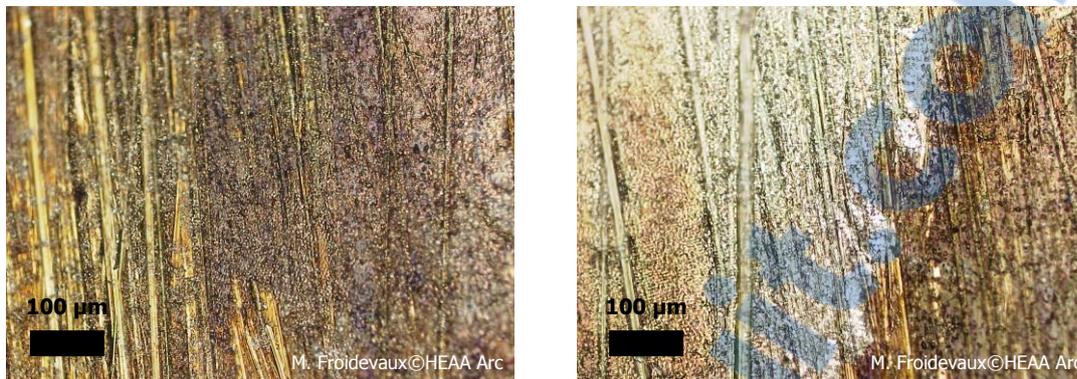
Figure 71 - 72 Microphotographs (200x magn.) of a laser cleaned (highest fluence 1.12 J/cm^2) bare brass sample, showing a grainy surface aspect. Figure 71 shows the darker area, induced by a less energetic part of the laser beam. On figure 72, the boundary of the laser beam spot is clearly visible : the white grainy area indicates where the beam is more energetic.

7.1.2.2.   Cuprite samples

Initially, the cuprite samples before laser cleaning showed a red-brown colour, with a few small nitrate crystals remaining from the artificial patination process.[213] Some yellow metallic spots were apparent on brass and bronze samples, maybe due to the partial dissolution of the oxide layer by the nitric acid used to remove nitrate crystals from the surface.[214]

After laser cleaning, optical microscopy revealed a shiny grey aspect visible on all laser cleaned cuprite samples, at each fluence level.

- Artificial cuprite on copper samples (figure 73-74) showed the most extensive surface discoloration, increasing with fluence and becoming shinier. Increasing fluence also produced visible marks of the laser beam due to the variations in intensity inside the beam itself.

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[213] See Chapter 6.1.1.1.
[214] See the un-cleaned samples in Appendix 8.2.
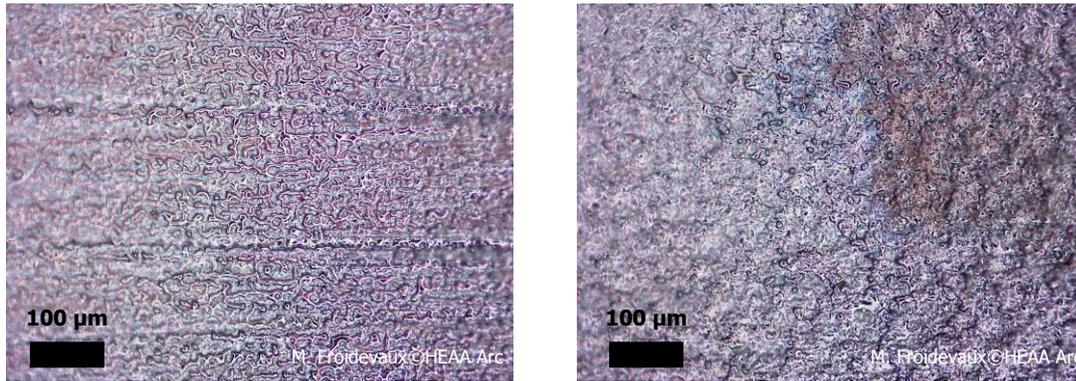
Figure 73 - 74 Microphotographs (200x magn.) of laser cleaned copper surface, at the lowest fluence (0.61 J/cm^2) and at the highest fluence (1.12 J/cm^2). An extensively grey surface is visible, which does not seem to be removed with increasing fluence.

- Cuprite on brass (figures 75-76-77) showed grey areas mixed with exposed metal, visible as small yellow stains. Such metallic zones were already present before laser cleaning, but newly exposed metal was visible after laser cleaning at the boundaries of the laser irradiated zone.[215] Blue areas, similar to burnt spots, appeared at the medium fluence (figure 76) and turned brown at the highest (figure 77). The grey areas seemed to be partially removed with increasing fluence.
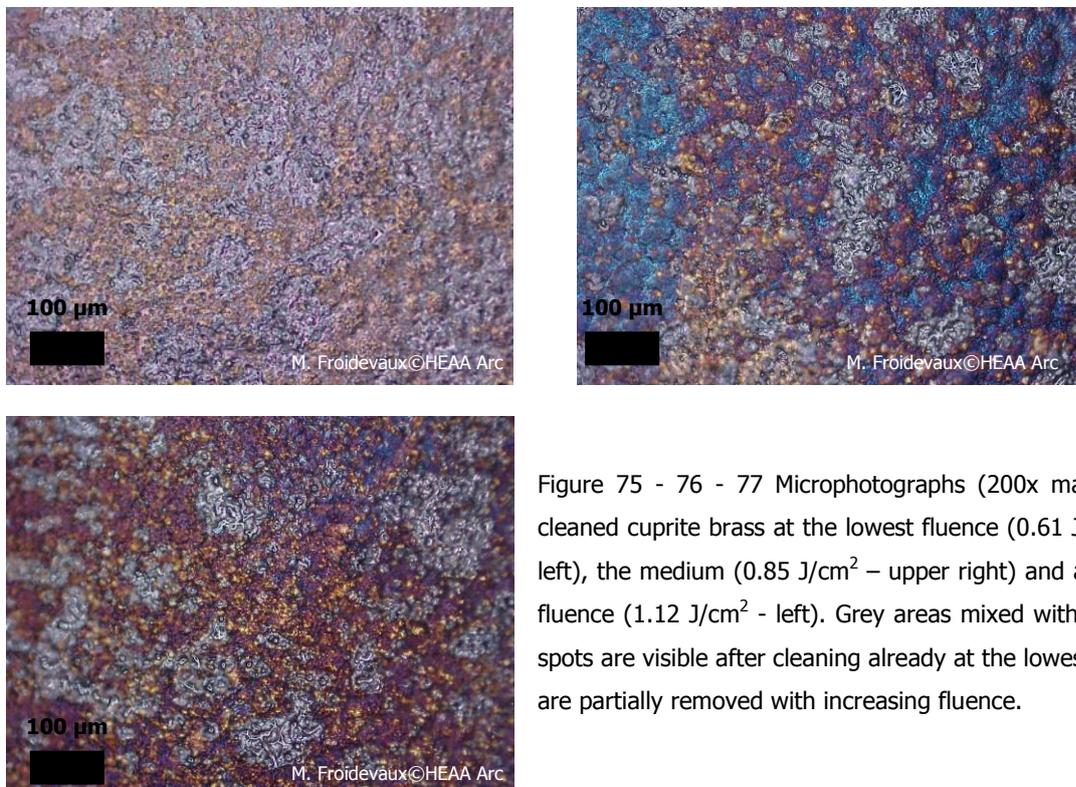
Figure 75 - 76 - 77 Microphotographs (200x magn.) of laser cleaned cuprite brass at the lowest fluence (0.61 J/cm^2 – upper left), the medium (0.85 J/cm^2 – upper right) and at the highest fluence (1.12 J/cm^2 - left). Grey areas mixed with yellow metal spots are visible after cleaning already at the lowest fluence and are partially removed with increasing fluence.

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[215] See Appendix 8.2.

- Despite being the less extensively discoloured metal, cuprite on bronze samples (figures 78-79) showed some grey areas, partially removed with increasing fluence, mixed with red and yellow areas (probably some exposed metal). Metallic areas were already present before laser cleaning, but newly exposed metal was visible after laser cleaning at the boundaries of the irradiated zone.
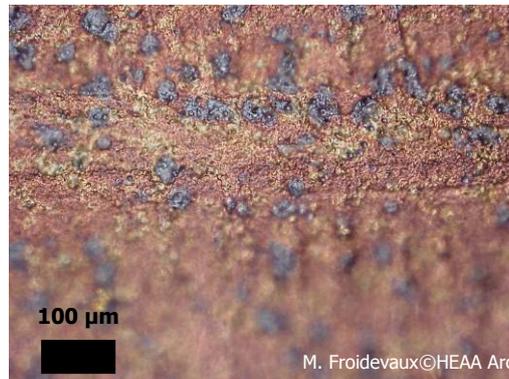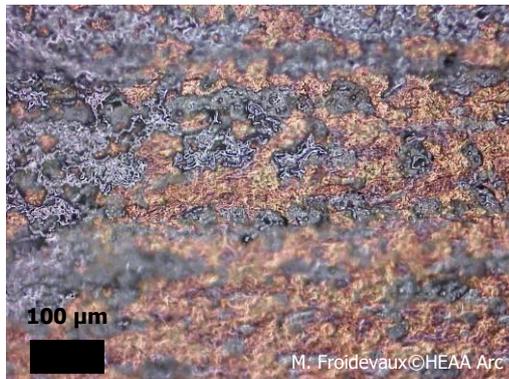
Figure 78 - 79 Microphotographs (200x magn.) of laser cleaned cuprite bronze at the lowest fluence (0.61 J/cm^2 - left) and at the highest fluence (1.12 J/cm^2 - right). Grey spots are visible, mixed with red and yellow areas (probably metal), and are partially removed with increasing fluence.

7.1.2.2.1. Results

Laser interactions with a cuprite surface are much stronger than with a bare metal surface. This can be explained by the fact that the higher reflectivity of metals prevents most of the laser beam to penetrate inside the material and a large part of the beam is reflected back. Although some melting occurs, surface modifications on bare metal are minimal. But sample surfaces behave differently when covered with cuprite.

The grey areas revealed on artificially oxidized samples under optical microscope seem definitely to result from laser / oxide / metal interactions, as no such discoloration appears on bare metal samples. The oxidized metal surface also behave differently depending on the type of alloy :

- On copper, the grey areas are perfectly uniform and are not removed with increasing fluence. No metal is revealed at the beam boundaries.

- On brass and bronze, the grey areas are removed with increasing fluence while some of the underlying metal is revealed at the beam boundaries.

This difference could be the result of a lower adherence of the artificial cuprite layer on brass and bronze compared to copper. That may be explained partly because Cu_2O could be more strongly bound to a pure copper structure than to its alloying elements, and partly because it seems that pure copper forms oxides very easily when heated. Unfortunately, no sufficient time was available during
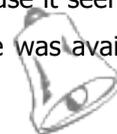
this research to determine exactly why the alloys behave so differently. The important point to keep in mind is that each metal may behave in a different way and, therefore, previous tests and metal analysis could be of great help before laser cleaning a copper alloy artwork, in order to identify the alloy and attempt predicting how the surface would behave. It could also be interesting to compare laser cleaning tests on the three alloys after exposure to atmospheric corrosion in real conditions.

7.1.2.3.   *Cuprite cross-sections*

Metal cross-sections of the cuprite samples were cut in order to try measuring the thickness of the cuprite layer and the amount of material ablated by laser cleaning. Unfortunately the microscope LEICA LEITZ®DMR, available at the National Conservation Centre, did not allow a magnification high enough to detect the cuprite layer on the sample surface. Such observations were carried out later by Dr. Peter Northover from the Department of Materials of the University of Oxford (UK) with a more powerful LEICA® microscope used for metallography, allowing a higher magnification (>1000x).

The samples used for these cross-sections were : 1 cuprite-copper sample before laser cleaning, 1 cuprite-brass sample before laser cleaning, 1 cuprite-brass sample before laser cleaning with copper nitrate crystals (coming from the artificial patination solution) and 1 cuprite-copper sample laser cleaned at 0.85 J/cm^2. The samples were mounted in an epoxy resin and then polished with a grinder.

These observations first helped to identify the exact nature of the oxide layer. As chemicals are often unpredictable, the artificial recipe used to form cuprite could have produced a different compound and it seemed necessary to assess its nature before going on with chemical analysis. Examination of crystalline corrosion products under high magnification is often the first step to establish their identity. Under bright-field reflected light microscopy, most corrosion products appear grey, while examination under polarized reflected light often reveals the real colour of the corrosion products.[216] For Dr. Peter Northover from the Department of Materials of the University of Oxford (UK), the red crystals visible under polarised light were undoubtedly the expected copper oxide, Cu_2O. This initial affirmation was later confirmed with the help of chemical analyses (XRD, XPS).

Under high magnification (1000x), the oxide layer was clearly visible. Polarized reflected light was used as it allowed a clear detection of the red cuprite crystals. Figure 80 (copper) and figure 81 (brass) show the red oxide layer, although not very uniform with more or less thick areas of approximately 1-2 and 4-5 µm (1 µm = 0,001 mm) and with metal coming through at some places. Such an irregular surface was obtained after dissolving the nitrate crystals formed on the copper oxide surface after the artificial patination process. The nitrate crystals gave to cuprite a grey colour which

[216] Scott, 2002, p.78.

disappeared after dissolving the crystals in a warm solution slightly acidified with nitric acid, but which also slightly attacked the copper oxide layer and exposed some metal.[217]

By comparison, a sample still covered with nitrate crystals was observed and showed a very even and uniform surface (figure 82). This proves that the nitric acid used to remove the crystals did slightly attack the oxide surface.
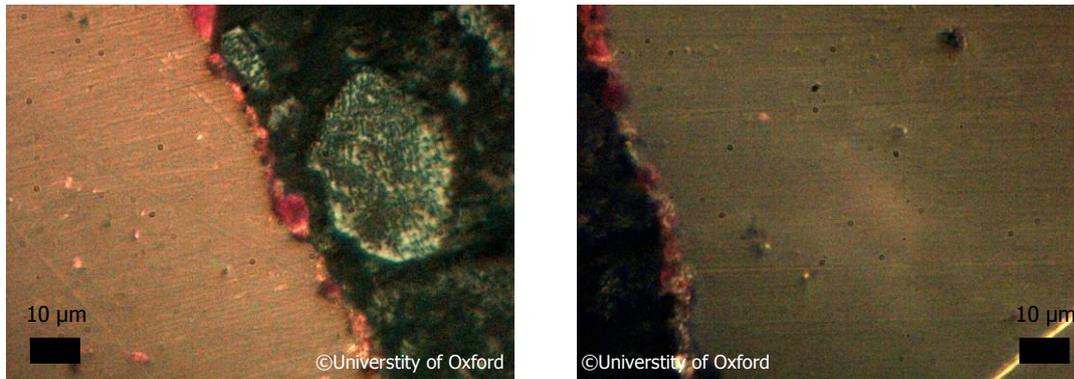
Figure 80 - 81 Polarized light microscopy (1000x magn.) of cross-sections of copper (left) and brass (right) samples showing an irregular and coarse cuprite layer. The black area represents the mounting resin and the reddish surface the metal.
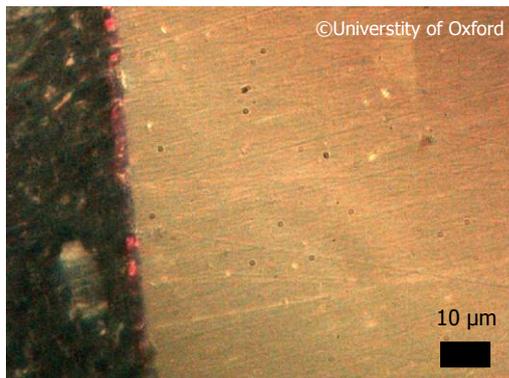
Figure 82 Polarized light microscopy (1000x magn.) of a cross-section of a cuprite-brass sample before dissolution of the nitrate crystals. The black area represents the mounting resin and the reddish surface the metal.

A cross-section of the laser cleaned (0.85 J/cm^2) cuprite-copper sample was observed under both bright-field and polarized reflected light. This surface had turned darker under laser radiation. Polarized light (figure 83) showed less red cuprite crystals than with the un-cleaned samples, although some oxide is still present. Bright-field light helped detecting the oxide layer, visible on figure 84 as a grey layer.

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[217] See Chapter 6.1.1.1.
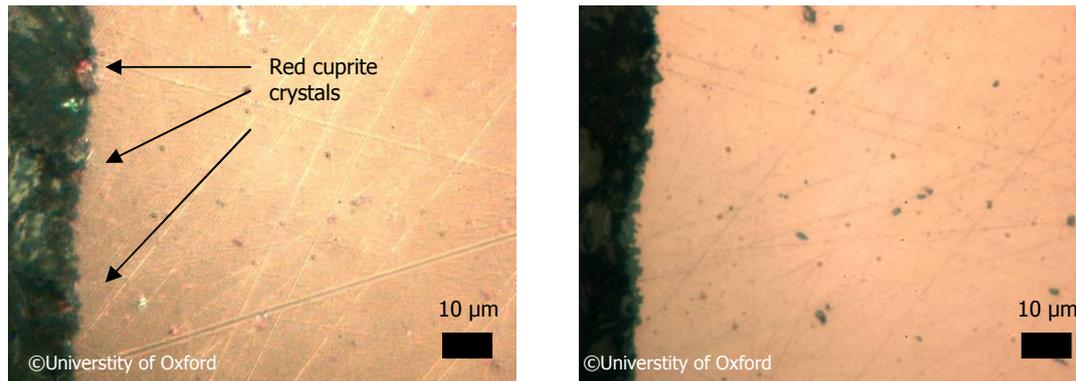
Figure 83 - 84 Polarized (left) and bright-field (right) reflected light microscopy (1000x magn.) of a cross-section of a cuprite-copper sample laser cleaned at 0.85 J/cm^2. Some cuprite crystals are visible under polarized light. The black area represents the mounting resin and the reddish surface the metal.

7.1.2.3.1. Results

Before and after laser cleaning, these images show a very irregular and coarse cuprite layer, instead of a nice regular film. The metal surface is covered with heterogeneous cuprite crystals of various sizes (from 1 to 4 µm). Moreover, there seem to be more numerous small crystals than large ones, and some metal may appear at places where no crystals are visible.

At last, the thickness of the laser cleaned oxide layer does not seem to have changed much compared to the layer before laser cleaning, as can be observed under 1000x magnification. The amount of ablated material due to laser cleaning seems to be so small that it cannot but measured on the micrometric scale.

7.1.2.4. "Spot by spot" laser tests

As was previously noticed by naked eye observations and then under optical microscope, the aspect of the laser irradiated area is different in the centre than at the beam boundaries. This is due to the fact that the central area receives more pulses, which greatly overlap, while the boundaries receive less pulse. Moreover, the laser beam does not show a homogeneous distribution of the energy and more or less intense zones ("hot spots") are easily detectable on the laser spots. Both effects are responsible for the aspect variations across the laser cleaned area. For example, on laser cleaned bare brass, the laser beam is divided in light areas (where the laser beam is highly energetic) and dark areas (where it is less energetic) (figures 71-72). With cuprite-brass and bronze samples, some exposed metal is visible at the boundaries of the laser irradiated area, but almost none in the centre and nowhere on the cuprite-copper samples (see Appendix 8.2.). Such variations in intensity inside the laser beam are important as they may cause localised different laser interactions with the substrate.

In order to understand the aspect variations on the samples and determine the impact of one single pulse on the substrates, "spot by spot" laser tests were carried out on a bare brass sample, which was the bare metal most reactive to laser radiation, as well as on cuprite-copper, brass and bronze samples. As previously mentioned in chapter 6.2.2, the number of pulses per unit area, using the x-y table cleaning technique, was calculated to be ~12 pulses, which means that each spot of the surface was irradiated by ~12 laser pulses. Then, the spot by spot test was achieved by firing each sample 12 times with one single pulse at a time, at the medium fluence of 0.85 J/cm^2, observing and recording the surface aspect after each individual pulse. Samples were each time placed at the exact same position for the next pulse.

The complete recorded microphotographs are presented in Appendix 9. The most significant results are as follows:

- *Bare brass sample :* the lighter zone, induced by the more energetic area of the laser beam, appeared already with the first pulse and turned always brighter with the increasing number of pulses. The boundary of the more energetic zone turned darker after 9 pulses. The grainy aspect, previously detected with the naked eye, was visible all across the surface from the first pulse (light, dark areas, centre and boundaries).

- *Cuprite-brass sample :* the first pulse produced a uniform grey spot, evenly distributed all over the surface. The intensity variations already appeared after the second pulse. After 7 pulses, the central area and the boundaries changed in colour, grey turning to blue, becoming brighter with the increasing number of pulses.

- *Cuprite-copper sample :* The increasing number of pulses led to a grayer and shinier surface. The intensity variations appeared from the second pulse. The higher intensity in the beam removed more grey areas and let the metal appear, while a lower intensity increased the formation of grey areas.

- *Cuprite-bronze sample :* the first pulse already revealed a yellow spot which may be exposed metal, as cuprite seemed to be partially removed by the laser. The surface generally showed less grey areas than on the other alloys covered with cuprite. The amount of grey did not change with increasing pulses, but was mostly removed where the laser beam was more intense, exposing the metal. On the lower intensity area, the surface turned redder / pinker with increasing pulses.
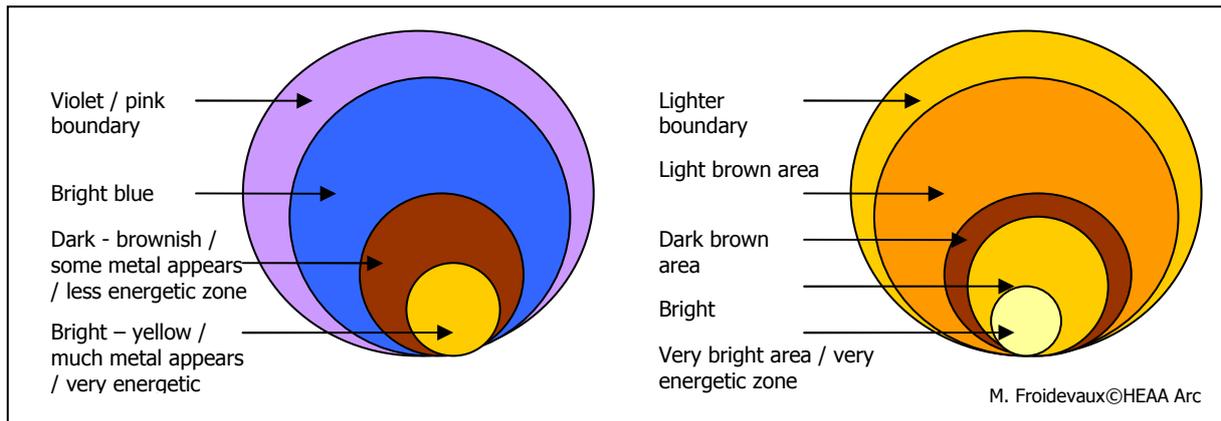
Figure 85 Schematic aspect of the laser spot shape on cuprite brass (left) and bare brass (right) samples after 12 successive laser pulses.

After these spot by spot laser cleaning tests, the general results are as follows.

- *On bare brass :* Already after 1 pulse, a general grainy aspect is visible all across the laser spot,. Moreover, variations in intensity in the laser beam create different intensity areas on the laser spot after only 2 pulses. The more energetic area in the laser seems to be aggressive to the metal surface.

- *On cuprite samples :* Only 1 single pulse is sufficient to produce the discoloration effect. The grey colour develops and becomes shinier with increasing number of pulses, except on bronze, on which the grey colour seems to be removed with more pulses. Moreover, intensity variations in the laser beam create different intensity areas on the laser spot after only 2 pulses. The more energetic area in the laser beam removes the grey areas and exposes metal in each case.

7.1.3.   Visible spectrophotometry

Visible spectrophotometry was used to determine the absolute surface discoloration, which means the difference between the colour of an un-cleaned surface and the colour of a laser cleaned one. The colour variations are of course considered at each fluence level used for laser cleaning. This technique was also used to establish the extent of the reversibility which occurs after laser cleaning oxidized copper alloys objects, as the surface seems to revert back with time to the original red-brown colour of cuprite. By definition, this supposed reversibility process means that the modification induced by laser is chemically unstable. Any sign of reversibility may suggest that the material is evolving over time to a more stable state.

Spectrophotometric measurements were undertaken using a desktop spectrophotometer (X-Rite Color Digital Swatchbook®[218], measurement spot diameter 4mm, measurement time 2sec.). Practically, a bright light source is scanned across the sample surface. This light is then reflected and the spectral intensity of its reflection at each wavelength of the visible part of the electromagnetic spectrum (400-700 nm) is detected by a sensor. The first measurements were taken on un-cleaned cuprite samples to obtain reference values.

In order to determine the absolute discoloration extent, to get an idea of the degree of reversibility and the length of time needed for this process to occur, spectrophotometric measurements were taken on each cuprite sample laser cleaned at each fluence level, a few days after cleaning. Then, the laser irradiated surfaces were measured once a week during 12 weeks to observe an eventual reversible effect. During these 12 weeks, the samples were kept in non-sealed plastic bags to minimize further oxidation with air and they were regularly removed for observation. The results show the spectra of the reflected visible light, randomly measured on 10 different spots on the sample taken all across the irradiated area.

N. B. Initial measurements on bare metal samples have also been carried out but such surfaces were so reflective that important variations in the recorded intensity appeared from one scan to the other. The light was scattered in different directions, depending on the position of the detector. As such, no significant or reliable results were obtained and so, it was chosen not to include them in this report. Moreover, brochantite samples were obtained too late and so, no spectrophotometric measurement could be done on these.

It also has to be mentioned that the background colour spectrum is only an approximate representation and as such, the wavelengths may not correspond exactly to the colours shown.

7.1.3.1.   *Extent of the discoloration*

Each cuprite sample showed a large difference in reflectivity between un-cleaned surfaces (UC) and each fluence level of the laser cleaned surfaces. Using visible spectrophotometry, the discoloration effect was characterized on most cuprite samples as a slight increase in reflectivity in the blue part of the spectrum (400nm-500nm).

7.1.3.1.1. Cuprite-copper samples

Artificial cuprite-copper samples (figure 86) show a strong decrease in the red part of the spectrum (650-700 nm) after laser cleaning and a slight increase in the blue part (400-450 nm). These samples show the most extensive discoloration, the surface turning totally and uniformly grey under laser

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[218] See Appendix 17.

radiation. The increasing intensity corresponds to increasing fluence and indicates that the surface becomes shinier.
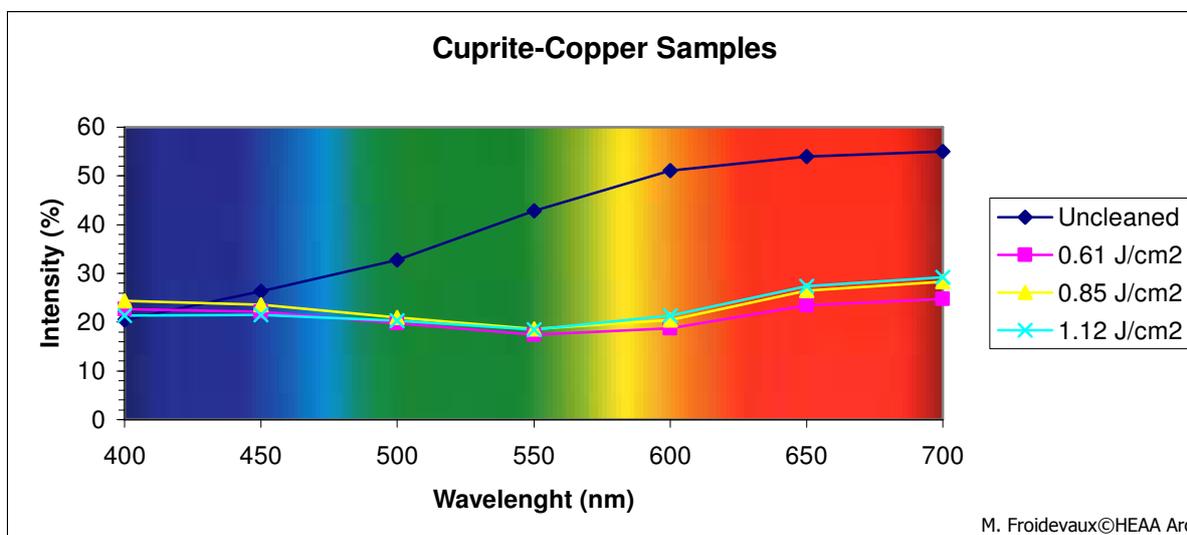
Figure 86 Visible spectrophotometry graph showing the extent of the discoloration effect on cuprite-copper samples, un-cleaned and laser cleaned at 0.61, 0.85 and 1.12 J/cm^2.

7.1.3.1.2. Cuprite-brass samples

The discoloration of brass samples covered with artificial cuprite (See Appendix 10.1 figure 121) is less pronounced than on copper. As was observed under optical microscope, the discoloration was less uniform, showing yellow metallic spots at 0.61 J/cm^2 and bright blue stains at 0.85 J/cm^2, which turned brown at 1.12 J/cm^2. To confirm this, the intensity in the blue part of the spectrum (400-450 nm) is the highest at the lowest fluence, as the sample shows a grey and shiny surface. At the middle fluence, the steeper spectral line in the blue part confirms the apparition of blue spots on the surface. At the highest fluence level, the surface is definitely browner and more matte, with more grey areas removed by laser. This can be determined as the line is steeper in the red part than in the blue. The low intensity of this spectral line also indicates that the surface has definitely become more matte.

7.1.3.1.3. Cuprite-bronze samples

The discoloration effect is still different and less marked on bronze samples covered with cuprite (See Appendix 10.1 figure 122). As these surfaces show the less extensive discoloration, the intensity values of the laser cleaned samples do not really differ from those of the un-cleaned samples. The intensity in the blue part of the spectrum (400-450 nm) decreases with increasing fluence, confirming the observations under optical microscope, which indicated that more grey areas were removed by laser at higher fluence levels. Respectively, the intensity in the red part (650-700 nm) is higher with increasing fluence. Moreover, the laser cleaned spectral lines become steeper in the yellow part of the

spectrum (600 nm), which confirms the exposition of some metal, as was also visible under optical microscope.

7.1.3.2. *Reversibility process*

Spectrophotometry measurements also indicated that the discoloration effect was a temporary phenomenon, as it slightly faded over a period of 12 weeks, slowly turning back to a more reddish colour. On all samples, this reversibility was assessed, more or less evidently depending on the sample. But in general, the results were not spectacularly significant and this effect could better be shown as a slight tendency to reverse back. Possibly, this reversibility effect would have been more pronounced if the samples had been in contact with air during the time of the analysis, instead of being enclosed in plastic bags between each measurement session. A more significant result was brought by the evident decrease in reflected intensity on all samples, indicating that the surface had become more matte with time.

Both effects are undoubtedly due to the oxidation process naturally occurring on the cuprite surface by contact with air. In fact, new red copper oxide crystals begin to form directly after laser cleaning : crystals first form rapidly after radiation, leading to the formation of small irregular crystals, and form more slowly after some time, leading to the formation of larger and nicely shaped cuprite crystals. This gradual growth of cuprite crystals certainly causes the surface to become matte and redder.

Further measurements, carried out on a longer period of time (for example 1 year), would certainly lead to more pronounced results in this reversibility effect than what is presented here. At the moment it is not known if the discoloration totally reverts back after a longer period of time. One could presume that these surfaces will completely turn back to red, as oxidation is a permanent process and the growth and size of cuprite crystals would increase with time, increasing the red colour on the laser cleaned metal surface.

The spectrophotometry spectra of the cuprite samples, laser cleaned at the lowest fluence (0.61 J/cm^2) are presented here. The spectra of the samples laser cleaned at the medium (0.85 J/cm^2) and highest (1.12 J/cm^2) fluence levels can be found in Appendix 10.2.

7.1.3.2.1. **Cuprite-copper samples**

The reversible effect is visible on a cuprite-copper sample laser cleaned at 0.61 J/cm^2 (figure 87). By comparison of the spectral lines between the first and the twelfth week, the reflected intensity slightly decreased within weeks and the gap between the lines was more pronounced in the blue part (400-450 nm) than in the red part (650-700 nm). This indicates that the sample surface became more matte and slightly more blue.
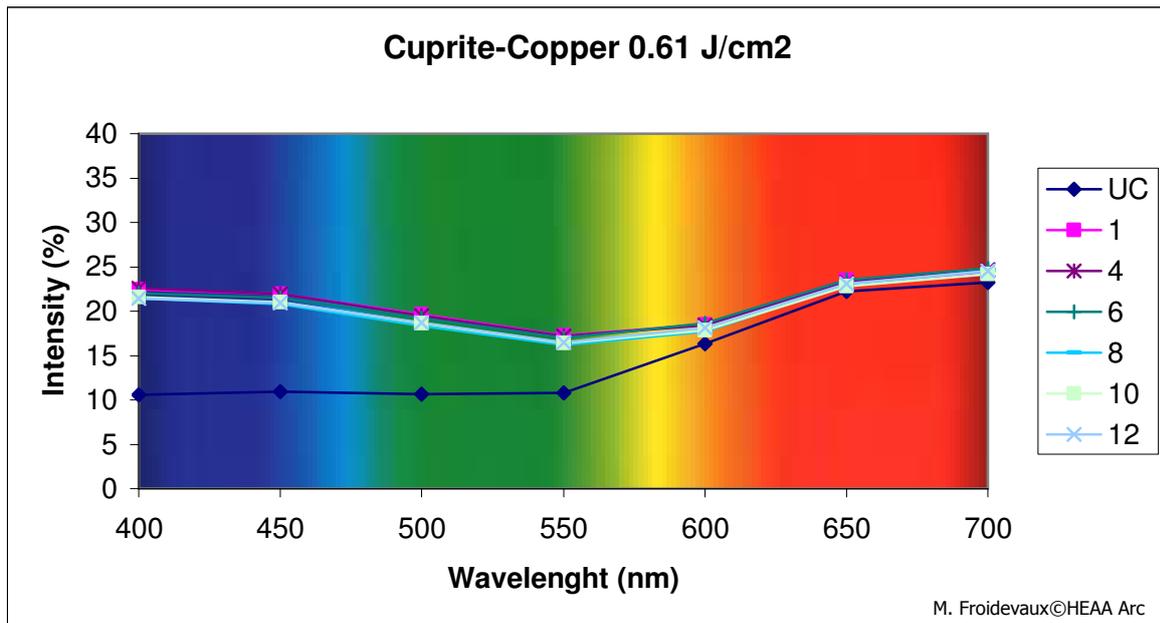
Figure 87 Visible spectrophotometry graph showing the reversible effect of the discoloration on cuprite-copper samples, laser cleaned at 0.61 J/cm^2, during 12 weeks.

At 0.85 J/cm^2 (See Appendix 10.2.1 figure 124), the reversibility effect is nearly not visible in the blue part of the spectrum, as the spectral lines cover each other. In the red part, the spectral lines show a tendency to move up and become steeper, indicating a slight evolution to the red colour.

At 1.12 J/cm^2 (See Appendix 10.2.1 figure 125), the intensity uniformly decreases with weeks, indicating that the surface becomes more matte. Not reversible effect is detected by spectrophotometry on this sample as well.

7.1.3.2.2. Cuprite-brass samples

With cuprite-brass samples, a slight decrease in intensity within weeks occurs again at 0.61 J/cm^2 (figure 88), indicating that the surface becomes more matte. The gap between the lines is larger in the blue part of the spectrum (400-450 nm) than in the red part (650-700 nm), indicating a slight reversibility effect.
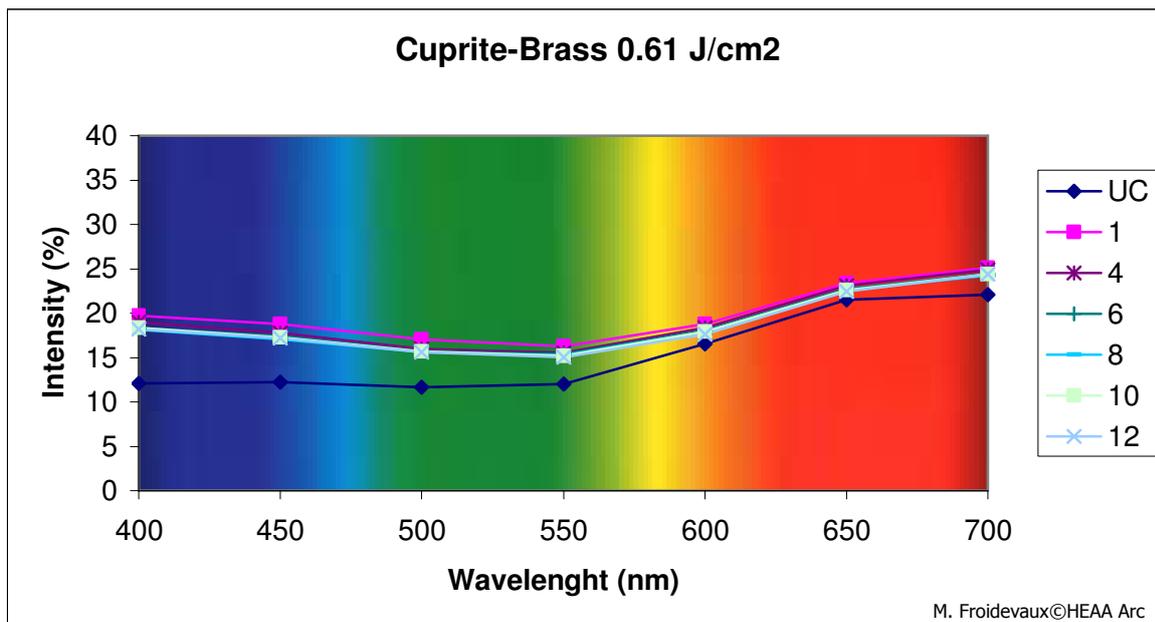
Figure 88 Visible spectrophotometry graph showing the reversible effect of the discoloration on cuprite-brass samples, laser cleaned at 0.61 J/cm^2, during 12 weeks.

Similarly, at 0.85 and 1.12 J/cm^2 (See Appendix 10.2.2 figure 127-128), the spectral lines become less steep in the blue part week after week, and much steeper in the red part (650-700 nm), indicating that the surfaces become redder. The reflected intensity is also very low, indicating a much more matte surface.

7.1.3.2.3. Cuprite-bronze samples

With cuprite-bronze samples, the variations are even less pronounced. At 0.61 (figure 89), 0.85 (See Appendix 10.2.3 figure130) and 1.12 J/cm^2 (See Appendix 10.2.3 figure 131), a decrease in intensity indicates that the surface becomes more matte. The reversibility of the discoloration process is not visible maybe because very little grey zones had initially formed on bronze samples. The steepest spectral lines occur in the yellow part of the spectrum (600 nm), as some yellow metal was already exposed before laser cleaning.
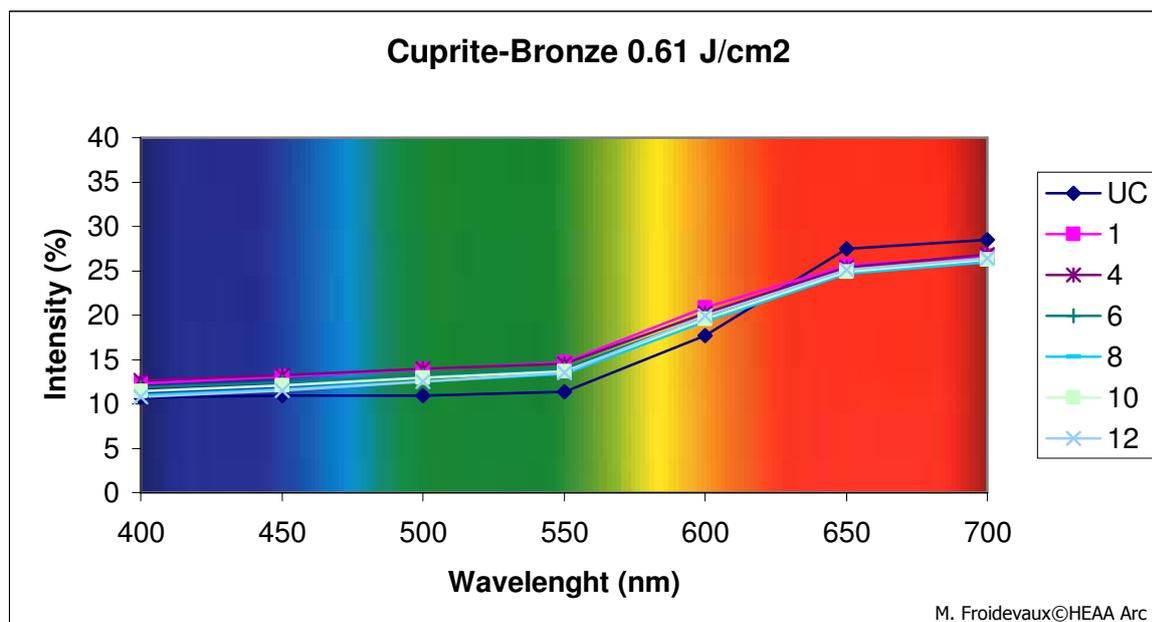
Figure 89 Visible spectrophotometry graph showing the reversible effect of the discoloration on cuprite-bronze samples, laser cleaned at 0.61 J/cm^2, during 12 weeks.

7.2. Chemical analyses

Chemical analyses allowed the study of surfaces on a scale that cannot be detected with the eye and requires specific and highly accurate analytical equipments. Optical analyses needed to be completed with techniques allowing topographical (SEM), elemental (EDX) crystalline (XRD) and ultra-sensitive molecular (XPS) analyses.

7.2.1. Scanning Electron Microscope (SEM)

SEM was used to perform surface topographical analysis. This technique allows a wide magnification range from 20x to 650'000x depending on the type of equipment. In SEM, electron beams are used to scan the surface of a sample kept under vacuum. Very precise topographical imaging can be obtained in this way and SEM can be coupled to EDS (see Chapter 7.2.2) to give the elemental composition of a surface. With SEM, the surface of a sample is scanned by a focused beam of high-energy electrons. The electron beam interacting with the material leads to a variety of signals (secondary electrons, backscattered primary electrons, emission of X-Rays, etc.) which are specific of the material analysed. In this way, high resolution images can be acquired.[219]

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[219] Ferretti, 1993, p.43-46; http://www.nrel.gov/pv/measurements/scanning_electron.html

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The SEM system employed at the National Conservation Centre was an Akashi Beam Technology, model ABT-55® linked with the software IScan 2000. Metal samples were kept untouched every time before, during and after laser cleaning to avoid contamination by fingers and they were enclosed in sealed bags to avoid air contamination. For the analysis, they were stuck on cylindrical stubs and held in position by conductive carbon tape before being placed in the vacuum chamber.

7.2.1.1.   *Bare metal samples*

Traces of localized melting were observed on bare copper, brass and bronze laser cleaned at each fluence level 0.61, 0.85 and 1.12 J/cm^2 (figures 90 to 95), which could have been induced by the heat produced by laser cleaning. As laser may produce heat levels high enough to locally melt the surface, the heat introduced by laser radiation seems to exceed the melting point of each alloy (1084°C for copper, 900-940°C for brass and 850-1000°C for bronze).[220]

Melting is visible on the following SEM microphotograph under the form of burst bubbles and craters of fused metal. It is observable especially where the metal surface shows imperfections (flakes, streaks). Copper and bronze only show little melting appearing at the lowest fluence (0.61 J/cm^2) and not much more extensive melting at the highest fluence level (figures 90 to 93). Bare brass shows more extensive melting already from 0.61 J/cm^2 and very extensive melting at the highest fluence (1.12 J/cm^2) (figures 94-95). This also confirms the higher reactivity of brass which was noticed with optical analysis, due to a lower reflectivity of this surface.
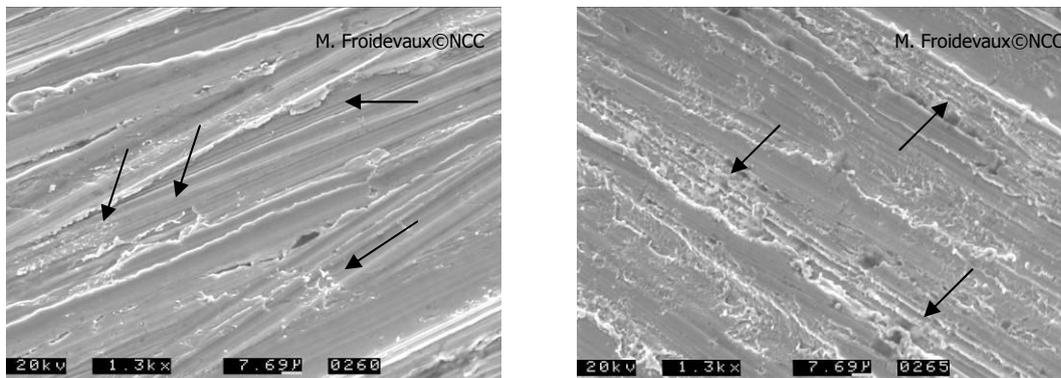
Figure 90 - 91 SEM microphotographs of bare copper after laser cleaning at 0.61 (left) and 1.12 J/cm^2 (right), showing little melting at surface imperfections. Signs of melting are visible as small craters and drops.

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[220] See Appendix 6.
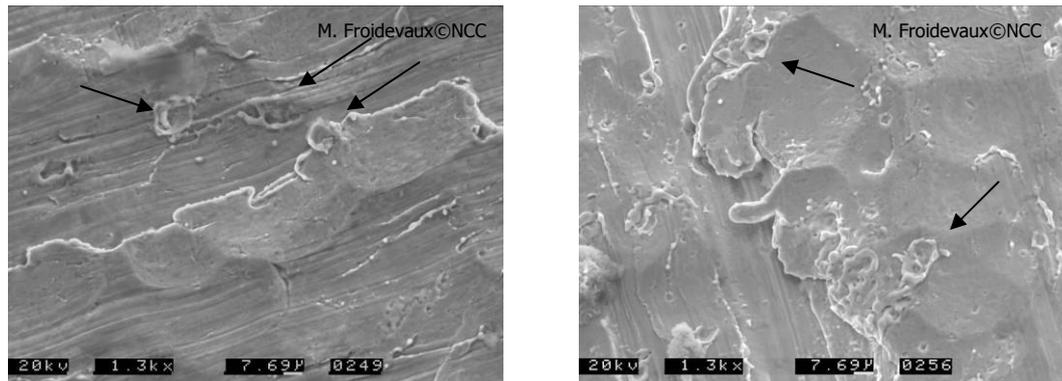
Figure 92 - 93 SEM microphotographs of bare bronze after laser cleaning at 0.61 (left) and 1.12 J/cm^2 (right), showing little surface melting at surface imperfections. Signs of melting are visible as small craters and drops.
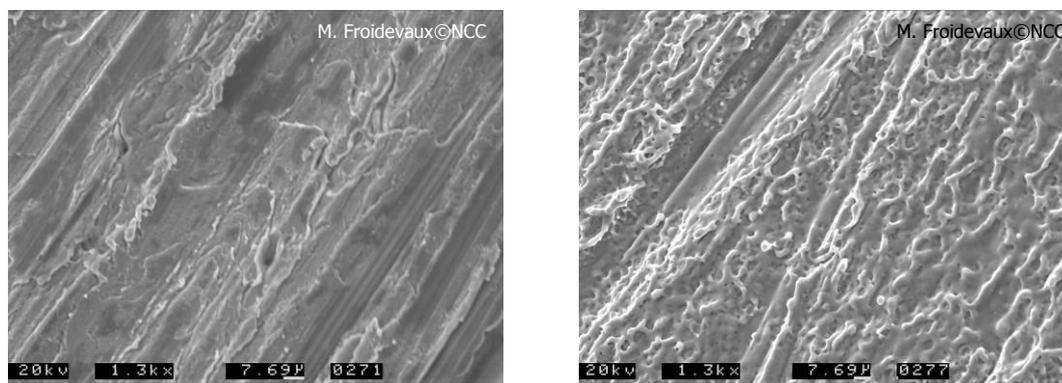
Figure 94 - 95 SEM microphotographs of bare brass after laser cleaning at 0.61 (left) and 1.12 J/cm^2(right), showing more melting than on copper and bronze at the lowest fluence and extensive melting all across the irradiated surface at the highest fluence.

7.2.1.2. Cuprite samples

Samples covered with cuprite layers showed extensive melting across the whole irradiated surface, at each fluence level and on each alloy (figures 96-101). This was visible as globules of melted material formed. Melting is much stronger on cuprite surfaces than on bare metal surfaces. This is due to the higher absorptivity of an oxidized surface compared to a bare metal surface, even a rough one, which reflects a consequent part of the laser radiations.

At the lowest fluence (0.61 J/cm^2), the shape of the cuprite crystals is still detectable after melting, especially with copper (figure 96) and even more with brass (figure 100). Increasing fluence leads to more extensive melting of the surface.

As the melting point of the alloys samples is lower than the melting point of cuprite (1508°C for cuprite, 1084°C for copper, 900-940°C for brass and 850-1000°C for bronze)[221], one can assume that superficial metal has melted as well, even slightly before cuprite. Globules may then be made of a

[221] See Appendix 6.

mixture of cuprite and metal, which crystallized after surface cooling in a tightly linked and chaotic magma.
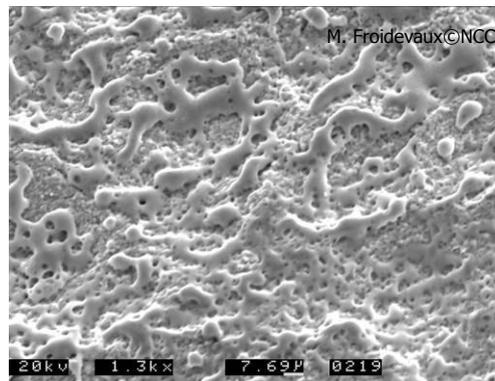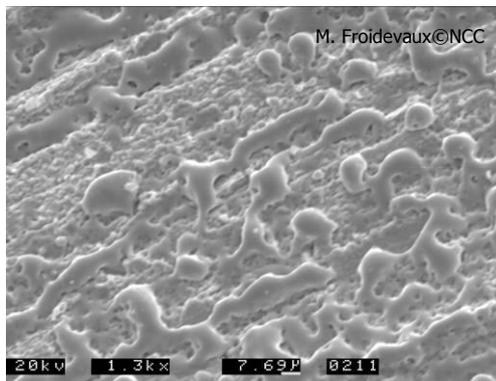
Figure 96 - 97 SEM microphotographs of the overall melted surface on a cuprite-copper sample after laser cleaning at 0.61 (left) and 1.12 J/cm^2 (right).
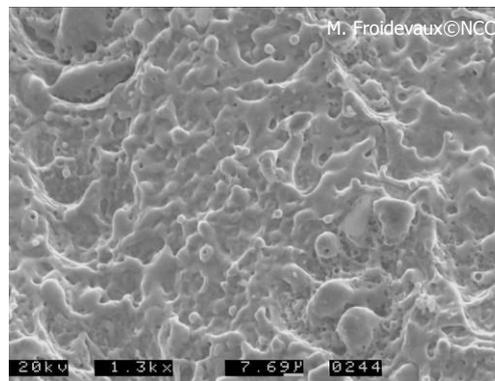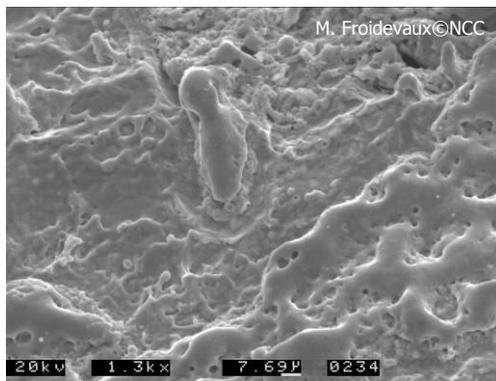
Figure 98 - 99 SEM microphotographs of the overall melted surface on a cuprite-bronze sample after laser cleaning at 0.61 (left) and 1.12 J/cm^2(right).
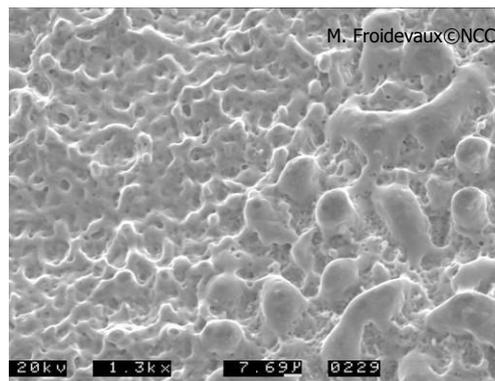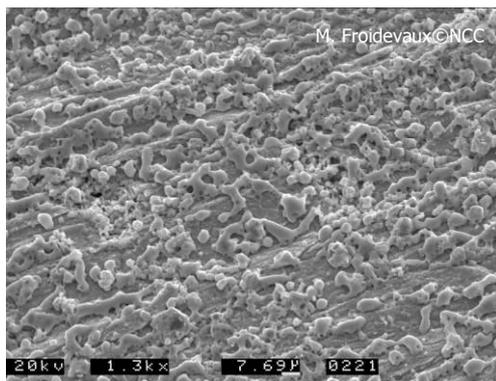
Figure 100 - 101 SEM microphotographs of the overall melted surface on a cuprite-brass sample after laser cleaning at 0.61 (left) and 1.12 J/cm^2 (right). The shape of the cuprite crystals is still clearly detectable at 0.61 J/cm^2.

7.2.1.3. *Cross-sections observations*

Initially, the idea of studying laser cleaned cross-sections of samples was to use half-cleaned samples. The cuprite samples of copper, brass and bronze, as well as bare metal samples were laser cleaned using the usual x-y rastering table technique, at each fluence level (0.61, 0.85 and 1.12 J/cm^2), while covering half of the surface. This would have avoided the creation of a "less cleaned" area, which corresponds to the boundary area which received less pulses. The objective was to obtain a cross-section with two directly adjacent levels, a well-definite step between non-cleaned and laser cleaned areas, which would allow the measurement of the amount of material ablated by laser (figure 102).
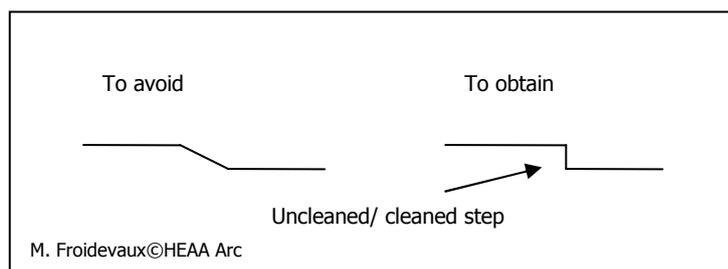
Figure 102 Schematic representation of the ideal cross-section of a laser cleaned sample with a definite step, allowing an easy measurement of the amount of material ablated from the surface.

Traditional optical microscopy, using the LEICA LEITZ®DMR available at NCC, was not able to detect the cuprite layer, as the magnification range was too low. Therefore, SEM high resolution imaging was used, at it was supposed to detect it. Once laser cleaned, the samples were mounted in an epoxy resin and polished to observe the cross-sections. Due to mounting in the resin, the metal conductivity was too low to acquire high resolution imaging under the SEM. To avoid this, the cross-sections had to be coated with a thin film (50nm-500Å) of carbon[222]. The carbon coater employed was an EMITECH®K250.

Unfortunately, no signs of laser cleaning were detectable under the SEM. The maximum magnification which could be obtained was 1.3 kx, so probably a higher magnification would have detected the level of laser cleaned / un-cleaned areas. But even at such a magnification, no distinct step was visible on both cuprite and bare metal samples. Regarding the cuprite layer, this could be due to the fact that the artificial oxide layer was very irregular, with more or less thick cuprite crystals aggregates. Therefore, no significant ablation level could be verified. But this is a good result for the conservation field, as this means that the ablated layer is very thin, being not easily detectable even under high magnification.

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[222] The advantage of using carbon coating is its cheap price, it allows a good image resolution and is invisible to most x-rays. As gold coating allows high quality imaging but blocks all x-rays, carbon coating was chosen to prepare the cross-sections to SEM and EDS exposure. http://www.uno.edu/pegmatology/coater.html; http://www.emsdiasum.com/microscopy/products/euiqpment/carbon_coater.aspx

7.2.2.   Energy Dispersive X-Ray Spectroscopy (EDS)

EDS is an analysis technique which is often coupled to a SEM equipment. It provides a qualitative and quantitative elemental analysis by ionization of the sample atoms, in an interaction volume of about 1µm (depends on the high voltage of the system and the density of the sample). Detecting the emitted X-rays allows the determination of the chemical composition. Thanks to this method, it was possible to get the elemental composition of the cuprite layers and of the bare metal samples in order to qualitatively determine eventual variations in the elements concentration, before and after laser cleaning.

The X-rays analyser at the NCC was an Oxford Instruments® system, with a thin window SiLi detector, resolution 138eV, model 5079 and using the Link ISIS 300 as software. The EDS spectra were obtained by scanning the target area at a magnification of 1 KX and at a voltage of 20 KV. The spectra show the X-ray counts relative to their energy. The peaks in the spectra allow identifying and quantifying the elements present in the area exposed to the electron beam.

The problem with the scanning method is that the elements are detected on a large scanned surface and not on a fixed and precise spot. As the oxide surface after laser cleaning is very irregular and coarse, the scanner sometimes meets a large cuprite crystal, sometimes a small one, sometimes it meets the metal surface and the detector produces an "average" of this variable surface topography. Such variations of the oxide layer produce large imprecision. Hence, no quantitative values could be given (done by measure of the area under the peaks), because such "average" values would not be reliable to determine the amount of ablated material after laser irradiation. The results given by the EDS analysis are then only qualitative (done by comparison of the height of the peaks), but they confirm the results given by the other analytical techniques.

7.2.2.1.   Bare metal samples

In the case of bare metal samples, no change in the elemental composition and approximate concentration are detected after laser cleaning. The spectra are identical for copper and bronze before and after cleaning at 0.61, 0.85 and 1.12 J/cm^2. The brass spectra show a slight variation due to the deposition of impurities which were removed by laser: the presence of C, O, and K peaks are typical for organic substances (grease) and were probably deposited by fingers. These peaks partially disappear after laser cleaning at 0.61 J/cm^2 and are completely removed at 0.85 J/cm^2 (see Appendix 12.1.).

7.2.2.2.   Cuprite samples

The EDS spectra of the cuprite samples show that the different alloys behave very similarly (see Appendix 12.2.). In each case (copper, brass and bronze), the O peak at 0.5 KeV is well marked

before laser cleaning, indicating the presence of the oxide layer. After laser cleaning at the lowest fluence level (0.61 J/cm^2), the O peak strongly decreases to become nearly negligible. This indicates that some of the oxide layer is removed by laser. The O peaks don't seem to decrease further with increasing fluence, except for bronze, where the O peak is still well marked after cleaning at 0.61 J/cm^2 and becomes negligible only after cleaning at 0.85 J/cm^2 and 1.12 J/cm^2. This result confirms what was observed under optical microscope, as the grey areas which appeared after laser cleaning were removed with increasing fluence and this effect was much less visible on copper and on brass. In all cases, the main Cu peak (Cu-K) at 8.2 KeV increases after cleaning at 0.61 J/cm^2 and does not seem to change with increasing fluence. On brass, the Zn concentration at 8.5 KeV increases as well and on bronze, the Sn concentration at 3.5 KeV increases, while some Zn is detected mainly at 8.5 KeV.

The decrease in O indicates that the oxide layer is partially removed by laser cleaning. Some oxide always remains because O is still detectable after laser cleaning at 1.12 J/cm^2, but in a lower quantity and is not uniform across the sample. As was observed and confirmed with other analytical methods, the oxide layer is very irregular and coarse, even more after laser cleaning, and EDS may have produced spectra done on an average of X-rays signal, when meeting large cuprite crystals, small one or metal, as is shown in figure 103.

The increase in metallic elements (Cu, Zn, Sn) indicates that some metal is exposed after laser irradiation. The higher concentration of these elements means that the oxide layer has been locally removed, revealing the metal, or that is has become thinner and metal is detected through it, or even that EDS has detected metal mixed with cuprite inside the globules of melted material. All three effects probably happen. As the melted surface is very uneven, where the globules are large, the EDS interaction volume of detection remains in the globule, where some cuprite mixed with metal is detected. Where the globules are small, the interaction volume also consider the underlying metal, which is detected. Where no globule is present, only metal is detected. This also confirms the observations under optical microscope, in which some exposed metal was clearly visible.
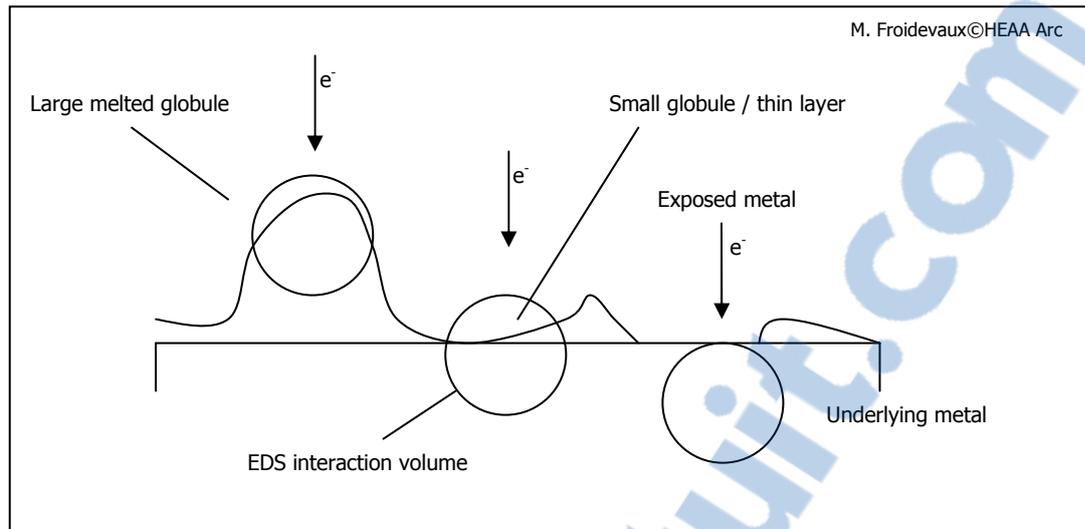
Figure 103 Schematic representation of the volume (approx. 1µm) interacting with the laser cleaned of samples covered with copper oxide. This shows the topography variations of the surface after laser cleaning: large globules, small globules, thin layer of melted material, exposed metal.

7.2.2.3. EDS elemental mapping

An elemental mapping analysis was performed on a cuprite copper sample, using the SEM for the selection of the target surface, and the EDS analyser, bombarding electrons on the surface and detecting X-rays typical for each element in a 1 µm depth. This technique produces a map being representative of the atomic repartition in a predefined surface. The selected analysed surface was a cuprite copper sample laser cleaned at the medium fluence, 0.85 J/cm^2 (figure 104). On the picture, extensive melting was visible with numerous globules.

The element maps (figure 105) show the atomic repartition of Cu and O, which constitute the Cu$_2$O layer. The CuKa map is determined by the main peak of the acquired spectrum, corresponding to the main electron shell (K, L, M, etc.) of the Cu atom. The maps showed that the Cu and O atoms, detected on an interaction volume of about 1µm, were relatively uniformly distributed all across the irradiated surface. Unfortunately, the elemental maps were too noisy and, therefore, not accurate enough to get a reliable result. The acquisition time should have been much elongated (approx. half an hour) in order to detect elements very precisely and obtain a reliable result.

a)   b)
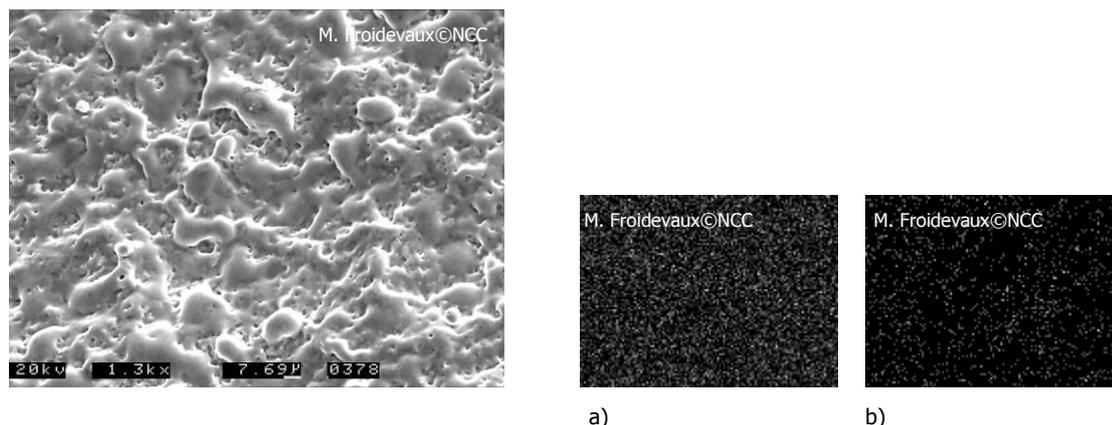
Figure 104 (left) Reference SEM photomicrograph of melted cuprite copper after laser cleaning at 0.85 J/cm$_2$.

Figure 105 a) CuKa map, main Cu peak – b) Oxygen map.

7.2.3. X-Ray Diffraction (XRD)

XRD allows the compositional analysis of crystalline materials, in a qualitative point of view. It is not suitable for amorphous products. More precisely, it is used for identifying crystalline phases present in solids or powder materials. As most corrosion products are crystalline, XRD is commonly used for their identification. It also allows the analysis of the structural properties of a material (grain size, stress, phase composition, crystal orientation or defects). In this method, a beam of X-rays bombards a sample from various angles. The X-rays are diffracted as they are reflected from successive plans formed by the crystal lattice of the material. By varying the angle of incidence, a characteristic diffraction pattern appears which is used to detect the presence of a crystalline element by comparing it with an international reference data base.[223]

XRD was used in the frame of this research first to assess the artificial oxide product on the sample to be really the copper oxide Cu_2O and then to determine if the laser cleaned area on a cuprite copper sample still shows crystalline components or if it has turned amorphous.

XRD was carried out on an artificial cuprite copper sample, before and after laser cleaning. The XRD analysis of un-cleaned cuprite copper sample was carried out by Dr. P. Muralt and his team from the Department of Materials Sciences of the Swiss Federal Institute of Technology of Lausanne (EPFL-Switzerland), while the analysis of laser cleaned cuprite sample (fluence 0.85 J/cm^2) was carried out by Dr. Peter Northover from the Department of Materials of the University of Oxford (UK). Both spectra are visible in Appendix 13.

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[223] Ferretti, 1993, p.35-42; http://www.nrel.gov/measurements/xray.html

7.2.3.1. *Identification of the crystalline compounds*

As the position of the peaks translates the type of crystalline material, the analysis on the un-cleaned sample suggested that the artificial oxide layer was definitely the copper oxide Cu_2O.

Moreover, the obtained spectra, compared to the XRD reference database, revealed the cuprite to have randomly formed during the artificial corrosion process. The same random structure was also evidenced on the laser cleaned sample.

7.2.3.2. *Determination of the crystalline structure*

Furthermore, by comparing the oxide layer of the un-cleaned and the laser cleaned samples, an identical crystalline structure was evidenced. This second result means that the crystallinity of cuprite Cu_2O is not affected and is even still highly detectable after laser irradiation, at least in 1 µm depth, which is the typical detection depth of the XRD analysis. Cuprite has not turned amorphous, which means that it is still in its initial crystalline form and laser has not transformed it. This shows that even though surface melting occurs, the globules visible on the SEM micrographs (see Chapter 7.2.1.2) are made of recrystallized cuprite, mixed with some of the underlying melted metal.

As XRD goes 1 µm in depth, this also suggested that the grey aspect could be produced by a very superficial product (< 1µm), as no chemical change corresponding to that colour was detected, or by an optical effect resulting from melting.

7.2.4. X-Ray Photoelectron Spectroscopy (XPS)

XPS[224] is a qualitative and quantitative technique which involves the irradiation of a material with X-rays and measures the kinetic energy and the number of the photoemitted electrons. Each photoemitted electron shows a typical binding energy which is specific of the emitted atoms and their bonding states. This technique requires ultra high vacuum (UHV) and detects all elements except hydrogen and helium. XPS provides chemical information about the elements and distinguishes chemical arrangements, such as molecular composition, bindings or oxidation states. The characteristic peaks correspond to the electronic configuration within the atom (1s, 2s, 2p, 3s, etc.). It is a very sensitive technique as it gives information on superficial layers of less than 10nm.[225]

This technique was used within the frame of this project because we needed to have a closer look on the cuprite surface (Cu_2O), in the sub-micron scale, to understand the impact of laser on a copper alloy surface and the discoloration effect. Because the previous analytical techniques were limited to a

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[224] Also called ESCA "Electron Spectroscopy for Chemical Analysis".
[225] Mathieu *et al.,* 2003, p.21-44 ; http://www.nrel.gov/pv/measurements/xray_uv_photoelectron.html

depth on the micron scale, it seemed necessary to investigate the top layers of cuprite with the help of a very sensitive technique like XPS.

A cuprite-copper sample was used in that analysis, partly because this metal showed the most extended discoloration after laser cleaning; partly because copper does not contain alloying elements and as such, it would give the most legible spectrum, compared to brass or bronze. The sample was laser cleaned with an Nd-YAG laser under similar conditions than previously conducted (1064nm, 0.63Hz, 10ns, rastering x-y table) at the medium fluence level of 0.85 J/cm^2. Before, during, and after irradiation, the sample was kept untouched to avoid fingers contamination. Just after exposure, it was enclosed in a sealed bag to minimize air contamination.

XPS analysis was carried out one week after laser irradiation by Dr. H. J. Mathieu and his team from the Department of Materials Science, at the Polytechnic University in Lausanne (EPFL). It was important to do the analysis as soon as possible, in order to minimize contamination and oxidation of the sample for the analysis. The spectra were obtained from different areas on the cuprite copper sample: laser cleaned and non laser cleaned. A slightly naturally oxidized copper sample was also used as a standard. The first analysis was carried out on the sample as received, the following ones after a surface treatment called *sputtering*[226] (etch time 180s, sputtering 3 min). The XPS system employed provided an irradiation with the monochromatic K-alpha aluminium X-rays (AlK$_\alpha$), emitting at 1486eV.

7.2.4.1. *Qualitative results*

7.2.4.1.1. Peaks identification

By comparing the obtained XPS spectra to literature references, major and minor copper compounds present in the oxide layer of the copper sample have been identified. Figure 134 in Appendix 14 shows the characteristic XPS peaks of Cu_2O, CuO and $Cu(OH)_2$ which were used to evidence their presence in the oxide layer of our sample. It seems important to underline that each compound detected by XPS has a very precise peak position and that a slight shift of only a few eV may sometimes indicate the presence a different compound.

The following XPS spectrum of the copper sample after laser cleaning shows three distinct copper compounds in the oxide layer, Cu_2O, CuO and $Cu(OH)_2$ (figure 106).

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[226] Sputtering is the removal of surface contaminants by bombarding the surface with argon ions (Ar$^+$) before the analysis.
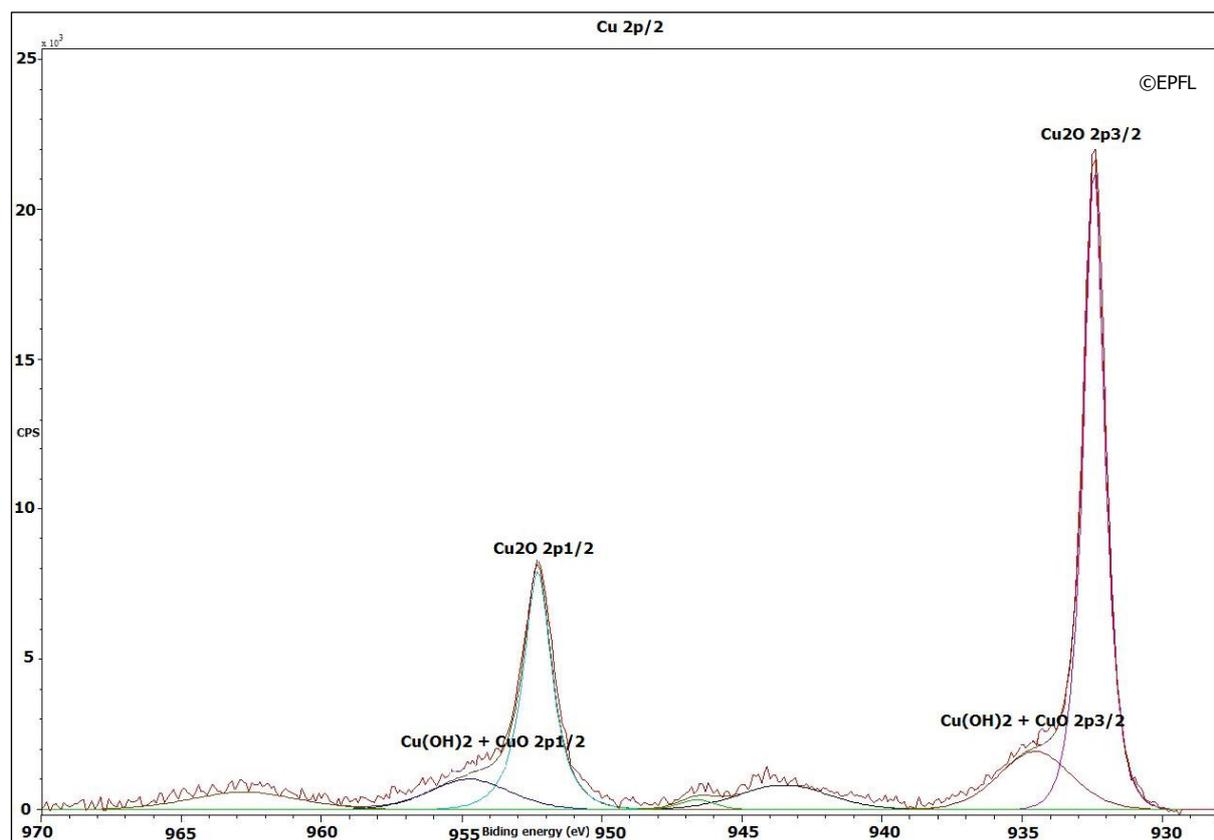
Figure 106 XPS spectrum of Cu 2p in the laser cleaned area of the copper oxide layer, showing the presence of Cu_2O, $Cu(OH)_2$ and CuO.

Cuprite

Cu_2O peaks, **cuprite**, have been identified by XPS as the major compound in the surface layer on the copper samples, before and after laser cleaning (figure 106). Two main peaks are visible on the spectrum at 952 and 932 eV, clearly assessing the presence of cuprite Cu_2O. The presence of this copper oxide as the major compound is also shown with the Auger spectrum of laser cleaned area (See figure 136 in Appendix 14) and with the oxygen spectra O 1s (See figure 138-139 in Appendix 14), taken from the laser cleaned area of the sample.

Tenorite and copper (II) hydroxide

CuO, tenorite, and $Cu(OH)_2$, a copper salt, seem to coexist in the oxide layer and have been evidenced in a much lower quantity than Cu_2O under the form of *shake up* peaks of the main Cu_2O peaks (figure 106). These are satellite peaks which sometimes accompany the main peaks. As they are often present in metal oxides spectra, shake up peaks can be used to identify metal oxides.[227] On the Cu 2p spectrum (figure 106), shake up peaks are clearly visible, corresponding to CuO and to

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[227] Mathieu *et al.*, 2003, p.29-30.

$Cu(OH)_2$. $Cu(OH)_2$ is present before and after laser cleaning, but CuO seems to appear with laser cleaning, or at least is much increased.

- Shake up peaks of **CuO**, **tenorite**, are mostly present in the laser cleaned samples. It is hard to affirm that it already existed before laser cleaning, as it could be partly covered by other peaks. On the laser cleaned samples, two small "shoulders" typical of CuO (see figure 134 in Appendix 14 for reference) are located at 955 and 934eV on the Cu 2p spectrum and are visible on figure 106. Two other "shoulders" may be hidden in the main Cu_2O peaks. On the oxygen spectrum O 1s (see figure 138 in Appendix 14), the laser cleaned oxide layer shows a CuO shake up peak at 529.4 eV. Figure 137 in Appendix 14 shows the O 1s peak before laser cleaning of the oxide layer. No CuO has been detected, or may be present in a very small quantity and be hidden in the main Cu_2O peak.

    By comparing figure 137 and figure 38 in Appendix 14, one can see that some more CuO was formed by laser cleaning, as figure 137 does not show the small CuO peak, even if $Cu(OH)_2$ and H_2O are present. The laser cleaned sample after sputtering (see figure 139 in Appendix 14) shows the removal of nearly all species except Cu_2O, which remains the major compound of the oxide layer. This indicates that CuO could have appeared with laser cleaning, but still in very low proportion (<10% CuO).

    While XPS analysis reveals the presence of CuO after laser cleaning, XRD analysis did not show any sign of tenorite. As XRD goes much in depth (1µm) than XPS (<10nm), one can assume that the small amount of CuO mixed with Cu_2O is located in and on the very top layer of the oxide surface.

- **$Cu(OH)_2$** is detectable before and after laser cleaning. As it is visible on the Cu 2p spectrum (figure 106), it is mixed with the CuO shake up peaks, in very low quantity. It is most visible on the oxygen spectra O 1s before (see figure 137 in Appendix 14) and after laser cleaning (see figure 138 in Appendix 14). This compound results from the exposure of CuO with H_2O to the air and forms very slowly, according to the following equation:

$$CuO + H_2O \rightarrow Cu(OH)_2$$
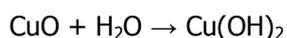
    As laser cleaning removes some of the water contained in the oxide layer, the $Cu(OH)_2$ content is proportionally higher than the water content after laser cleaning (figure 138 in Appendix 14).

Metallic copper

Metallic copper Cu appears on the laser cleaned area after sputtering (see figure 140 in Appendix 14). It is hardly detectable as it is mostly mixed with the Cu_2O peaks at 952 and 932 eV. Its presence can be explained first by the fact that metal is mixed with cuprite inside the globules formed by melting ; second, by the fact that sputtering, while removing contaminants from the surface, also removes thin layers of material and detects some underlying metallic copper. This also explains the surprisingly high Cu ratio compared to O (4:1) in the following quantitative results (see table 3).

7.2.4.1.2. Superposition of the peaks

As previously discussed, each compound detected by XPS has a very precise peak position and a slight shift of only a few eV may sometimes indicate the presence a different compound. This property was used to check if the peaks were perfectly superposed before and after laser cleaning, and so if the compounds had been modified by laser radiation or not.

By comparing the spectra of the sputtered samples before and after laser cleaning, which may contain nearly no contaminants, one can observe that all the Cu peaks are identical and can be perfectly superposed. The O peaks after laser cleaning show the same identical superposition, but the O peak before laser cleaning is slightly shifted to the left (shifting of +0.2eV), which is acceptable and corresponds to the error range of the XPS machine.

The perfect superposition of all the XPS spectra shows that most of the Cu and O atoms have not recombined themselves in a different molecular structure after laser cleaning. Cu_2O is still the major compound, although some CuO has formed very superficially in the oxide layer. Thus, the molecular structure of the copper oxide is slightly modified in surface because of the presence of CuO, while the underlying layer only contain Cu_2O mixed with some metallic copper.

7.2.4.2. Quantitative results

Here are the XPS quantitative results obtained on the artificially oxidized copper sample, before and after laser cleaning, on two different points in the laser cleaned area. Table 3 shows the results for Cu 2p and O 1s without sputtering, while table 4 shows the results after sputtering.

	Non laser cleaned area		Laser cleaned area point 1		Laser cleaned area point 2	
Peak	Cu 2p	O 1s	Cu 2p	O 1s	Cu 2p	O 1s
Atomic %	**19.92**	**24**	**31.93**	**27.39**	**32.42**	**27.65**

Table 3 Atomic percentage of the XPS analysis of oxidized copper, before and after laser cleaning, without sputtering.

Usually, the atomic ratio for the corrosion product CuO (tenorite) is 1:1 while for Cu_2O (cuprite) it is 2:1. Considered that and regarding table 1, the O ratio is extremely high. Before laser cleaning, it is higher than Cu (Cu 20% / O 24%) which indicates a large amount of carbon contaminants on the oxide layer, coming from the atmosphere and combined to O. After laser cleaning, the decrease of O respectively to Cu (Cu 32% / O 27%) indicates that laser cleaning removes some carbon contaminants, which then completely disappear after sputtering (see table 4).

	Non laser cleaned area		Laser cleaned area point 1		Laser cleaned area point 2	
Peak	Cu 2p	O 1s	Cu 2p	O 1s	Cu 2p	O 1s
Atomic %	**78.62**	**17.72**	**82.28**	**17.72**	**80.03**	**17.47**

Table 4 Atomic percentage of the XPS analysis of oxidised copper, before and after laser cleaning after sputtering (etch time 180sec; sputtering 3min).

Table 4 shows the quantitative results of the analysed sample before and after laser cleaning after sputtering (which means that all contaminants have been removed) on two different points on the sample. Sputtering has removed around 15-20 nm of the oxide layer.

The atomic percentage is around 17% for O and around 80% for Cu. This brings the atomic ratio for Cu and O to be respectively 4:1 and indicates an unusual high atomic ratio of Cu. The explanation for such a high Cu ratio may be the fact that the artificial oxide layer is initially very irregular, with metal being exposed or mixed with cuprite inside the melted layer. At some places, XPS directly detects metal and at others, it detects the copper oxide. Moreover, sputtering removes some of the superficial layer (around 15-20 nm) and where it is very thin, it may allow some metallic copper to be detected through. This result confirms the XPS spectra as well, where metallic Cu is detected (see figure 106).

For the same sputtering level, Table 4 also indicates a slight increase in the proportion of Cu after laser cleaning compared to O, which remains unchanged. This could mean that the oxide layer thickness has slightly decreased due to laser cleaning, allowing more metallic copper to be detected. But the amount of removed material remains very small, which is acceptable from the conservation point of view.

7.2.5. Extra analysis: Diffuse and specular reflectance spectrometry

At this point of the project, two hypotheses had appeared which could explain the discoloration of the copper alloy surfaces covered with cuprite after laser radiation : a minor chemical change due to the formation of some tenorite (CuO), which colour is grey; an optical change induced by melting of the surface, producing a change in light reflection which is diversely perceived by the human eye.

The interpretation of an optical change as the explanation of the discoloration of surfaces covered with copper oxide was assessed with a final spectrometric analysis in the visible part of the spectrum, conducted by Christian Ban at the Applied Optics Laboratory from the Swiss Federal Institute of Technology (EPFL) in Lausanne (Switzerland). This analysis is similar to the spectrophotometric measurements conducted in 7.1.3, but it was achieved with a more precise tool which allowed the differentiation of diffuse and specular reflectance measurements.

The idea was to assess the optical change leading to discoloration by comparing the diffuse and specular reflectance of a copper sample before and after laser cleaning. The eye mainly perceives diffuse light reflected from the surface of a copper alloy monument, although a small part of the light is specularly reflected. If only specular light was reflected, the monument would appear very shiny. As the discoloration of surfaces covered with copper oxide seems to be mainly due to diffuse reflected light, as it is not a mirror surface, it was interesting to investigate the impact of the specular part reflected from the sample surface.

The reflectance spectra were recorded on a PerkinElmer Lambda® 19DM spectrometer with integrating spheres. Three different measurements were done: a) in diffuse reflectance, b) in specular reflectance and c) in diffuse and specular reflectance. The system consists of firing a light beam on the sample, which is then reflected on two dielectric mirrors, reflecting up to 99% in the visible part of the spectrum. The reflected light is totally diffused in a white chamber and is then measured by the detector. Such a system provides a measure of diffuse and specular reflections together. In order to get only diffuse reflection, the specular beam is cancelled by replacing one of the mirrors by a black template, absorbing all the specular light. In order to get only specular light, a different configuration of the mirrors and the sample needs to be found. This last measurement could not be maximized in order to get only specular light and a small part of diffuse light was detected.

A copper sample covered with artificial cuprite was used for this purpose, of which one part was laser cleaned and the other not. A mirror-like copper surface was used as a highly specularly reflecting reference.

7.2.5.1. Measure of diffuse reflectance

The graph is visible in Appendix 15, figure 141. The diffuse reflectance of the mirror-like copper surface is nearly equal to the diffuse reflectance of the laser cleaned area, which indicates that the part of specular reflectivity on the laser cleaned area is very low and that nearly only diffuse light is perceived by the eye. The grey discoloration is then mainly due to diffuse reflectance.

The laser cleaned surface shows a clear increase in the green-blue part of the spectrum. Compared to the mirror-like copper surface, it reflects less in the red. The reflectivity of the non oxidized mirror-like copper sample is high in the red part of the spectrum, as this metal is reddish, but falls as soon as it enters the green part.

The reflectivity in the red part is similar for both oxidized surfaces (laser cleaned and non laser cleaned), but the laser cleaned area reflects a little more, as some of the absorbing cuprite has been removed and melting has produced a more reflecting surface.

7.2.5.2. Measure of diffuse and specular reflectance

The graph is visible in Appendix 15, figure 142. Here, both diffuse and specular reflectance are measured.

The mirror-like copper surface shows a higher reflectivity compared to the oxidized samples, as it naturally reflects light specularly and that it is the specular reflectance which is detected. The oxidized copper, before and after laser cleaning, shows a large decrease in reflectivity compared to the mirror-like copper surface, which indicates again that mainly diffuse reflectance is responsible for their aspect.

Again, the laser cleaned area shows a slight increase in the blue part compared to the non-cleaned area. The reflection in the red part is similar for both oxidized samples (laser cleaned and non laser cleaned), but the laser cleaned area reflects a little more, as some absorbing cuprite has been removed and melting has produced a more reflecting surface.

7.2.5.3. Measure of specular reflectance

The graph is visible in Appendix 15, figure 143. Here, mainly specular reflectance is measured, although some diffuse reflectance is also detected. The initial configuration of the mirrors and sample had to be modified according to the position "sample-mirror-mirror", with the sample being the first one hit by the light beam.

The reflectance of the mirror-like copper surface falls when entering the green part of the spectrum, as the colour of bare copper is reddish.

The oxidized copper sample before and after laser cleaning shows a lower reflectance compared to the mirror-like copper sample, due to the high absorptivity of cuprite, which reflects poorly. But the laser cleaned area reflects more than the non-cleaned one, as its surface has become more reflecting due to melting. It also shows an increase in specular reflection in the blue part of the spectrum. The reflection in the red part is similar for both oxidized samples (laser cleaned and non laser cleaned), but the laser cleaned area reflects a little more, as some absorbing cuprite has been removed and melting has produced a more reflecting surface.

7.3.   Synthesis of the results

7.3.1.   Bare metal samples

Optical observations with naked eye and optical microscopy assessed that no discoloration occurred on bare metal samples, at any of the selected fluence levels, under laser irradiation at 1064 nm. Again the behaviour of the various copper alloys varied, with brass showing a much higher reactivity than copper and bronze, because of its lower reflectivity, or higher absorptivity. SEM indicated that melting occurred, strongly on the bare brass samples but less extensively on copper and bronze. Melting explains the grainy aspect visible under optical microscope on bare metal samples. Such small grains on the surface were microscopic marks of melting.

7.3.2.   Cuprite samples

Optical observations with naked eye and optical microscopy assessed that the samples covered with cuprite discoloured under laser radiation of wavelength 1064 nm, turning from a red-brown colour to a grey / purple tinge. The copper alloys behave differently, copper showing the most extensive discoloration and bronze the less marked. The discoloration was also characterized using spectrophotometry on most cuprite samples as an increase in reflectivity in the blue part of the spectrum (400nm-500nm).

Regarding the reversibility process, it has been evidenced that the discoloured aspect slightly reverts back to a more typical reddish colour in a 12 weeks period. What has also been detected with spectrophotometry and is maybe the most evident effect, is that the surface of all cuprite samples tarnishes, becoming more matt along the weeks following laser cleaning procedure. Both processes are the visible effect of the natural on-going oxidation of the metal surface in contact with air, during which new copper oxide crystals form on the surface.

Calculation of the cuprite thickness was only an estimate as the layer was too irregular and coarse. High magnification microscopy completed with other analytical techniques (XRD, XPS) have established that the artificial layer before laser cleaning was about 1-2 to 4 µm, depending on the

areas on the sample, but with more numerous small cuprite crystals than large ones and the layer being very thin at some places. It has been difficult to measure the thickness of ablated material by laser cleaning, as the surface was so irregular, but high magnification images did not show a large difference in thickness before and after laser radiation. The heat diffusion length being of 2 µm (see Chapter 5.2), it gives an idea of the depth of thermal effect produced by one pulse. But this value has been calculated using theoretical values for copper only and could not be obtained for brass and bronze. One could assume laser to have removed around 1-2 µm of the oxide, but really not much more.

Detected by SEM, melting may partially explain the discoloration effect of surfaces covered with cuprite. As was clearly visible on the SEM micrographs, melting leads to a modification of the surface topography, passing from a surface covered with small crystals to a layer covered with globules of melted material. This change in surface topography, becoming less rough, induces a different reflection of light, compared to an un-cleaned surface. This is perceived by the eye as a colour change and could explain the grey discoloration. The combination of metal, cuprite and surface state play a role in the diffusion of light and in our visual perception.

EDS showed that some cuprite was definitely removed by laser radiation and evidenced its irregular and coarse nature. It also showed that some metal was detected inside the melted layer and was locally exposed to the atmosphere, at the places where cuprite crystals were initially absent or completely removed by laser.

XRD showed that the chemical structure of cuprite was not affected by laser cleaning, as no change in the crystalline structure was detected before and after laser cleaning. The XRD results complete the SEM results, showing that the melted globules visible on the SEM micrographs are made of recrystallized cuprite mixed with some of underlying metal.

XPS analysis evidenced that Cu_2O remains the major compound present in the oxide layer before and after laser cleaning. After laser cleaning, some CuO, tenorite, is formed, which may be explained by the fact that tenorite forms at high temperatures, like the one induced by laser. The presence of CuO in the oxide layer, which natural colour is grey-black, could partially explain the effect of the discoloration after laser irradiation. Even though its proportion is so small (<10%), its location on surface and its colour could explain the grey aspect. This also contributes to say that the discoloration of surfaces covered with copper oxide does not seem to be due to a major chemical change, as the formation of tenorite is so tiny, and that it could also be an optical change due to melting.

Diffuse and specular reflectance spectrometry showed that the optical aspect was a crucial factor in the explanation of the discoloration effect. As cuprite is a rough and very absorbing material, only little reflection occurs when it is exposed to light, moreover mainly diffusely. The partial removal by

laser radiation of this highly absorbing red material increases the reflectivity of the surface, as highly reflecting metal is revealed and some is mixed with cuprite inside the melted layer. The presence of metal may also explain the shiny aspect of the surfaces exposed to laser radiation.

7.4. Discussion

7.4.1. Possible interpretation

The results previously exposed have contributed to understand the discoloration of surfaces covered with cuprite after exposition to laser radiation and an interpretation can be presented. The discoloration effect may occur as follows:

1. The sample surface is irradiated with laser light at wavelength 1064 nm, pulse length 10 ns, repetition rate 0,63 Hz.

2. Part of the laser beam is absorbed inside the oxide layer.

3. A thin oxide layer is removed by rapid thermal expansion[228] and melting of the underlying cuprite crystals and metal occurs. Globules form on the surface, in which cuprite and metal are mixed. A small amount of tenorite form, localized on top of the melted surface, which may contribute to the grey colour appeared after laser radiation of the surface.

4. At the end of the laser pulse (10ns), the surface cools down and freezing of the globules occurs. Cuprite and metal recrystallize inside the globules.

5. As a result of surface melting, which produces a topographical change of the surface, the diffuse reflectance of light appears different than before laser irradiation. The grey aspect is perceived.

6. Immediately after irradiation and during the following weeks, visible signs of on-going oxidation are visible on the laser cleaned cuprite surface. Reoxidation of the surface begins, very quickly because of the heat induced by laser and therefore, very chaotically. Microcrystals form first, growing in size with time. Newly formed red copper oxide crystals make the surface slowly revert back to the more typical aspect of cuprite. The roughness of the surface is modified again and light is gradually reflected in the same way than it was before laser cleaning.

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[228] See Chapter 4.3.3.

The cuprite surface before and after laser cleaning is schematically presented as follows in figures 107 and 108.
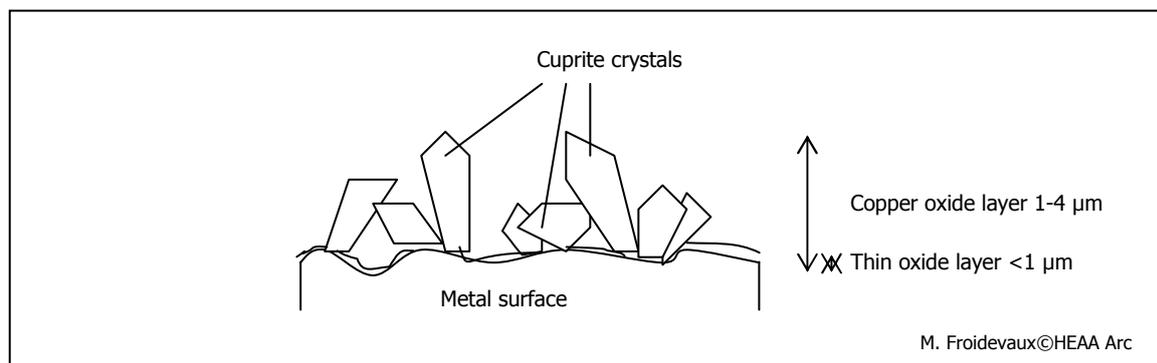
Figure 107 Schematic representation of the oxide layer before laser cleaning. The metal surface is covered with crystals of different size and a thin oxide layer (Cu_2O) on the metal.
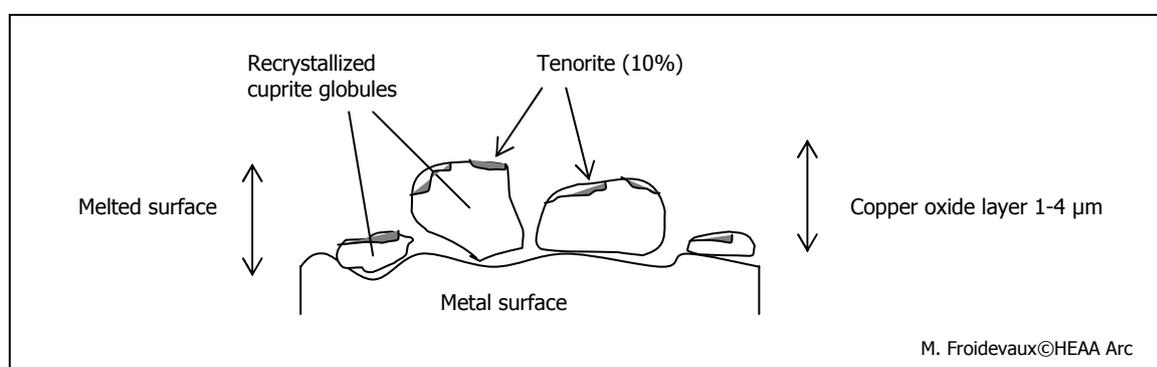
Figure 108 Schematic representation of the oxide layer after laser cleaning. The thin oxide layer has been removed by laser, revealing bare metal. The cuprite crystals have melted and then have recrystallized under the form of globules, presumably in which some metal is mixed. Tenorite is present on the top layer of the globules.

Thanks to high precision analytical methods, it has been established that laser radiation does nearly not change the chemical structure of cuprite, as only a small amount of tenorite is formed at a very thin depth. An important chemical change may then not be responsible for the discoloration effect. It seems most probable that it is also due to optical changes. Three hypotheses regarding optical changes have come out during the course of this research, which may be tightly linked and responsible for the discoloration effect, in addition to the presence of the small amount of tenorite:

- The grey / purple aspect may be due to a modification of the light diffusion. This physical process is similar to the one responsible for the blue colour of the sky.[229] Light diffusion is more important in the shorter wavelengths (blue part) and depends on the particles size, in this case, the cuprite crystals. As the colour of metallic copper is orange / red, it mainly

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[229] http://perso.orange.fr/philippe.boeuf/robert/physique/cielbleu.htm ;
http://www.meteo.org/phenomen/cielbleu.htm

reflects red. A large quantity of blue is absorbed but a small amount of blue and green is also reflected. As a result, cuprite, which lies on copper and which is partially transparent, absorbs blue and appears red before laser radiation.

Initially, the roughness of the cuprite surface is high and the crystals are large. Laser radiation provokes a decrease of the surface roughness (with formation of microcrystals due to immediate re-oxidation) and as a result, a change in light diffusion. As was previously mentioned, light diffusion is more important in the shorter wavelengths (blue part) and depends on the size of the crystals. White light diffused on microcrystals may then make it appear greyish / bluish. Within time, the copper oxide crystals go on growing, become larger, surface roughness increases again and hence, longer wavelengths (red part) are diffused, giving again a red colour to the surface.

- Another point that needs to be mentioned is that the human eye is naturally much more sensitive to the yellow, green, blue and violet part of the spectrum compared to the red part.[230] This means that with a surface reflecting on the same scale in the red and in the blue, the eye's perception of the blue will be much stronger than the red. On the reflectance spectra obtained in chapter 7.2.5., the laser cleaned area of the sample always shows a slight increase of reflectivity in the blue part, which may counterbalance and exceed the reflectivity in the red. This can be a secondary explanation of the grey / purple aspect of cuprite induced by laser radiation.

- The shiny aspect can be explained by melting, which modifies the surface topography by forming globules of mixed metal and oxide and leads to a decrease of the surface roughness. This provokes the deviation of light and increases reflectivity. The presence of metal mixed with cuprite in the form of globules may also explain the shiny surface aspect.

Moreover, the very absorbing layer of cuprite is partially removed by laser, locally revealing metal, whose reflectivity is much higher than the copper oxide.

7.4.2.   Influence of the results on the conservation practice of copper alloys with laser

From a conservation point of view, the results obtained in this research are positive. The discoloration effect of surfaces covered with cuprite was investigated in order to determine if it introduced massive damage or modification in the copper corrosion products of outdoor monuments, and the impact it would produce on the conservation practice.

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[230] http://www.ndt-ed.org/EducationResources/CommunityCollege/PenetrantTest/Introduction/lightresponse.htm

Objectively, slight damage has been noticed on the artificial samples, as melting occurs on the surface. But such a consideration should be taken with care for the following reasons:

1. Even though melting occurs on the samples covered with copper oxide, the layer has not suffered strong chemical modifications, as cuprite is still present in its crystalline state. Moreover, the formation of tenorite should not be an issue, as this copper oxide is even more stable than cuprite and will not be aggressive to the metal.

2. The samples used in this research have been artificially oxidized. This supposes that a surface corroded in real outdoor conditions may react differently, as such copper oxides products are often thicker, mixed with other corrosion products, inclusions and various contaminants. The fact that a small amount of metal melts with cuprite under the laser effect would maybe not happen on a real oxidized surface. Indeed, Philip Platt from the School of Materials Science and Engineering (University of Liverpool, UK)[231], also conducted at the NCC an analysis of the microstructure of a copper sample corroded in real outdoor conditions. He established no discernable heat affected zone in the bulk metal microstructure after laser irradiation at 1064 nm under the exact same conditions than the ones exposed in this report. It has to be mentioned again that the oxide layer artificially created was very thin, irregular and that exposed metal was already visible before laser cleaning. It is possible that a thicker and more uniform layer would not affect the metal underneath or produce less surface melting.

3. Optical changes are responsible for the discoloration effect, due to the topographical modification resulting from melting and due to the partial removal of cuprite, optically modifying the perception of the colour to the eye. This surface colour change will disappear with time thanks to the natural oxidation process occurring between the oxide and the air. The discoloured surface will slightly revert back with time to its initial red-brown typical colour.

4. Another important point to underline, which was revealed by the "spot by spot" laser cleaning tests, is that the intensity variations inside a single laser pulse is consequent and may be considered problematic. Indeed, the high intensity zones in the laser beam may remove cuprite, exposing metal, while low intensity generally produces a more grey aspect but does not expose metal. Obviously, such variations lead to localised different and unexpected interactions with the substrate, which may cause damage in the areas where the laser beam is very energetic. Hence, surface melting seems to be more extensive in such high intensity areas where more cuprite is removed, exposing metal. This is easily visible on cuprite brass and bronze samples, which show yellow spots of exposed metal, but even on cuprite copper,

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[231] Platt, 2007, p.51.

of which the totally grey surface also shows some metal coming through under optical microscope. From a conservation point of view, if the grey discoloration may appear as a side-effect of laser cleaning, the exposition of metal due to laser is a more important issue as the oxide layer is not preserved. Preservation of the oxide layer is fundamental because it plays the role of a natural protection against aggressive atmospheric conditions and other alteration factors. Removing the corrosion products to the metal is the thing conservators would always avoid.

Moreover, such variations in intensity may slightly falsify the fluence calculation, as it is made from an average of high and low intensities inside a single laser pulse. The obtained fluence values may then be less accurate, with laser exposed areas where fluence would in fact be lower or higher than what it should.

Practically, laser cleaning of artworks requires powerful laser systems which show the disadvantage of such variations in intensity. Certainly these systems will be improved in the future and such variations avoided. But at present and in the reality work, when handled by skilled conservators on real copper alloys surfaces, laser cleaning may not be so harmful. First because the layers to remove are much thicker on real sculptures than on artificial samples and the metal surface would not be reached so quickly. Second because laser cleaning of corroded artworks may require much less pulses than for the laser tests carried out in this research (< 12). Even though laser cleaning of copper alloys is not self-limiting like on marble, a skilled conservator can reduce the number of pulses to achieve a good cleaning level while minimizing the discoloration and the effects which are linked to it (melting, metal exposure).

8. Conclusion

Before concluding, it seems necessary to propose a few recommendations and ideas for the further research that will be undertaken in the field of lasers and copper alloys.

- **Equipment:** The use of a beam homogenizer could be useful in order to produce an even fluence level, without hot spots, across the beam cross-section. Such tools may reduce the power of the laser system but may allow the determination of a precise fluence all across the sample and thus, a safer and more accurate cleaning.

  It could be good as well to use an x-y table, like the one used here to clean the metal samples, which moves constantly instead of in steps. This would help producing a smoother rastering pattern. These two proposals may improve the results in the field of research under laboratory conditions.

- **Artificial corrosion:** During this project, it has been noticed that there is a lack of documentation regarding artificial corrosion formation for conservation or scientific purpose. It has been very complicated and time-consuming to find the right way to create artificial layers, as each author proposes its own recipes, often without giving all the necessary details. This was verified with the trials achieved to form artificial brochantite, which unfortunately was formed too late during this project. Such recipes may also produce a few surprises, like the nitrate salts deposition on the artificial cuprite surface. For further researches, it would be helpful to spend enough time testing various methods. In the case of artificial cuprite, it would have helped avoiding the nitrate crystals deposition due to the saturated solution, which required the dissolution of the crystals with acid. It would have been an advantage to keep the initial more regular oxide layer and see less apparent metal.

  Having a more regular copper oxide layer would also have allowed the accurate measurement of the thickness of ablated material. As the layer was so irregular, with metal coming through at some points, it was not possible to determine a precise level of cleaning. A very even cuprite surface would probably show it and allow an accurate measurement.

- **Further research:** what would be interesting to go on with the present research is to deepen the exposed hypothesis of light diffuse reflectance influencing the colour of the laser cleaned surfaces, as at the moment no scientific research could be carried out to assess it. Further spectrometric measurements and study of the surface roughness would help understanding the exact optical processes.

It would also be interesting to go on with measurements of the reversibility process over a longer period, in order to define if the discoloration totally reverts back or only to a certain extent.

Then, it could also be helpful to achieve similar laser tests on the same kind of copper alloys (copper, brass and bronze), but after prolonged exposure to real atmospheric conditions. Comparing their behaviour would be a good complement to the results obtained here on artificial samples. It would also allow the measurement of the layer ablated by laser. It could also be interesting to try explaining why the alloys covered with cuprite behave so differently under laser radiations.

At last, the use of femto-second laser cleaning is now under investigation and appears very promising.[232] This type of pulsed laser offers even shorter pulse duration (100 fs) and as such, thermal ablation processes can be avoided. It may be interesting for the cleaning of copper alloys, as very short pulse duration may allow a lower penetration depth inside the bulk material and reduce the depth of affected zone in the metal surface. This may also reduce melting or even avoid it.

At the term of this research, it seems that the various objectives exposed previously in this paper have been reached:

- The accurate observation and analysis of the laser cleaned copper alloy surface, both oxidized and corrosion-free, has evidenced that there could be large variations depending on the type of substrate, mainly on the type of alloy. The nature of the alloy, the surface state and preparation of an artefact may strongly influence how laser light will interact with it. This needs to be kept in mind by conservators and all the people dealing with laser cleaning treatments on copper alloys. Metallurgical analysis of the alloy composition can be a useful way to attempt predicting how a material will react under laser radiation. Of course, if this kind of analysis cannot be achieved, careful preliminary tests must be undertaken before any cleaning treatment with laser.

- The main questions concerning the appearance of the grey aspect due to laser radiation seem to have found an answer, or at list a plausible hypothesis. The discoloration effect seems to be mainly due to surface melting and decrease of the cuprite crystal density, which produces optical modification on the surface, perceived by the eye as a grey colour. The heat induced by laser radiation on the surface also produces the apparition of small amounts of tenorite

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[232] Barcikowski, 2000.

(CuO), a very stable copper oxide which grey-black colour may also be partly responsible for the grey appearance.

- The amount of ablated material seems to remain very small. In fact, the copper oxide layer before laser cleaning was very thin (a few microns) and irregular and it hasn't been possible to establish the quantity of removed material, as no significant level of cleaning could be measured, even with the help of high magnification tools. One can say that laser does not remove more than 1-2 µm of material, as no sign of cleaning was clearly detectable under high magnification and as the heat diffusion length was measured at 2 µm.

- The discoloration effect of the surfaces covered with cuprite is slightly reversible, as it turns back to a more typical red colour in a 12 weeks time. This is due to the re-oxidation of the surface in contact with the atmosphere.

Considering these results, even though some melting occurs superficially, laser cleaning is not more damaging than any other tool used today for the cleaning of copper alloys outdoor monuments. It may even be preferred to abrasive techniques, as what was observed in this report is that it only removes a very small amount of original material. Moreover, the discoloration effect is much less pronounced on real samples and the visual modification seems to be more acceptable, as it may indicate less extensive melting. For very fragile or thin copper alloy surfaces, laser cleaning may certainly be one of the most gentle and sensitive cleaning technique available today. The cleaning efficiency could even be increased by using laser complementarily to other methods.

The important point is, and this is the positive point, that conservators using laser to clean copper alloys sculptures might now become aware of what really happens on the surface and what may produce the discoloration effect on surfaces covered with cuprite. They know that some melting occurs on the surface, but at the same time they know that the oxide layer is not heavily chemically transformed and that the discoloration would revert back with time to a more reddish colour.

Each cleaning technique shows advantages and disadvantages and very often compromises must be done. But even though some melting occurs on a thin layer of the surface, laser may be the gentlest method to clean highly damaged and fragile copper and copper alloy monuments. Like for each object and material, it is the choice of the conservator to consider the object and its conservation state with its own ethics, priorities, objectives and the available budget, in order to determine the most suitable cleaning technique.

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10. Figures index

11. Tables index

12. List of units and symbols

Centi   cm

Milli   mm

Micro   µm

Nano   nm

Pico   pm

Femto   fm

α Optical absorption coefficient at a given wavelength λ $\left[cm^{-1} \right]$

A   Absorption of the surface at a given wavelength λ (no unit)

a Amplitude (of a wave)

c_p Specific heat capacity (at 25°C and constant pressure) $\left[{J}/{gK} \right]$

D   Thermal diffusivity$= \dfrac{K}{c_p \cdot \rho}$ $\left[{cm^2}/{sec} \right]$

f Frequency $\left[s^{-1} \right]$

Hz   Herz

I   Intensity or incident laser beam power density $= \left(\dfrac{\text{pulse energy}}{\text{pulse length} \times \text{beam size}} \right) \left[{W}/{cm^2} \right]$

J   Joule

K   Thermal conductivity $\left[{W}/{cmK} \right]$

l_α Optical penetration depth $\left[m \right]$

l_{τ} Heat diffusion length $[m]$

ρ Mass density $\left[g \middle/ cm^3 \right]$

r Radius $[m]$

t Time $[s]$

t   Pulse length $[s]$

τ_l Laser pulse length or pulse duration $[s]$

T Temperature $[K]$

T_m Melting point $[K]$

ΔT Temperature rise $[K]$

π Pi = 3,14

υ Velocity (of a wave) $\left[m \middle/ s \right]$

W   Watt

λ Wavelength of electromagnetic radiation $[nm, \mu m]$

Appendices

1. Basics of laser technique

1.1. Components of the laser system

The laser system is constituted of three essential components:

- The *lasing medium* is the material emitting the laser beam and it defines the wavelength to be generated. It can be a gas, a liquid, a glass, a crystalline solid or a semiconductor crystal, depending on the characteristic required for a specific application (purity, coherence, power, divergence).[233] The most common lasing medium used today in conservation is the crystalline solid state Nd:YAG laser, mainly because of its excellent thermal and optical qualities and because it is a reliable, versatile and simple laser, able to deliver high peak power. In Nd:YAG, the lasing medium is a rod[234] of yttrium aluminium garnet, a synthetic crystal ($Y_3Al_5O_{12}$). It is doped with neodymium ions present as an impurity, which would be excited by the pumping light source. [235] It can be used in continuous or in pulse mode, depending on the pumping source.

  Excimer laser[236] is another type often used in conservation. It contains a mixture of two rare gases which leads to a UV emission (193, 248, 308nm). Its use in conservation is limited to the cleaning of paintings, as the higher heat level from Nd:YAG lasers can cause extreme damages to pigments. It has to be used inside studios, as Excimer laser systems are very large and the gases very corrosive.[237]

- The *pumping source*, which aim is to excite the lasing medium in order to obtain a population inversion (see below). It can be a flashlamp for pulsed mode lasers like Nd:YAG, a continuous light, diodes or sometimes another laser.

- The *resonator* is the optical cavity containing the lasing medium. Two mirrors are located at its ends, which reflect the excited photons back and forth into the cavity, leading to the amplification of the laser beam. One mirror, partially reflective, allows the outcome of the laser beam.

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[233] Cooper, 1998, p.35-38 ; Hecht, 1992, p.3.
[234] Hecht, 1992, p.96. A range of crystals can serve as hosts, which must show properties such as transparency, ease of growth and good heat-transfer characteristics. Garnet and ruby are the most common crystalline solid state medium.
[235] Cooper, 1998, p.30, 36 ; Hecht, 1992, p.19, 96.
[236] Hecht, 1992, p.202. The lasing medium in Excimer laser is a rare gas halide, such as ArF, KrF, KrCl, XeF, XeCl. *"An excimer is a molecule formed by the association of an excited atom with another atom in its ground state"* (Cooper, 1998, p.37).
[237] Cooper, 1998, p.37, 82-83 ; COST Action G7, p.20.

The laser system also includes a cooling system (with air or water) and accessories such as Q-Switch, harmonics generators or/and beam homogenizer.
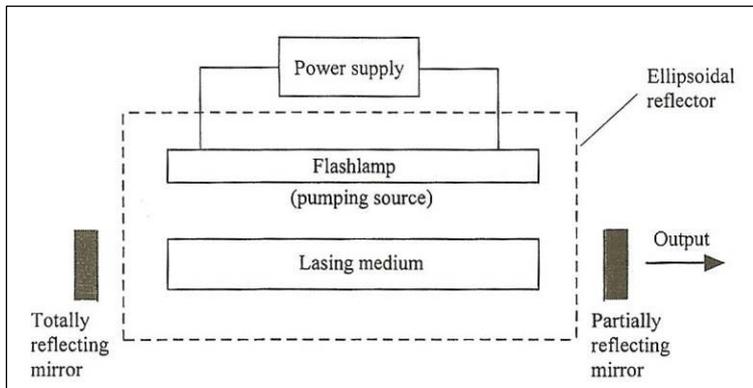
Figure 109 Schematic representation of a flashlamp-pumped Nd:YAG laser (From Cooper, 1998, p.30).

1.2. Pulsed / Q-Switched mode

In contrast to continuous mode, in which energy pumping is continuously applied, pulsed mode can be obtained by a pulsed pumping, such as a flashlamp. The laser pulse lasts approximately the time of the pumping.

One type of pulsed mode is called *Q-Switching* mode (or *giant pulse mode)* and it allows the generation of very short pulses (5ns-50ns)[238]. The shorter the pulse, the higher the peak power. Thus, the intensity released in a single pulse can be very high, but as the pulse is so short, heat doesn't propagate deeply through the bulk material.[239]
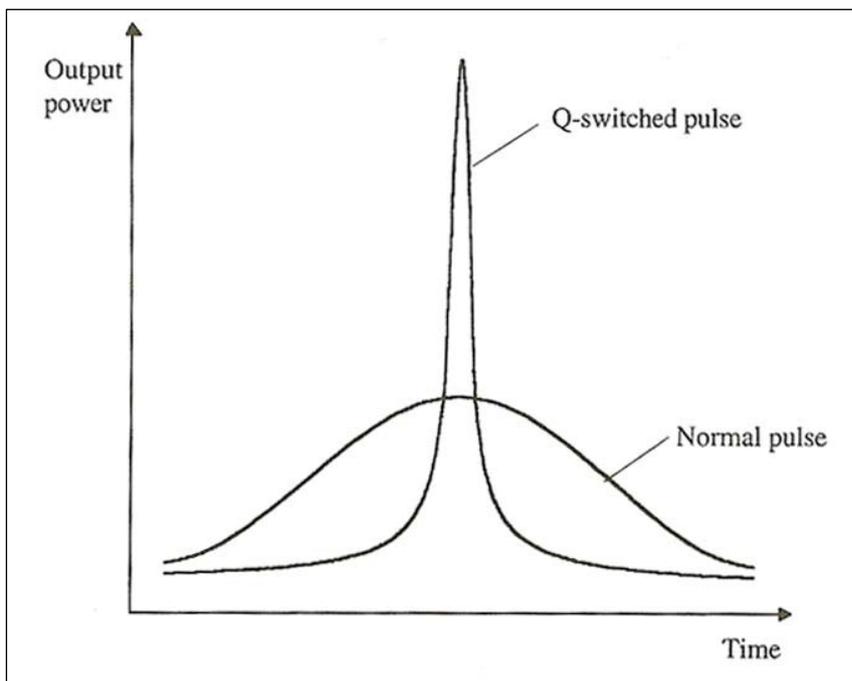
Figure 110 Schematic representation showing the difference in intensity between a Q-Switched laser pulse and a normal laser pulse (From Cooper, 1998, p.31).

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[238] Watkins et al., 1994, p.909 ; COST Action G7, p.3.
[239] Hecht, 1992, p.401.

1.3.   *Harmonics generation*

Some lasers can be modified to emit at different wavelengths, which are harmonics of the fundamental frequency. For example, the Nd:YAG can emit at 1064, as well as at the second harmonic 532, third harmonic 355 and forth harmonic 266 nm, respectively IR, green and UV wavelength. The harmonics are obtained by dividing the fundamental wavelength, respectively $\lambda/2$, $\lambda/3$, $\lambda/4$. This is achieved by passing the fundamental wavelength of 1064nm through a non-linear crystal, such as KDP (potassium dihydrogen phosphate).[240]

This device allows one to adapt the wavelength to the nature of the object or the material to remove, but shows the inconvenient of a loss of power.[241]

1.4.   *Singlemode / multimode lasers*

A single spot from a Nd:YAG laser is constituted of zones which differ in intensity. This variation in the distribution of the laser energy is a result of incoherent waves interfering inside the laser cavity and along the laser beam.

This phenomenon appears because Nd:YAG laser produces a *multimode* beam, which is common on pulsed laser[242]. *Multimode* lasers are more powerful than *singlemode* lasers, with a larger beam diameter but with a complex beam structure. In contrast, *singlemode* lasers (commonly continuous lasers) produce a round spot with a Gaussian intensity profile (TEM_{00}), which means that it is the brightest in the centre and becomes less bright at edges. *Multimode* lasers produce "multiple" beams arranged in a sort of structured pattern. The *multimode* beam profile would show numerous peaks of more or less high intensity, known as *hot spots*[243]. This property leads to an imprecision in the fluence level calculation of $\pm25\%$[244] and a safe cleaning appears more difficult to control.

Higher power of the Nd:YAG laser is desirable for laser cleaning applications, even if the beam quality is lower. In other applications, such as photochemistry, atomic, molecular and Raman spectroscopy, *singlemode* lasers are required, with a very pure and coherent beam[245].

A beam homogenizer[246] is an accessory that can help avoiding the beam variations in a *multimode* laser, as well as replacing the articulated arm delivery by a fibre optic.

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[240] Hecht, 1992, p.399 ; Cooper, 1998, p.34.
[241] Cooper, 1998, p.34 ; Hecht, 1992, p.45-47, 399.
[242] Bäuerle, 2000, p.83.
[243] Cooper & Larson, 1996, p.33 ; Cooper, 1998, p.62.
[244] Cooper, 1998, p.62.
[245] Cooper, 1998, p.33-34.
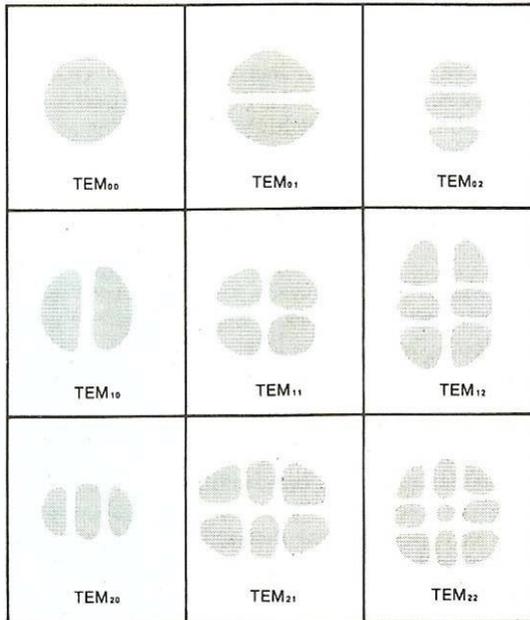
Figure 111 The first square shows the round laser spot of the singlemode beam (TEM$_{00}$). The following squares show the various patterns of higher order Gaussian beams. A multimode beam is a mix-up of such higher order beams (From Hecht, 1992, p.36).

1.5.   Generation of the laser radiation

The word *laser* is an acronym for « **Light Amplification by the Stimulated Emission of Radiation** ». This definition contains the basic principle of laser: "a laser amplifies light by a phenomenon known as stimulated emission"[247].

To understand it, one has to refer to the energy levels theory of atoms or molecules. When energy (light in the case of lasers, and more precisely light particles called *photons*) is absorbed by an atom or a molecule, the atom/molecule is transferred from its ground state, or ground energy level, to its excited state, or higher energy level. Emission, or energy release, occurs when the atom/molecule decays, which means that it returns to its more stable state, emitting photons. The emission of a photon can be spontaneous or stimulated.[248]

1.5.1.   Spontaneous and stimulated emission

In a **spontaneous emission**, atoms or molecules return to a lower energy level after a natural decay time (generally $10^{-10} - 10^{-3}$ sec.) without any external intervention.

In a **stimulated emission**, an arbitrary initial photon of adequate energy stimulates the emission of other photons, "*leading to a cascade of stimulated emission*"[249]. It has to be noted that the stimulated

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[246] Bäuerle, 2000, p.619-621.
[247] Cooper, 1998, p.21.
[248] Cooper, 1998, p.26-29 ; Hecht, 1992, p.23-31 ; www.shorelaser.com/About LasersDet.html
[249] Hecht, 1992, p.27.

photons rigorously have the same properties (frequency, direction) than the stimulating photons. This is the way laser light is produced.[250]
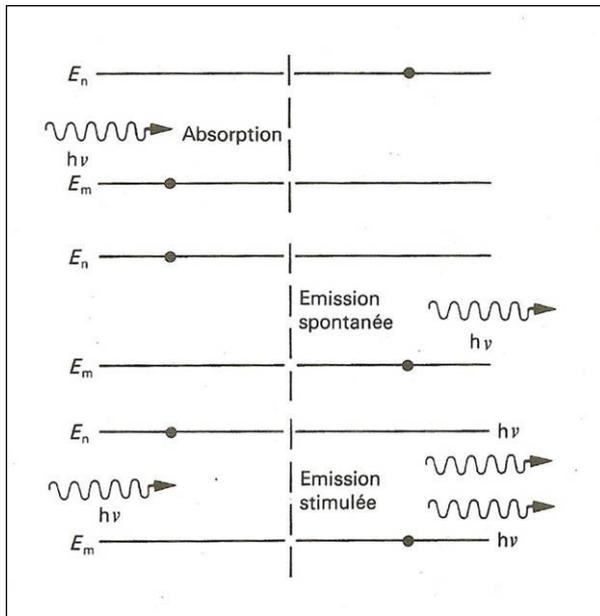
Figure 112 Schematic representation of spontaneous and stimulated emission of photons (From Dändlicker, 1981, p.13).

1.5.2.   Population inversion

For stimulated emission to occur, a population inversion needs to be created. This means that the atoms/molecules in the lasing medium have to be more numerous on the excited levels than on lower levels, which is contrary to the natural equilibrium. This is achieved thanks to the pumping source, which emits a high concentration of photons. This high energy is absorbed by the lasing medium and leads to a high increase of the number of excited atoms and molecules. This is the first step for amplification of the laser.[251]
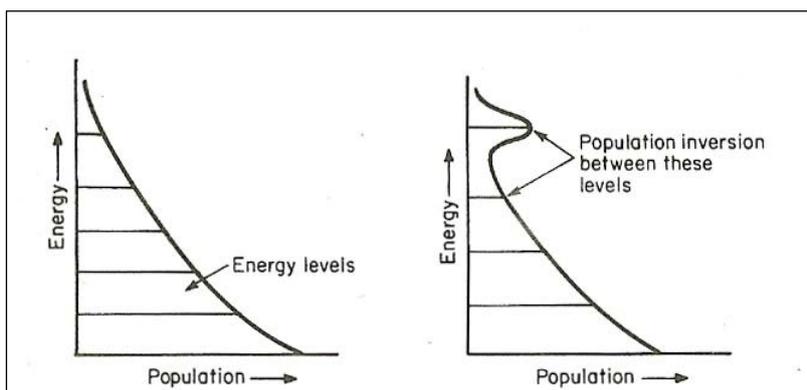
Figure 113 Distribution of populations in the energy levels at equilibrium (left) and during a population inversion (right) (From Hecht, 1992, p.28).

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[250] Cooper, 1998, p.28.
[251] Cooper, 1998, p.28-30.

1.5.3. Oscillation

The following excitation or amplification of the photons between the mirrors positioned at the ends of the resonator is called oscillation. The stimulation of the photons is increased and is concentrated in a beam oscillating back and forth between the mirrors.

Photons emitted out of the axis are lost and hence, only the along-axis photons provide the high concentrated and well-collimated beam.[252]

1.5.4. Generation of the laser beam

When the lasing medium returns to its initial stable state, laser light is produced. The laser beam goes out from the resonant cavity through one of the mirrors, which is partially transparent. It will be emitted as long as the lasing medium is excited.[253]

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[252] Cooper, 1998, p.30 ; Hecht, 1992, p.3.
[253] COST Action G7, p.3.

2. Laser safety

Properties of laser radiation (linearity, monochromaticity, coherence) make it a hazardous tool if no precautions are taken[254]. Laser cleaning systems are classified in the European laser safety standard IEC 60825-I. They are classified as class IV products, which means that the laser radiation emitted by such a product is hazardous to the unprotected eye when viewing directly, from a specular reflection or even from a diffuse reflection. Skin, fire and fume hazards can also be produced by such a class IV system.

- **Eyes:** The main hazard when dealing with lasers is done to the eye, as it is the most light-sensitive part of the body. The laser beam hitting the eye is focused to a point in the retina, where are located the cells responding to light. Depending on the wavelength of the laser, a different part of the eye will be touched (the retina with IR laser and the cornea with UV laser). Even a single short pulse (<1ms)[255] can cause permanent damage if it penetrates the eye. A single blink isn't quick enough to protect it against the beam.[256] Moreover, the laser beam remains hazardous a long way from the source (up to 100m).[257]

  To protect the eye, safety goggles must always be worn, with special filters adapted to the laser wavelength being used[258]. They have to fit well and to be covering enough to avoid beam specular reflections (from shiny surfaces) or diffuse reflections (from matte surfaces), sometimes coming from unexpected angles.[259] The fact that the infrared beam cannot be seen by the eye increases the possibilities of such reflections. Therefore, shiny objects (metallic tools, scaffoldings) have to be removed from the vicinity of the laser or covered with non-reflecting tape.

- **Skin:** Burns can be made to the skin exposed to laser light. A burn effect is produced at infrared wavelengths and photochemical damage with UV radiation. It is recommended to wear gloves, as well as a lab coat with long sleeves.

- **Inhalation:** Particles or fumes coming from the cleaned material have to be considered, as they can be extremely thin and can deeply penetrate the lungs or the skin. Sometimes hazardous waste products can issue from the cleaning process, like metallic compounds,

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[254] Coll., Introduction to Laser Cleaning of Artworks, p.14 ; Cooper, 1998, p.63-66 ; Hecht, 1992, p.8-10 ; COST Action G7, p.6-17 ; Vergès-Belmin *et al.*, 2003, p.263-266.
[255] Hecht, 1992, p.9.
[256] Vergès-Belmin *et al.*, 2003, p.264.
[257] COST Action G7, p.6.
[258] Different protective goggles have to be used when dealing with different wavelength due to harmonics generation.
[259] COST Action G7, p.7.

organic vapours, harmful bacteria, fungus, etc. An extraction system should be switched on and placed near the object during laser cleaning to absorb all the waste products.

- **Noise:** the rapid ejection of the material from the cleaned surface induces sound waves, perceptible as a "snapping" sound, which can be very loud. The long term effect of this type of hazard still hasn't been investigated.

- **Electrical shock:** Electrical hazard has to be considered, as a laser system usually includes a high voltage power supply. When the cooling system contains water, special attention must be due to eventual condensation or water loss. The laser system should never be opened by a person not trained for maintenance.

- **Other safety measures:**

It has to be noticed that all users of laser equipment must have received a specific training, in order to be aware of the potential hazards associated to the laser and follow the safe working procedures.

Users working for long periods of time with the laser shouldn't forget to take regular breaks.

As laser radiation is extremely powerful on large distances, the working area has to be controlled.

It should be enclosed in order to avoid hazards to peoples outside the laser zone.

Windows have to be blocked with an opaque material (black textile) which would absorb all the radiations.

Access has to be restricted and an interlock system has to be installed, which would turn the laser off when someone enters the area.

Hazard warning signs have to be displayed clearly and a warning light installed, which would indicate when the laser is operating.

Keys to the laser system have to be removed when it is not in use and stored in a separate room.

No other work has to be undertaken in the same area of the laser when it is in use.

All the equipment (laser system, warning lights, extractor, goggles) have to be maintained regularly and replaced or repaired if any technical problem is noticed.

3. Optical interaction of light waves with material

When laser light (and any light source in general) hits a surface, three different interactions occur: *absorption, reflection* and *transmission* of light (*refraction* occurs with light interacting with transparent bodies). The amount of each of these interactions will determine the optical appearance of the body, such as its shine and its colour.

3.1.   Absorption and reflection

Absorption and reflection are strongly linked. Light is always partially reflected and partially absorbed. The level of absorption depends on the wavelength of the light source and on the chemical and physical properties of the irradiated material. The surface roughness is an important parameter in both cases, as it influences the depth of absorption of the laser light inside the material and the amount of reflection at its surface. A rough surface of a given material, which reflects light in a diffuse way, absorbs much more of the energy from the beam than a very polished, mirror-like surface of the same material, which reflects light specularly and absorbs much less.[260]

Absorption plays the role of a filter for white light (which contains the whole visible spectrum), as the wavelengths perceived by the human eye are the ones reflected by the surface, while their complementary ones are absorbed. This property explains why Nd:YAG lasers are so widely used in conservation for laser cleaning purposes. The infra-red light emitted is often strongly absorbed by the dark layer of contaminants, while many underlying substrates absorb it very weakly and damage to the material to preserve is avoided.
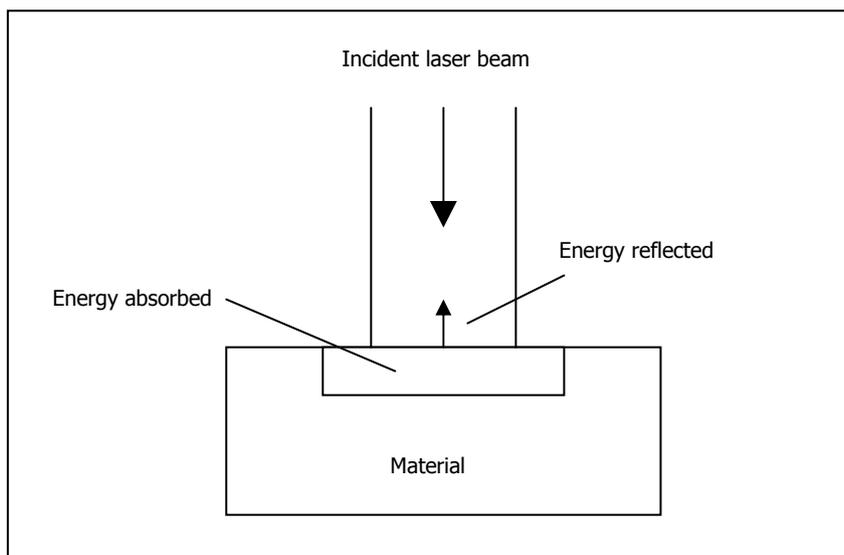
Figure 114 Schematic representation of absorption and reflection of a laser beam on a surface. (From Cooper, 1998, p.40).

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[260] Cooper, 1998, p.40-41.

Reflection can be more or less important. Here again, the roughness of the surface is of great importance with reflection. *Specular reflection* occurs when the incident beam hits a perfectly polished surface, producing a unique reflected beam. *Diffuse reflection* occurs on irregular surfaces, as the incident beam is reflected in all directions at a comparable intensity.[261] A surface will appear very shiny if a high quantity of light is reflected specularly, while a surface which reflects light diffusely will appear more matt.

M. Froidevaux©HEAA Arc

Incident light   Reflected light   Incident light

Working distance

100% specular reflection on a polished surface

100% diffuse reflection on a rough, matt surface
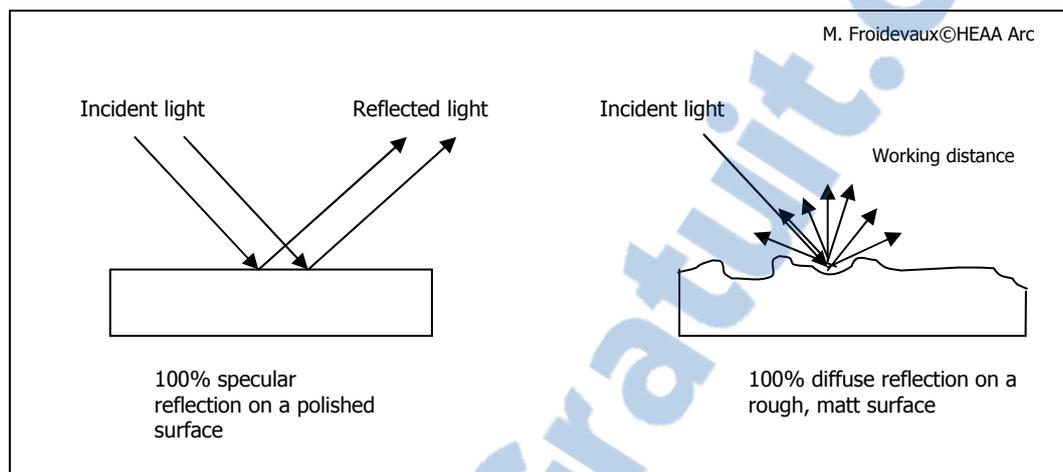
Figure 115 Schematic representation of specular and diffuse reflection from a surface.

3.2.   Transmission

Each visible colour is in fact either reflected light or light transmitted through a coloured material (for example pigments, loaded glass). The chemical structure of the material shows the property to absorb and reflect light selectively in different part of the visible spectrum. For example, crystalline materials may reflect light diffusely, in all directions, while their transparent or semi-transparent property may selectively transmit light. This may give a crystal its typical hue, by absorption of the complementary wavelengths (colour) of the visually detected colour.[262] Then, a red cuprite crystal appears red because the green-blue wavelength is absorbed and the red one transmitted.

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[261] http://fr.wikipedia.org/wiki/R%C3%A9flexion_optique
[262] Zuppiroli & Bussac, 2001, p.142.

4. Basics of metallography

Metallography is a science which consists in characterizing the microstructure of metal objects to determine its alloying properties, its manufacturing and sometimes its authenticity. A few introductive elements are presented here.

4.1.   *Grains*

In its solid state, a metal or an alloy shows a typical crystalline structure. This structure is mostly visible under the form of an aggregate of grains. This is a polycrystalline structure, where each grain is oriented differently. Grains are positioned directly in contact with each other, the contact point of which is named grain boundaries. 1 grain usually measures about 10 µm to 1 mm.

4.2.   *Phases*

When grains have different crystalline structures inside the same matrix, one says that different *phases* do exist. In the case of copper alloys, the microstructure comprises two ore more distinct phases. The elemental and chemical composition may greatly differ from one phase to the other.[263] For example, in copper and tin alloys, a two-phase structure is produced, as tin is only partially soluble in copper. This results in one phase constituted of nearly pure copper and the other richer in tin. With the addition of lead to copper alloys, both being insoluble into each other, the result is a phase constituted of globules of lead distributed in a matrix of copper.[264]

Inclusions, pores and cracks may also be present in the matrix and create chemical heterogeneities. This non-uniformity of the surfaces, with various phases, explains the different behaviour occurring on a metal object when it is exposed to a corrosive environment. These phases may result in localized or preferential corrosion of the least resistant phases, and galvanic corrosion can occur directly between the phases.[265]

Phase diagrams are a very useful way of recording information concerning the phase changes in many alloys systems. Such diagrams, with axes of temperature and composition, describe the different phases that may occur in an alloy. For more information refer to Avner, 1974, p. 155-224.

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[263] Pernot, 1999, p.65.
[264] Payer, 1992, p.108.
[265] Payer, 1992, p.108.

4.3. Technological impact on the metal microstructure

The appearance of the structure and the grains shape is also different regarding the surface treatment and technology used to create the object.

4.3.1. Casting

For example, the microstructure of cast alloys shows a dendritic structure, which is a tree-like structure randomly grown throughout the metal as it was cooling down, growing larger until they meet each other. The faster the cooling, the smaller the dendrites and so, the more resistant and harder the material[266]. Large and coarse dendritic structures produce a less resistant and softer metal. The growth of dendrites forms a phase different from the surrounding matrix, named segregation.[267]
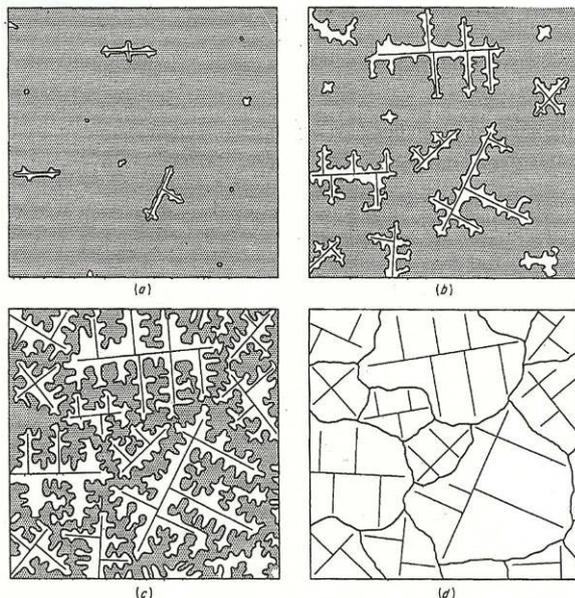
Figure 116 Schematic representation of the process of crystallization by nucleation and dendritic growth. a) nucleation; b) apparition of dendrites; c) dendritic segregation; d) grains (From Avner, 1974, p.95).

4.3.2. Working

Working refers to a number of methods which are used to change the shape of a metal by techniques such as hammering, drawing, turning, etc. Such treatments show a typical microstructure.

The grains, originally in a hexagonal shape, are flattened and dislocated to a certain point by cold-working, at which the metal becomes brittle. For further working, the metal must be annealed in order to restore ductility and malleability. The annealing process is performed by heating the material (generally until glowing) for an extended period of time and allowing it to cool slowly. This cyclic process can be repeated until the desired shape is obtained. Hot working is a combination of cold-

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[266] Avner, 1974, p.100-101.
[267] Henderson, 2000, p.209.

working and annealing, with the object being heated to red and then immediately annealed. Both processes will produce the same microstructure.

Characteristic parallel straight lines appear after annealing, named twin lines, traversing part or all of the individual grains. In heavily worked objects, strain lines may appear, which are a series of parallel fine lines in some of the grains.

Such treatments modify the properties of the metal, which strength and hardness increase while ductility decreases. The internal energy also increases, particularly at the grain boundaries, enhancing the risk for intergranular or stress corrosion, due to residual stresses resulting from working.[268]
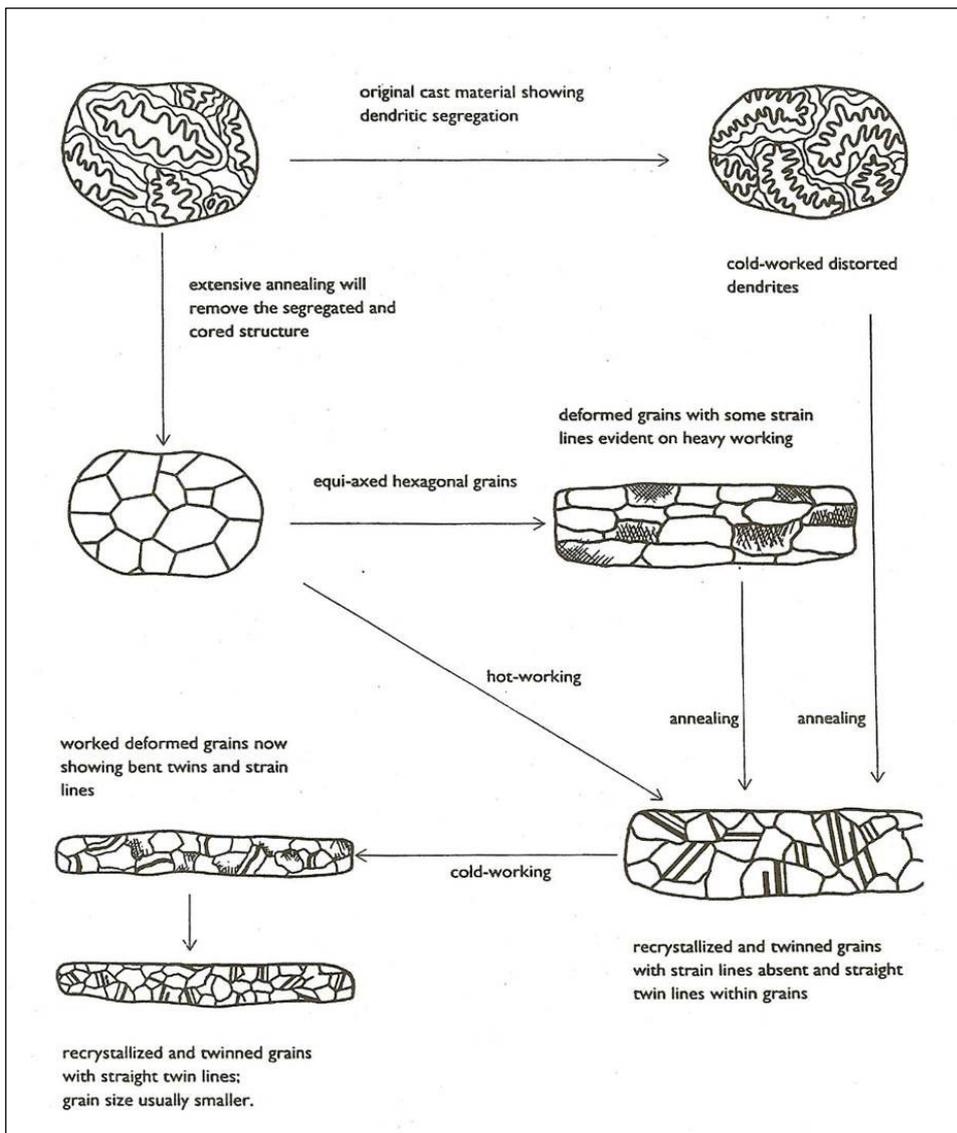
Figure 117 Schematic representation of the various working treatments and their effect on the metal microstructure (From Scott, 1991).

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[268] Avner, 1974, p.124-126.

4.4.   Microstructure observation

To observe this microstructure, one requires preparing the sample before using a metallurgical microscope. After being taken from the object in a way which avoids deformation and the use of heat, as this could modify the microstructure, the sample is mounted in a resin under vacuum and finely polished with always finer abrasive material (alumina, diamond, etc.). For the grains to become visible, a chemical attack needs to be performed, usually with an aggressive solution which will mark the grain boundaries or / and oxidize the grains surface. For copper and its alloys, the most common etching substances are aqueous ferric chloride, alcoholic ferric chloride or aqueous ammonium persulfate.[269]

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[269] Pernot, 1999, p.65.

5. Composition of the various copper alloys

5.1. Composition of the copper alloys constituting the Monuments to Queen Victoria and Lord Nelson

5.1.1. Brass ("commercial bronze")

Public Monument of Queen Victoria, Southport :

- Cu 86.8%

- Zn 11.9%

- Sn 0.8%

- Pb 0.2%

- Tiny traces of iron, nickel and arsenic

5.1.2. Copper

Public Monument of Lord Nelson, Liverpool :

- Cu 94.6-96.8%

- Zn 2.2-2.9%

- Pb 0.4-0.9%

- Tiny traces of iron, nickel, arsenic, silver, bismuth and sulphur

5.2. Composition of the copper alloys samples used for artificial corrosion and laser cleaning tests

5.2.1. Copper

- Cu 99%

- O_2 0.1%

5.2.2.   Brass

- Cu 58%
- Zn 30%
- Sn 0.3%
- Pb 1.5-2.5%

- Ni 0.3%
- Fe 0.3%
- Al 0.1%

5.2.3.   Bronze (« *gunmetal* »)

- Cu 85.5-85.76%
- Sn 7.38%
- Pb 2.19%
- Zn 4.67%
- Tiny traces of iron, nickel, antimony, phosphorus, sulphur, arsenic, bismuth, aluminium and silica

6. Table of metal properties for copper and its alloys

Table 5 From Bäuerle, 2000, Table II, p. 693.

Metal Properties						
	Symbol	**Copper**	**Brass**	**Bronze**	**Cuprite**	**Tenorite**
Absorptivity (of oxidized copper at 1064 nm) (no unit)	α	-	-	-	0.5	-
Absorptivity (of rough copper at 1064 nm) (no unit)	α	0,1-0,3	-	-	-	-
Absorptivity (of polished copper) (no unit)	α	0,04	-	-	-	-
Melting point (°C)	T_m	1084°C	900-940°C	850-1000°C	1508°C	1326°C
Density (g/cm^3)	ρ	8,94	8,5	8,8	6,1	6,3 – 6,4
Specific heat capacity (25°C) (J/gK)	c_p	0,39	0,38	0.36		
Thermal conductivity (W/cmK)	K	4	1,05	1,8		
Thermal diffusivity (cm^2/s)	D	1,14	0,33			

7. Technology

7.1.   Lost-wax process

Figure 118 From http://en.wikipedia.org/wiki/Lost-wax
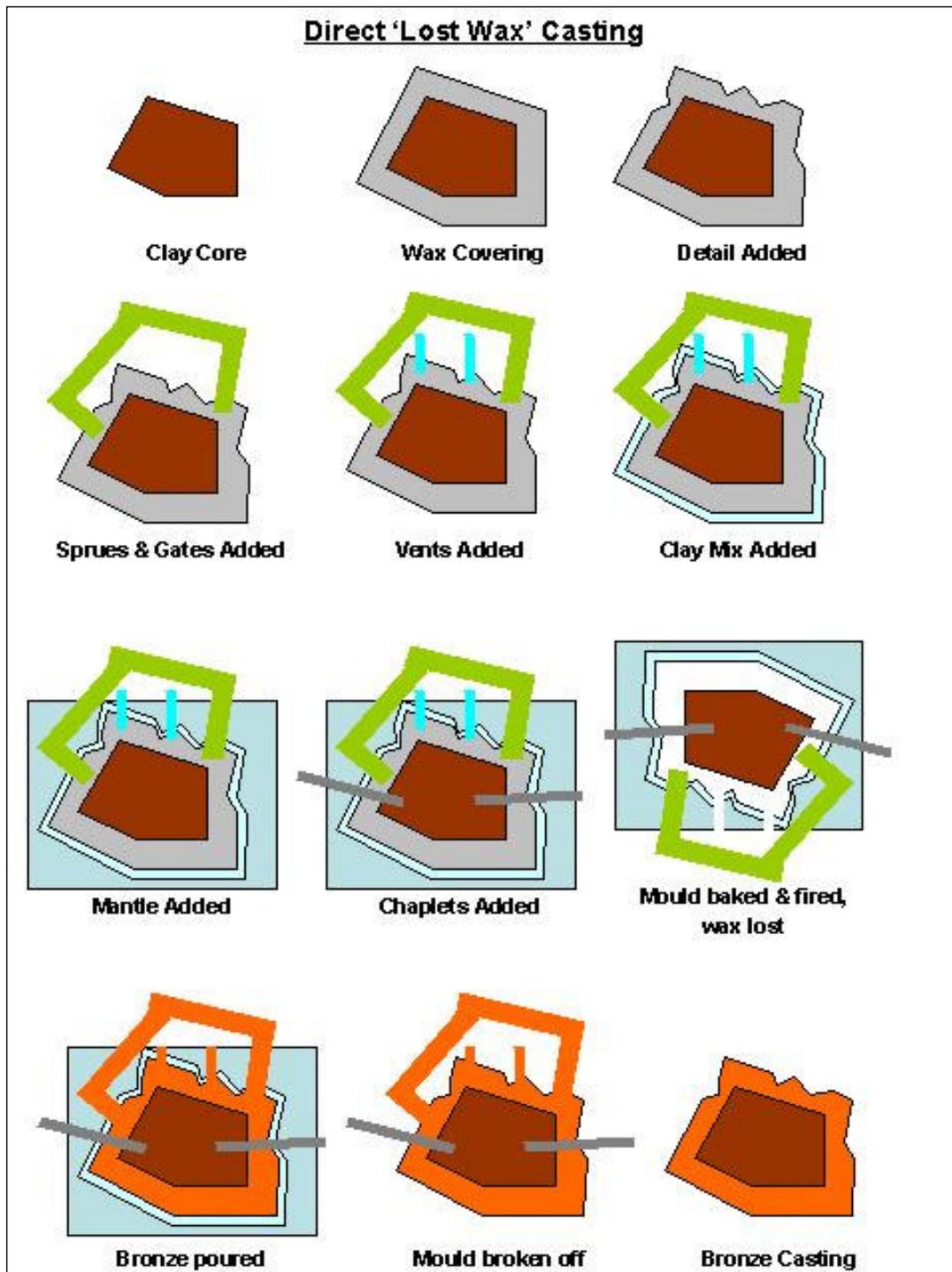
7.2.   Sand-casting process
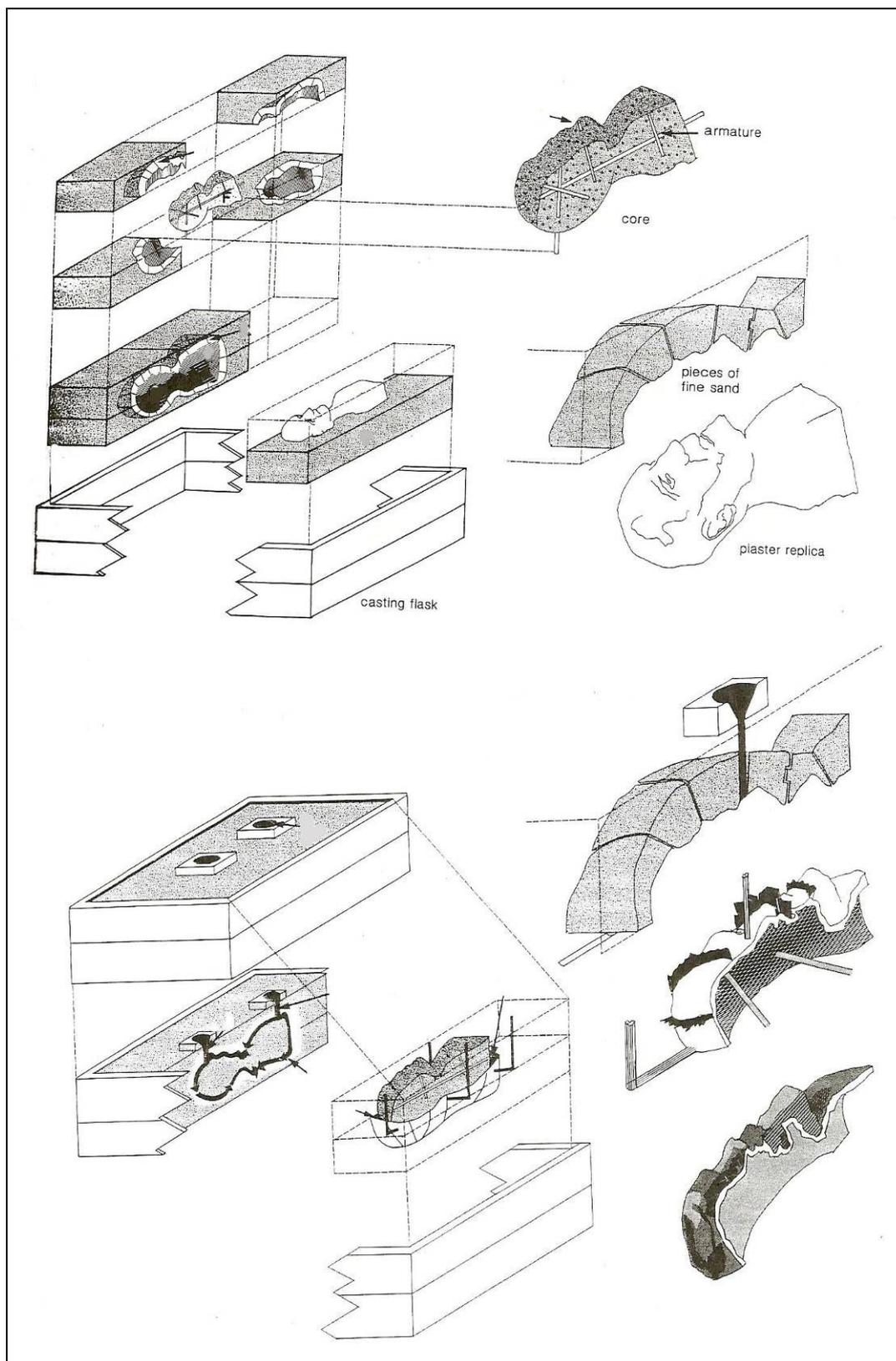
Figure 119 From Lins, 1983, p.9-10.

8. Optical microscope images

8.1.   *Bare metal samples*

Magnification: 200x

Copper	Un-cleaned	0.61 J/cm^2
	100 µm — M. Froidevaux©HEAA Arc	100 µm — M. Froidevaux©HEAA Arc
	0.85 J/cm^2	1.12 J/cm^2
	100 µm — M. Froidevaux©HEAA Arc	100 µm — M. Froidevaux©HEAA Arc

Magnification: 200x

Brass	Un-cleaned	0.61 J/cm^2
	0.85 J/cm^2	1.12 J/cm^2
	1.12 J/cm^2 – spot boundary	1.12 J/cm^2

Magnification: 200x

Bronze	Un-cleaned	0.61 J/cm^2
	0.85 J/cm^2	1.12 J/cm^2
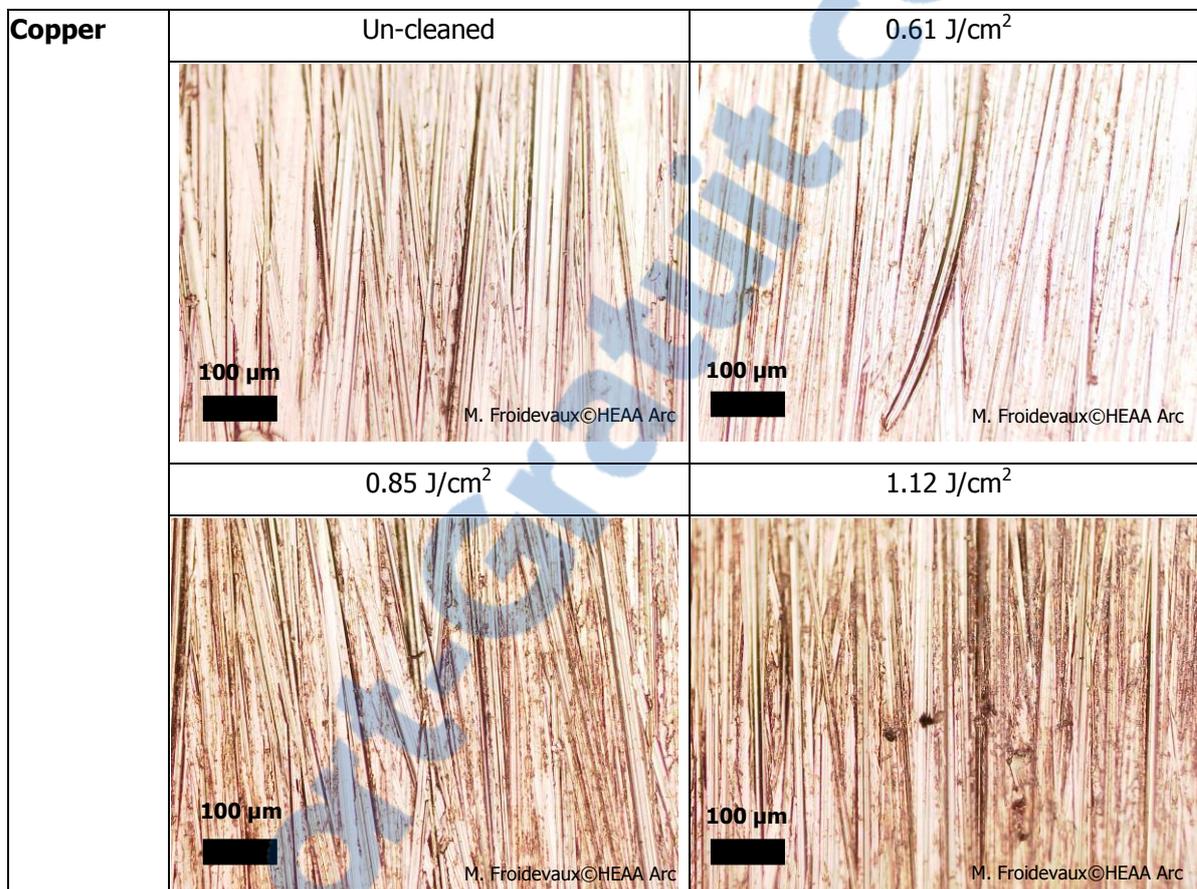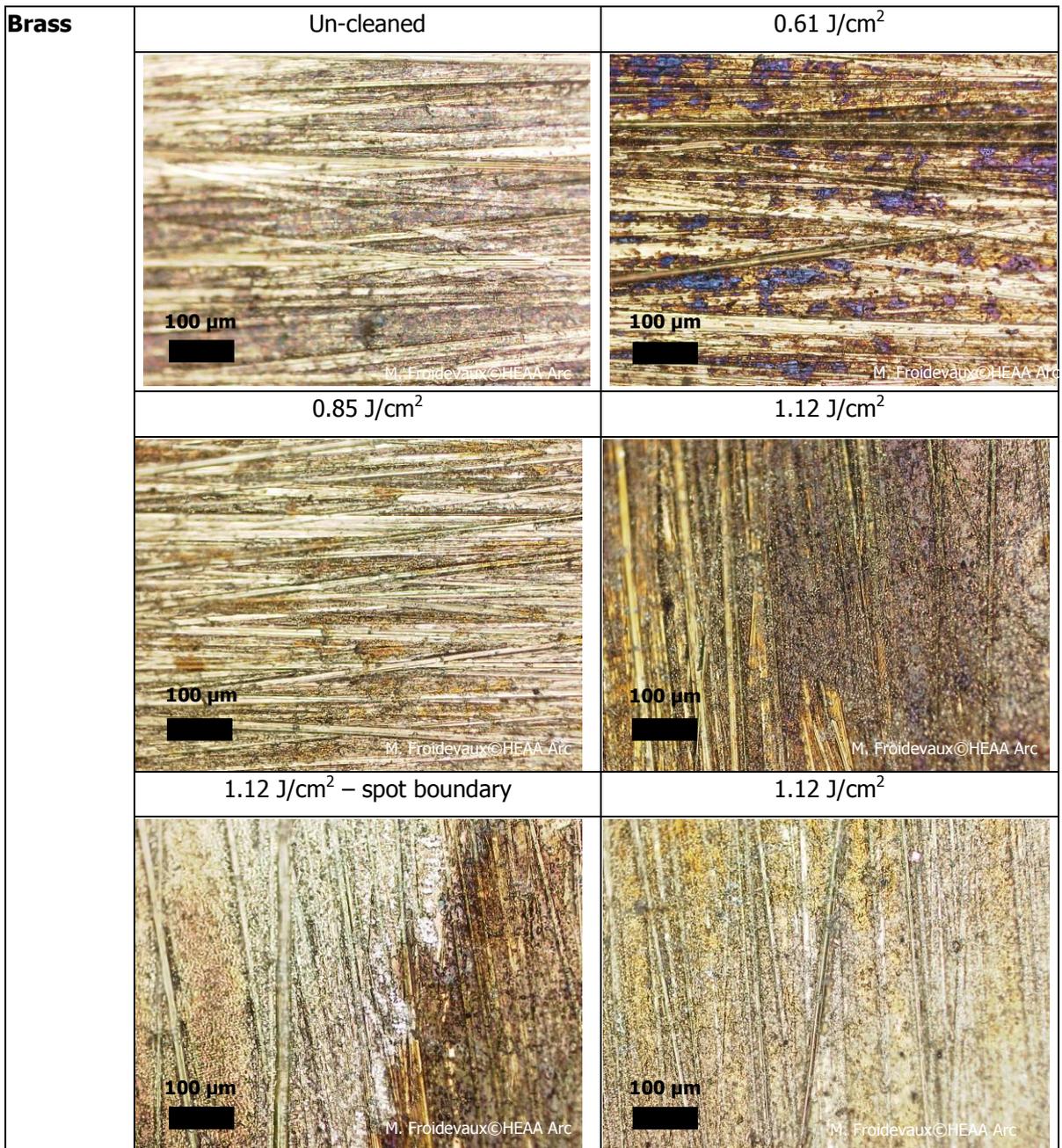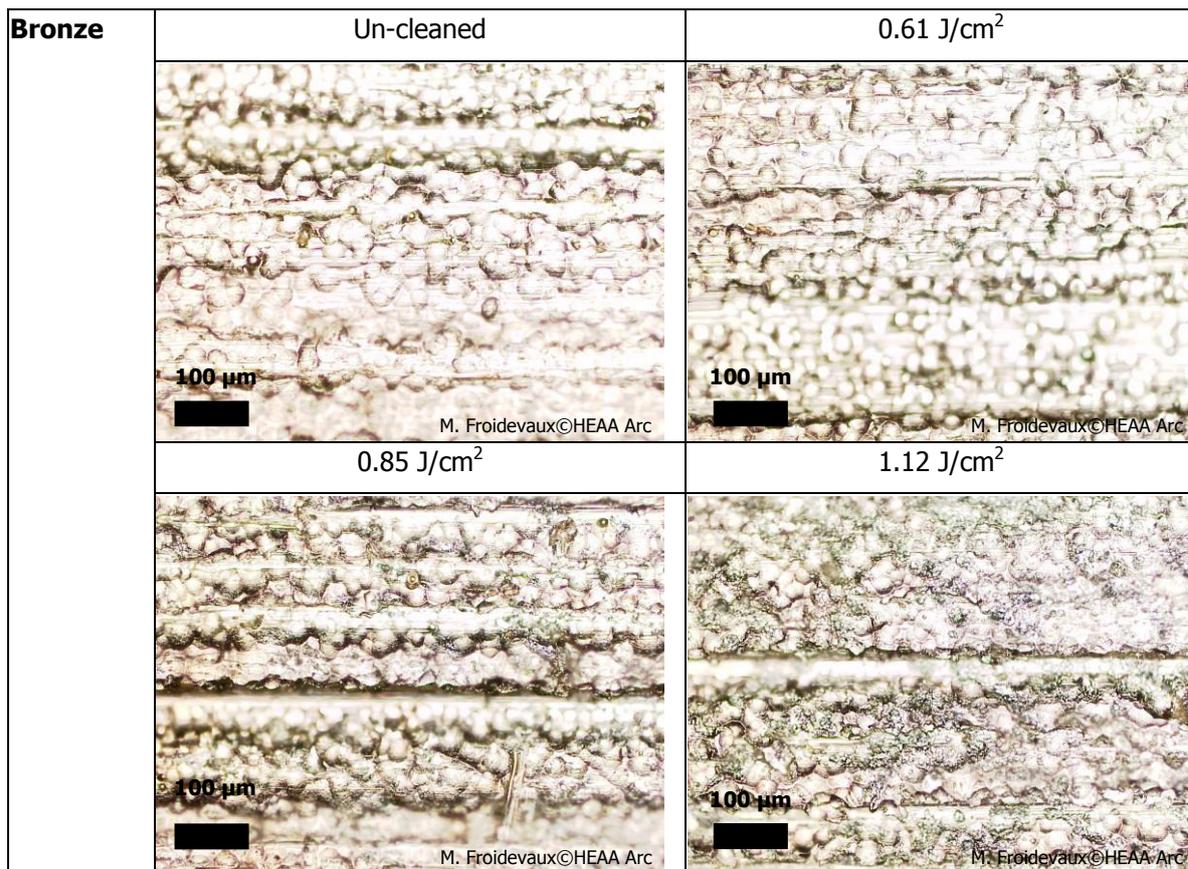
8.2. Cuprite samples

Magnification : 200x

Boundaries images : 100x

Copper	Un-cleaned 200x	0.61 J/cm^2 200x
	0.85 J/cm^2 200x	0.85 J/cm^2 boundary 100x
	1.12 J/cm^2 200x	

Brass	Un-cleaned 200x	0.61 J/cm^2 200x
	0.85 J/cm^2 200x	0.85 J/cm^2 boundary 100x
	1.12 J/cm^2 200x	1.12 J/cm^2 boundary 100x

Bronze	Un-cleaned 200x	0.61 J/cm^2 200x
	100 µm M. Froidevaux©HEAA Arc	100 µm M. Froidevaux©HEAA Arc
	0.85 J/cm^2 200x	1.12 J/cm^2 200x
	100 µm M. Froidevaux©HEAA Arc	100 µm M. Froidevaux©HEAA Arc
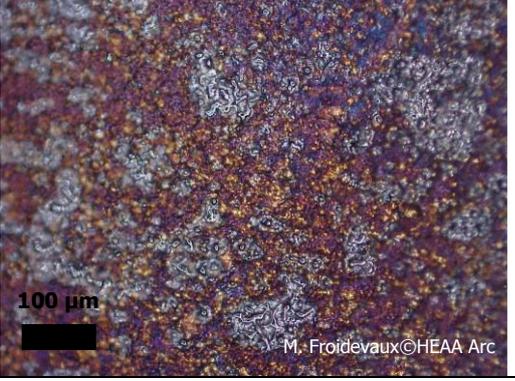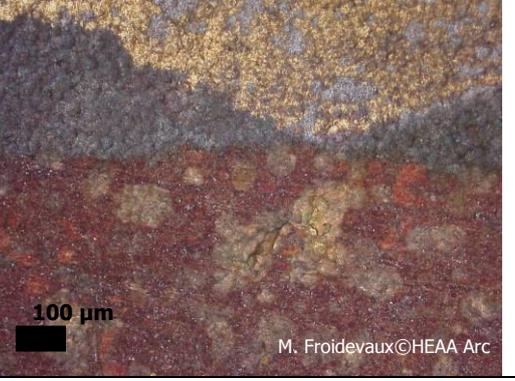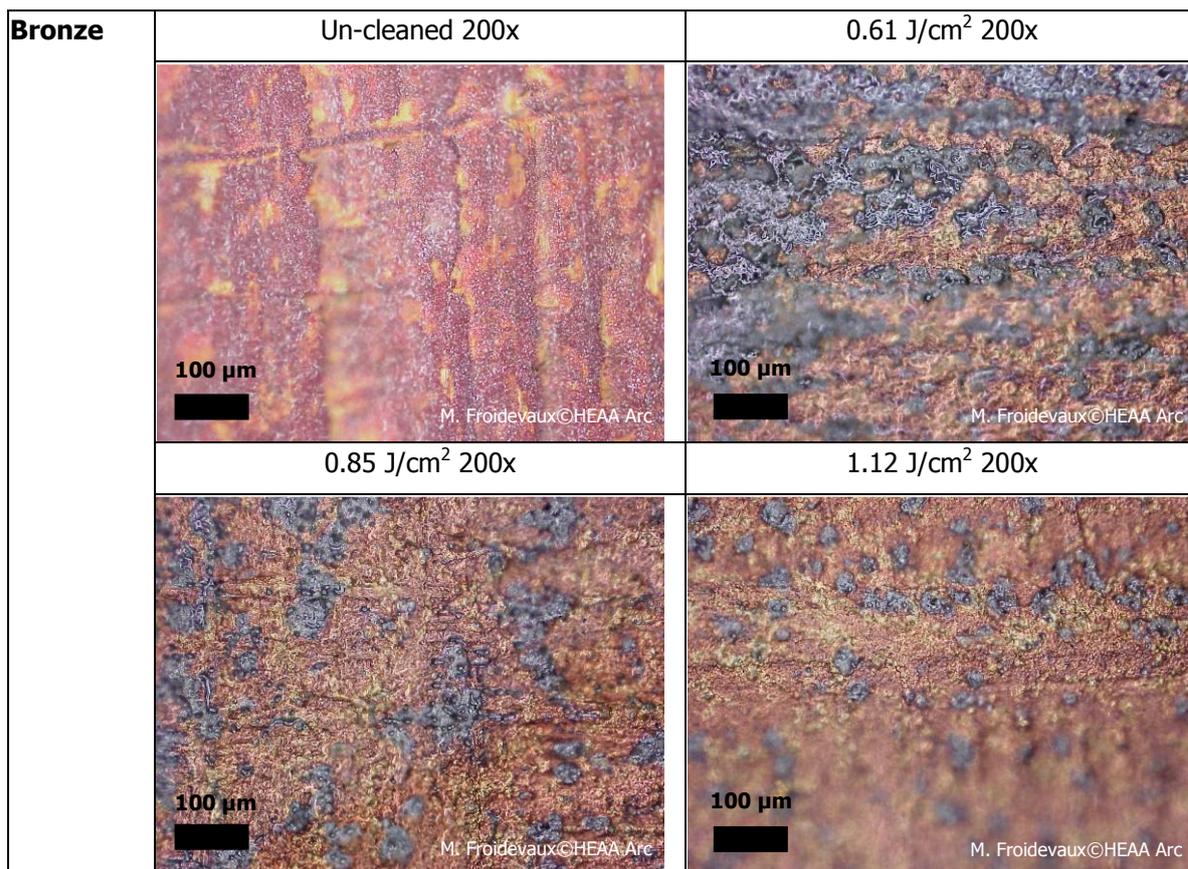
9. Spot by spot laser tests

12 successive laser pulses have been fired on each of the following metal substrates:

9.1. Bare Brass

M. Froidevaux©HEAA Arc
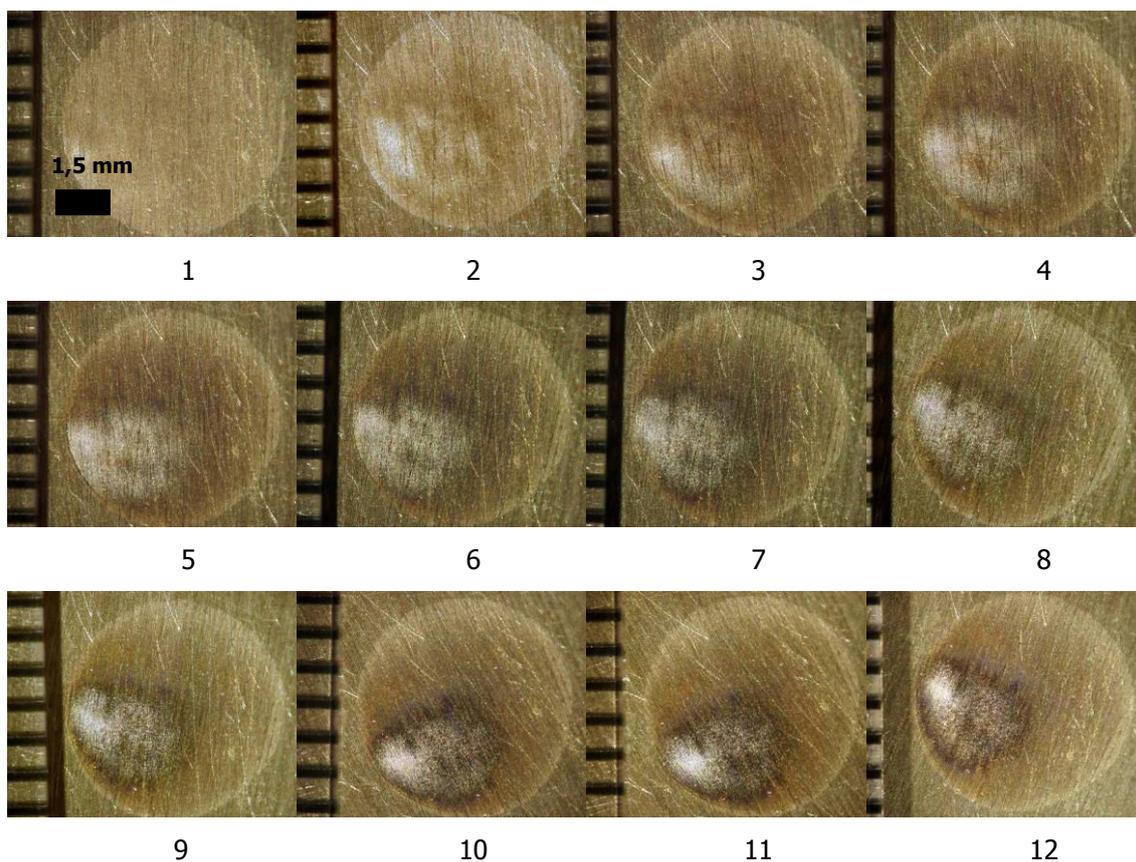
| 1 | 2 | 3 | 4 |

| 5 | 6 | 7 | 8 |

| 9 | 10 | 11 | 12 |

9.2. Cuprite Brass

M. Froidevaux©HEAA Arc
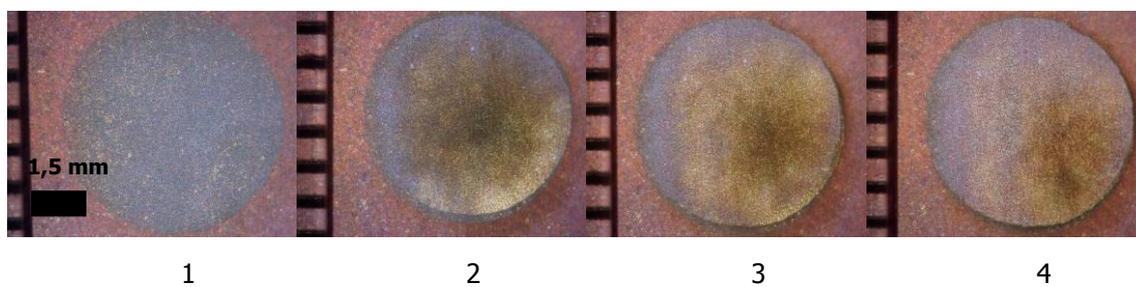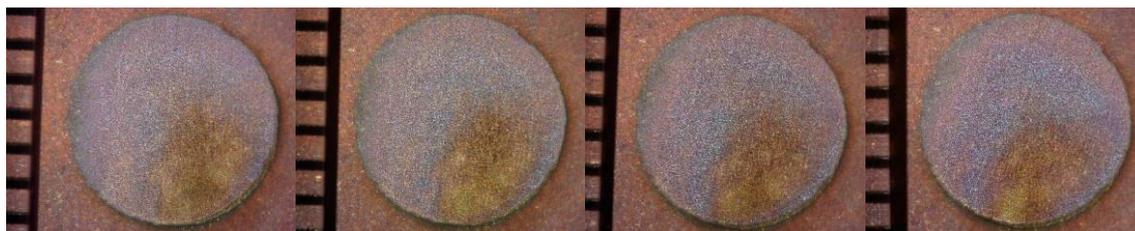
| 1 | 2 | 3 | 4 |

5   6   7   8

9   10   11   12

9.3. *Cuprite Copper*

M. Froidevaux©HEAA Arc
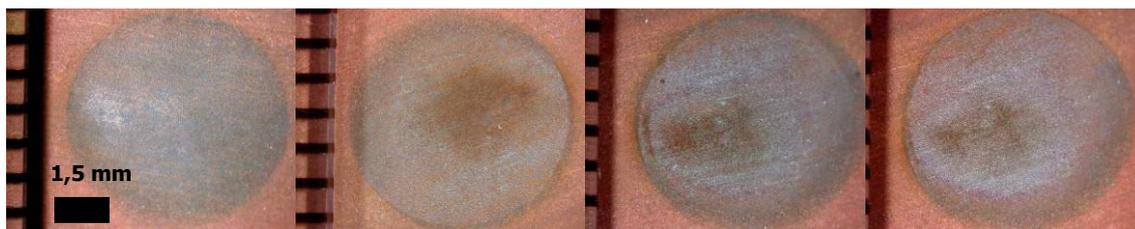
1   2   3   4

5   6   7   8

9   10   11   12

9.4. Cuprite Bronze

M. Froidevaux©HEAA Arc

1,5 mm

| 1 | 2 | 3 | 4 |

| 5 | 6 | 7 | 8 |

| 9 | 10 | 11 | 12 |
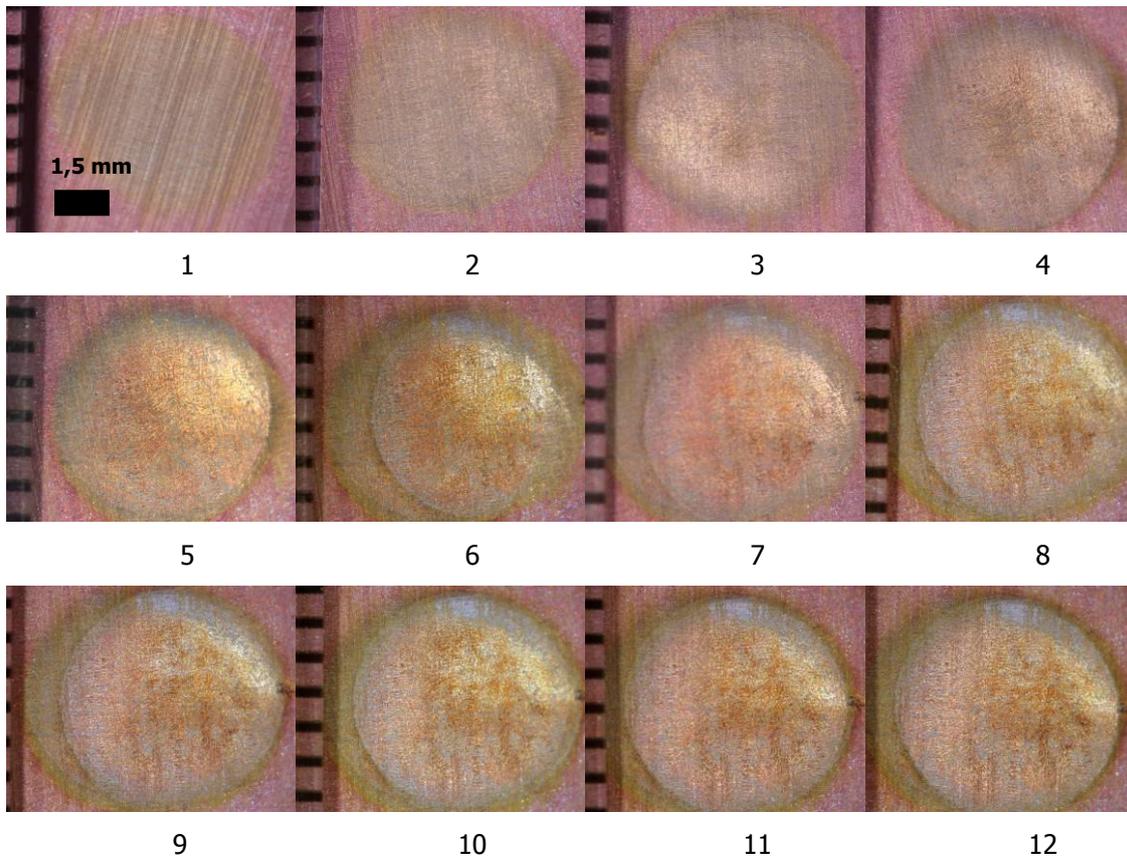
10. Spectrophotometry graphs

UC=un-cleaned

10.1. Un-cleaned / Laser cleaned cuprite samples at 0.61, 0.85 and 1.12 J/cm²
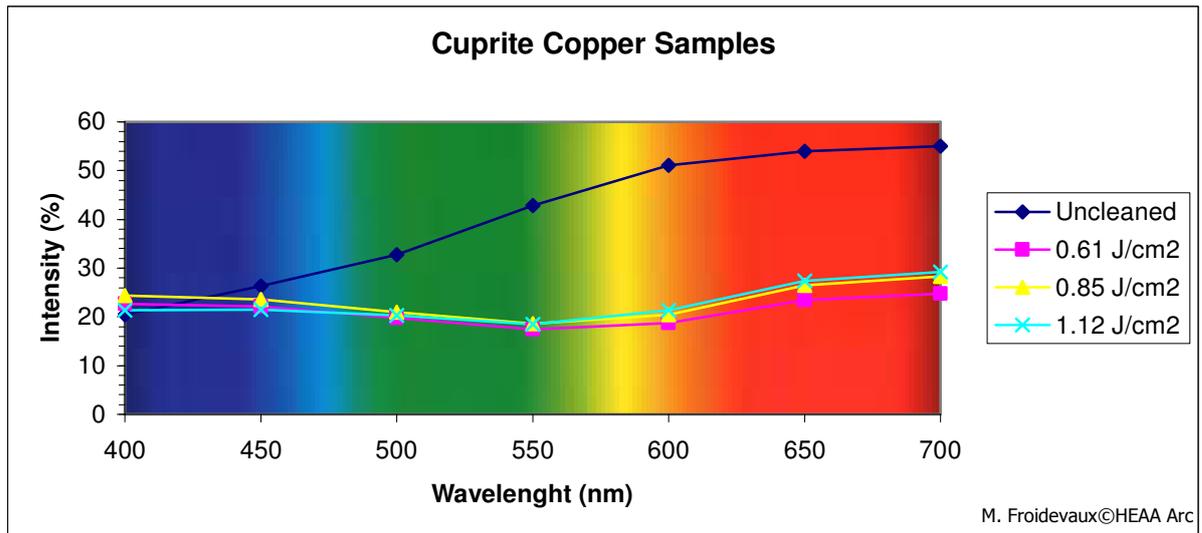
Figure 120 Cleaned / un-cleaned cuprite copper samples.
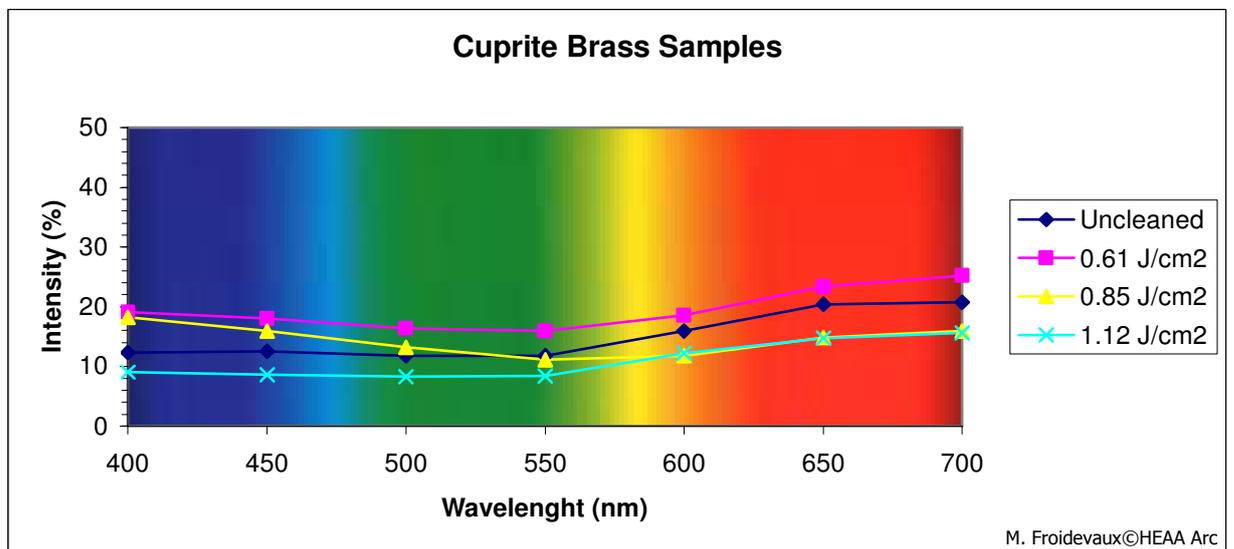
Figure 121 Cleaned / un-cleaned cuprite brass samples.
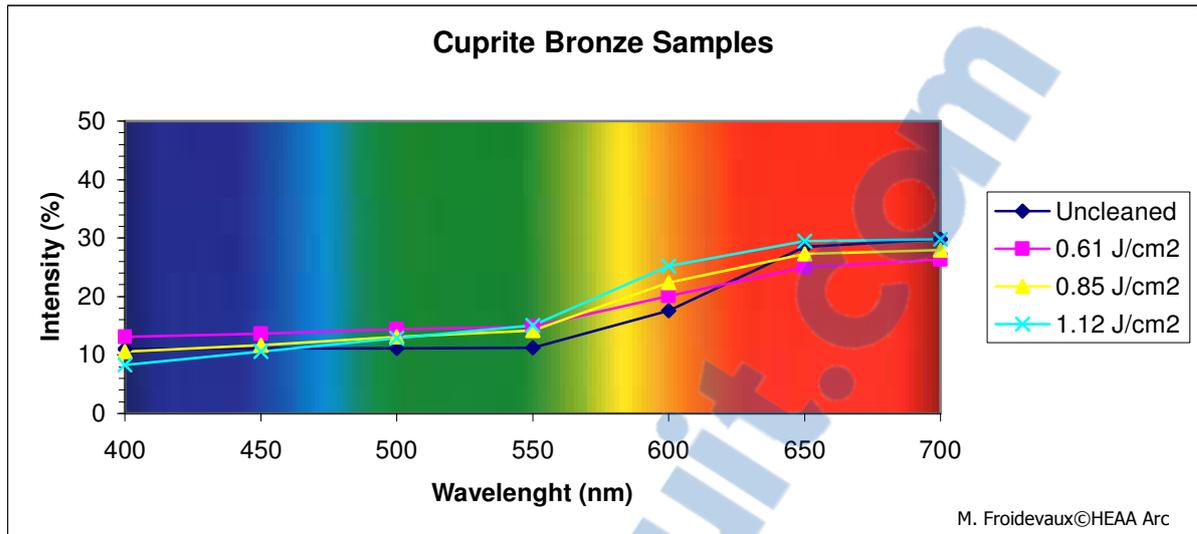
Figure 122 Cleaned / un-cleaned cuprite bronze samples.

10.2. Discoloration effect on 12 weeks

Remark: UC = un-cleaned

10.2.1. Cuprite copper
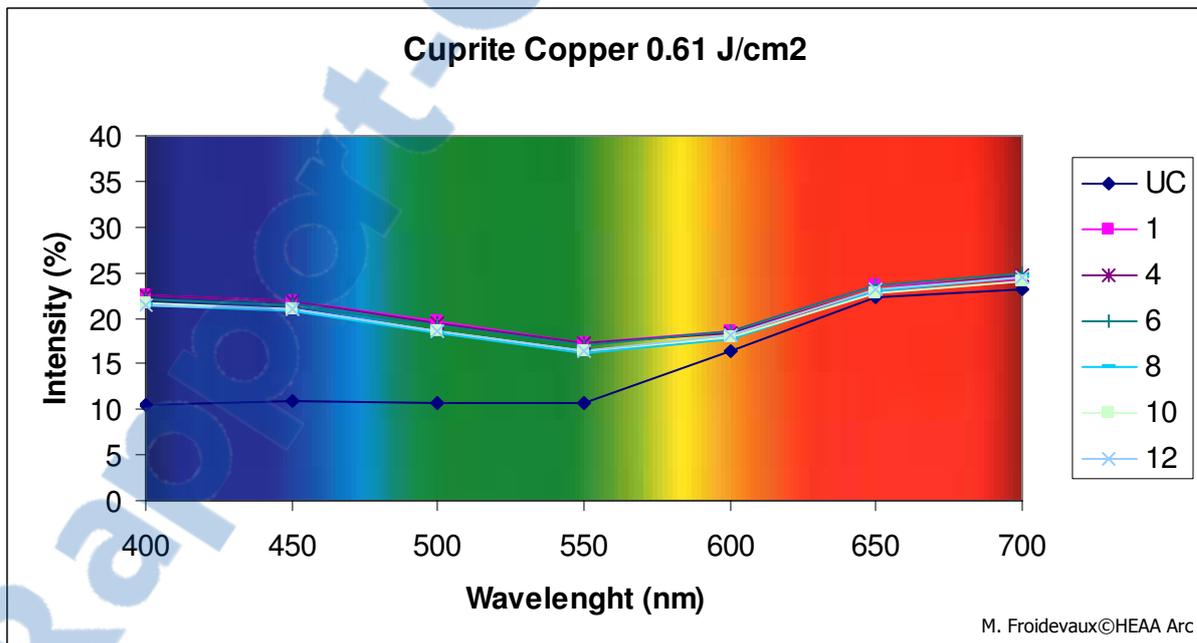
Figure 123 Reversible effect on cuprite copper after laser cleaning at 0.61 J/cm^2.
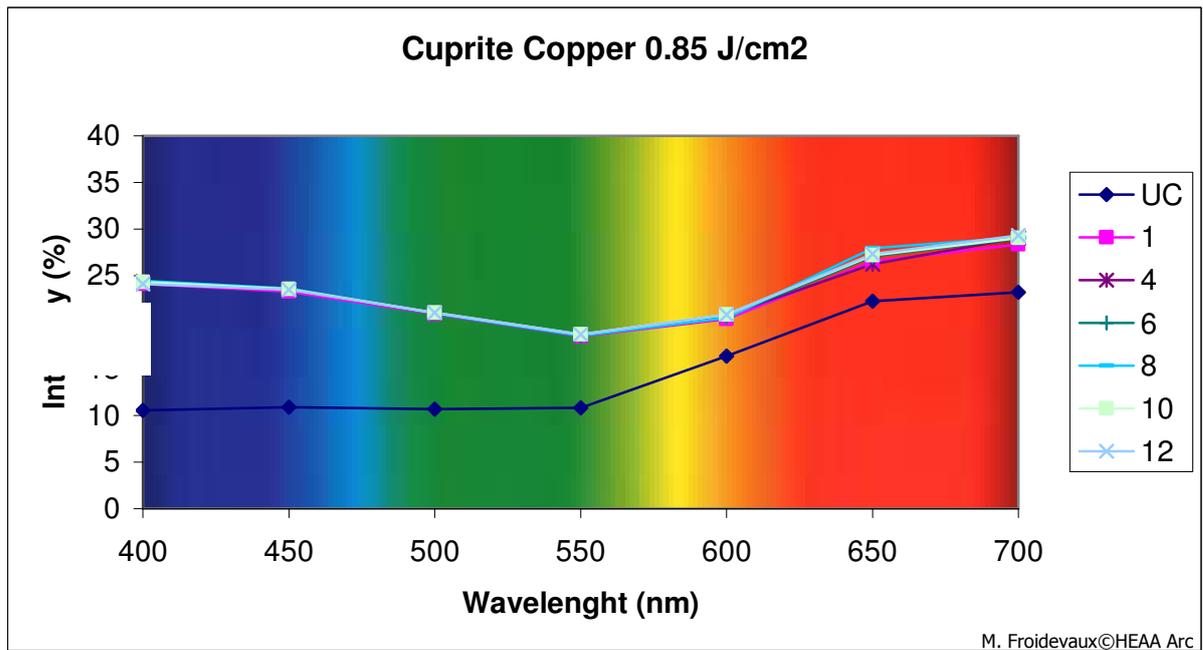
Figure 124 Reversible effect on cuprite copper after laser cleaning at 0.85 J/cm^2.
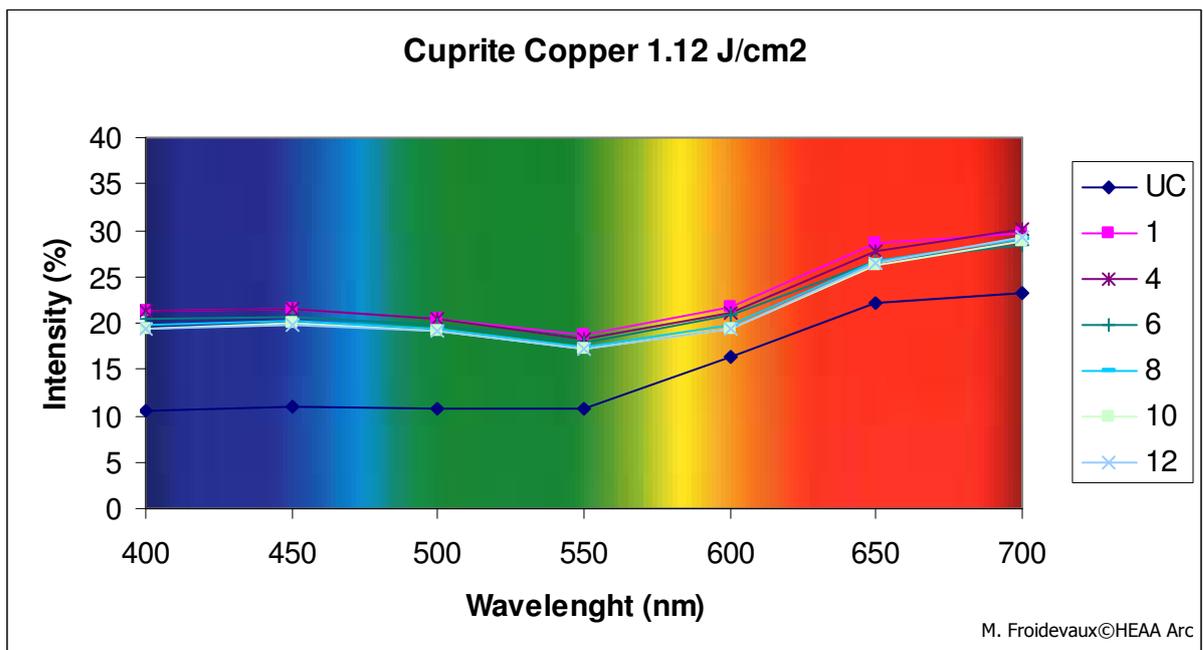
Figure 125 Reversible effect on cuprite copper after laser cleaning at 1.12 J/cm^2.

10.2.2. Cuprite brass
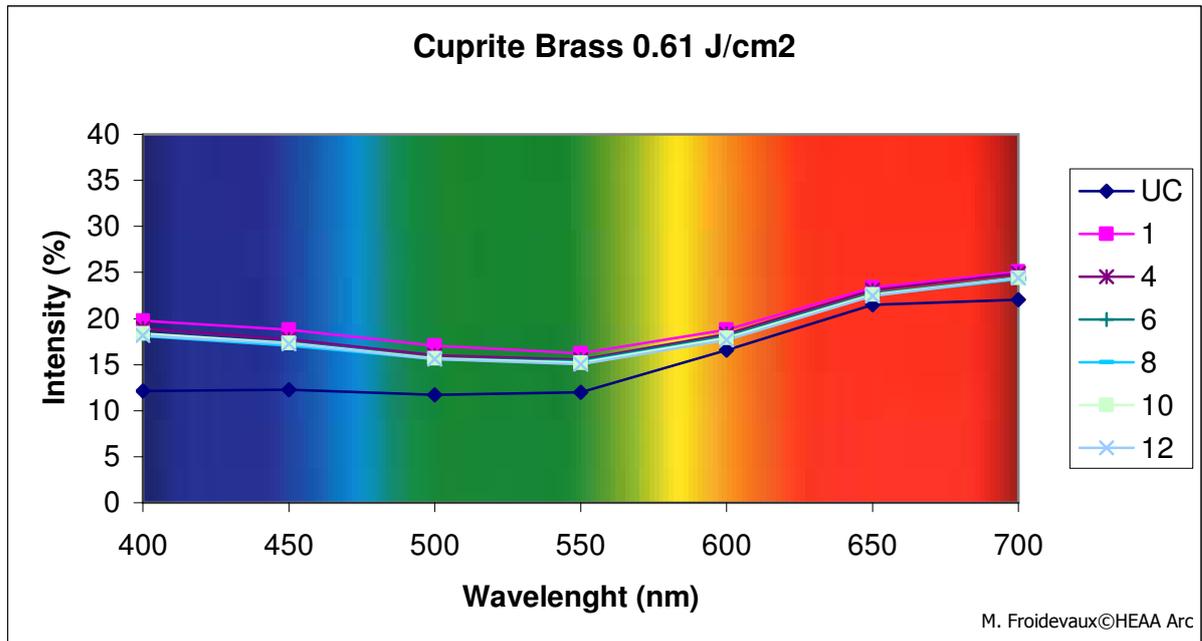
Figure 126 Reversible effect on cuprite brass after laser cleaning at 0.61 J/cm^2.
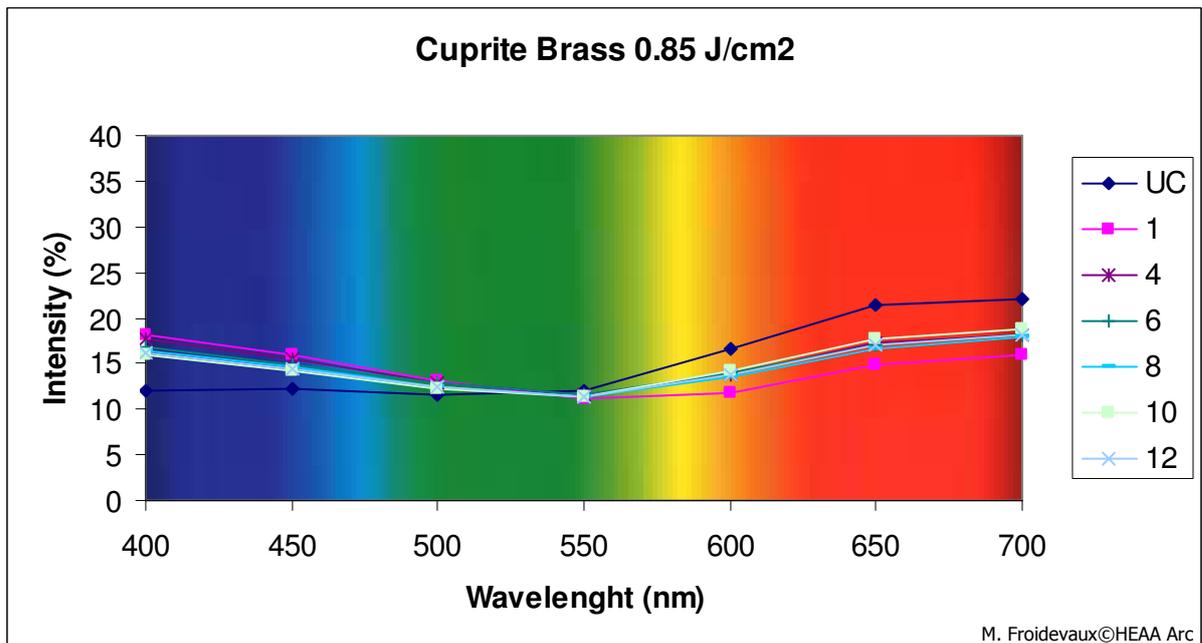
Figure 127 Reversible effect on cuprite brass after laser cleaning at 0.85 J/cm^2.
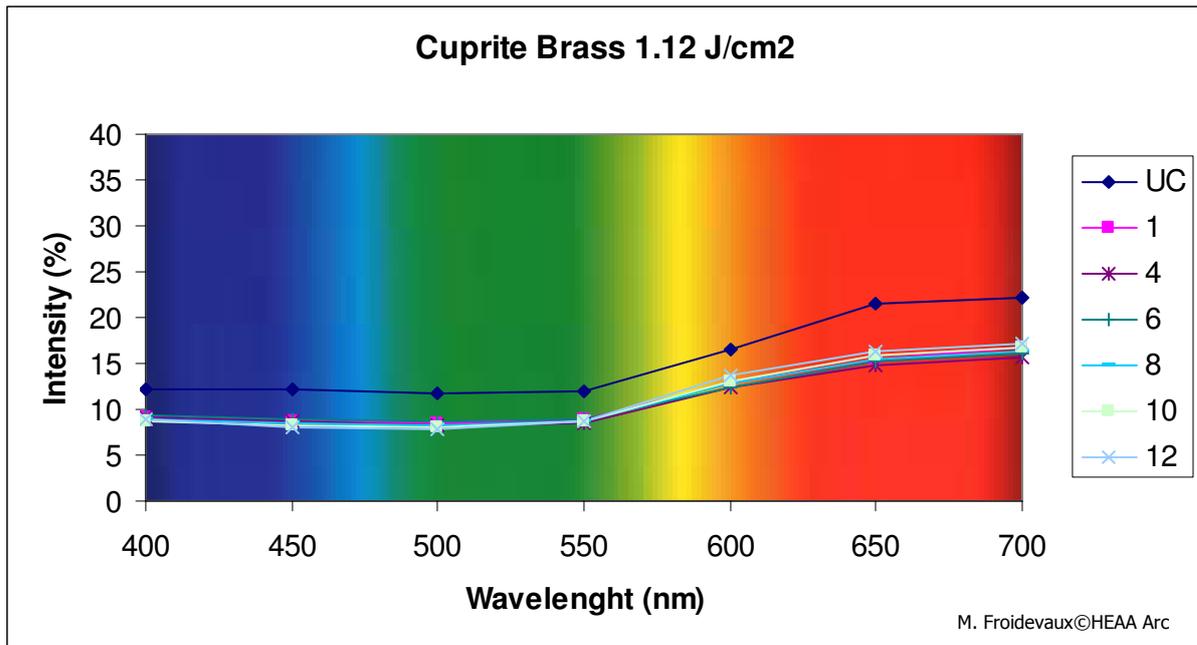
Figure 128 Reversible effect on cuprite brass after laser cleaning at 1.12 J/cm^2.

10.2.3. Cuprite bronze
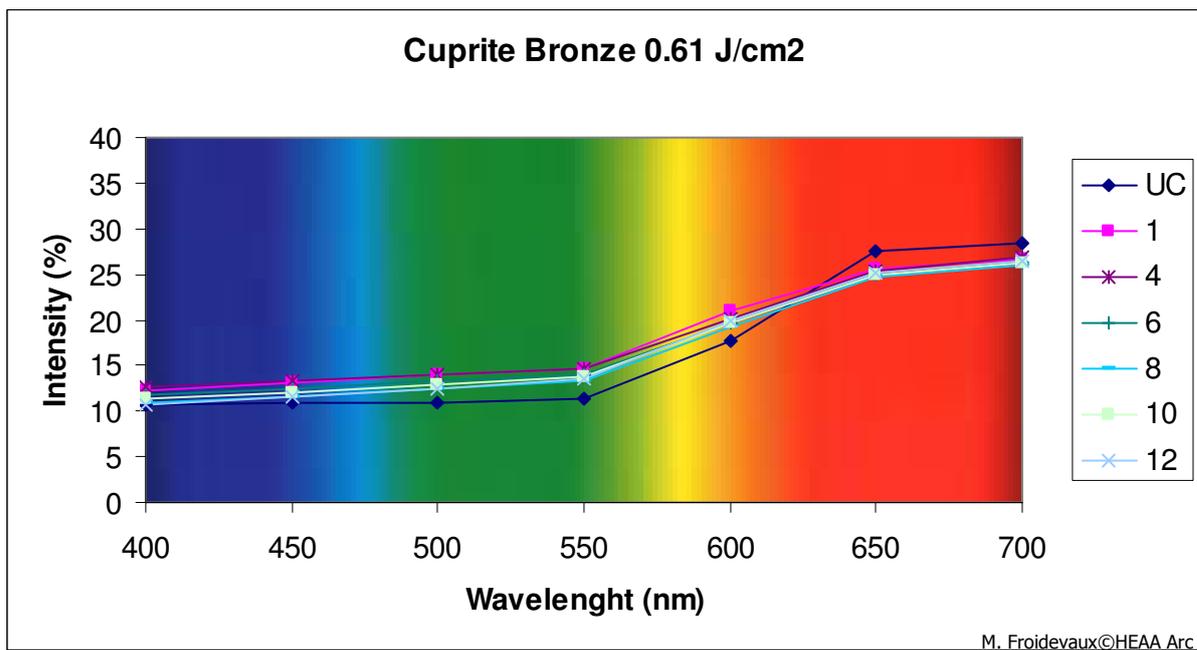
Figure 129 Reversible effect on cuprite bronze after laser cleaning at 0.61 J/cm^2.
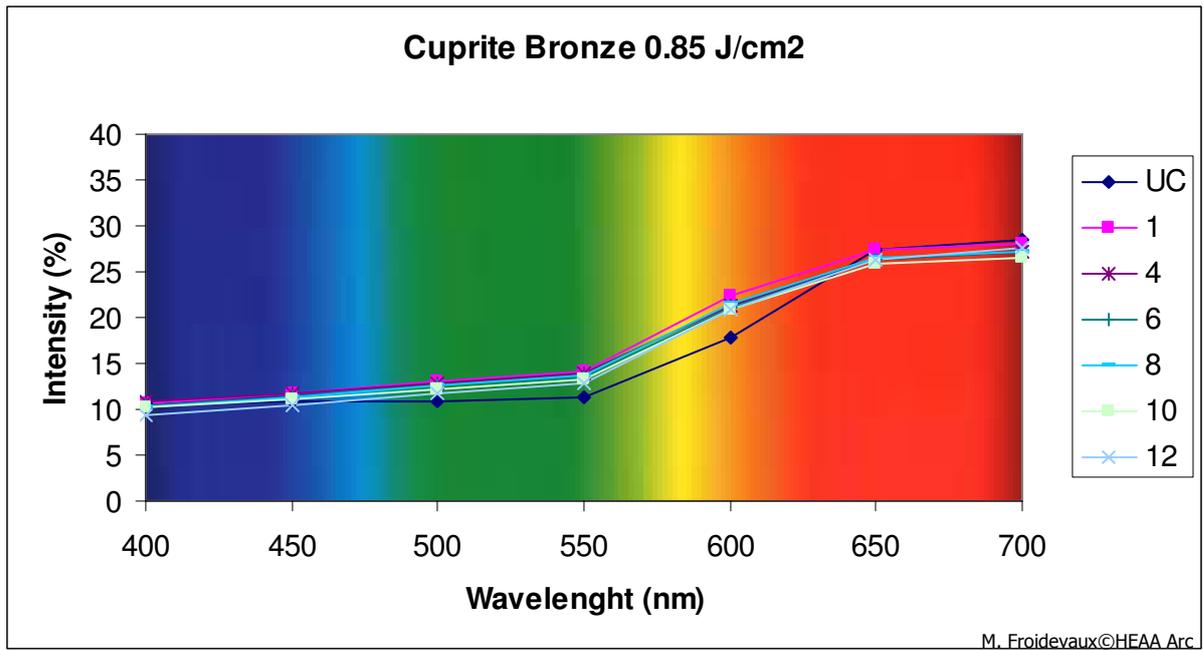
Figure 130 Reversible effect on cuprite bronze after laser cleaning at 0.85 J/cm^2.
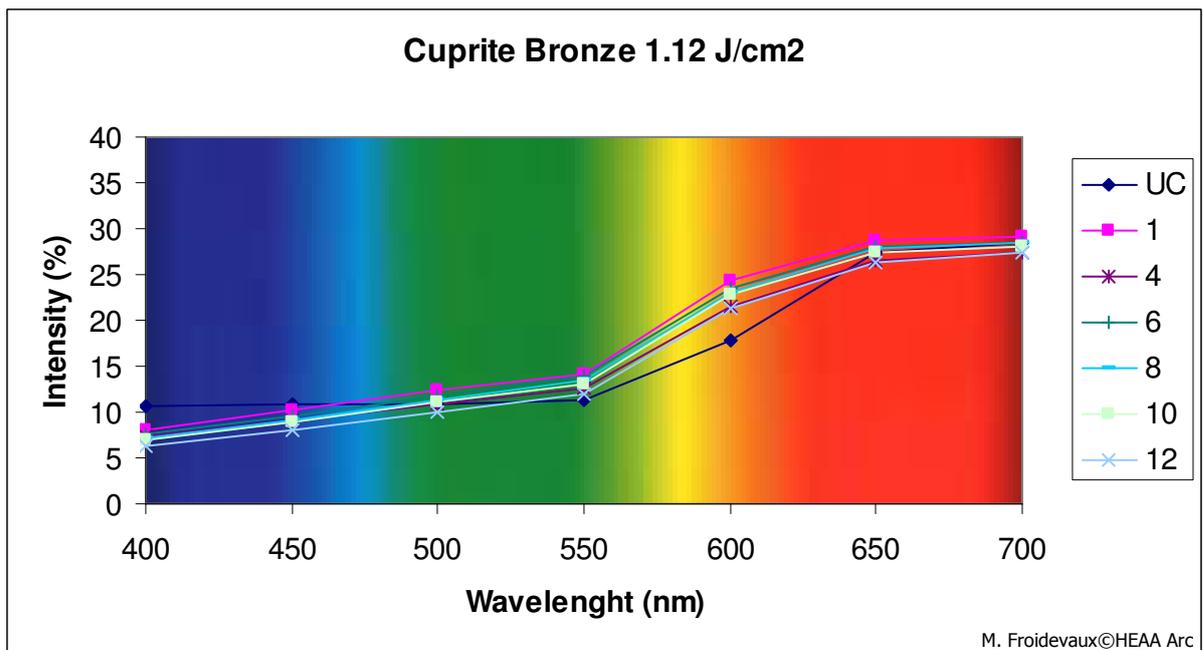
Figure 131 Reversible effect on cuprite bronze after laser cleaning at 1.12 J/cm^2.

11. SEM Images

11.1. Bare metal samples

11.1.1. Un-cleaned

Magnification 0.3Kx (left) and 1.3KX (right).
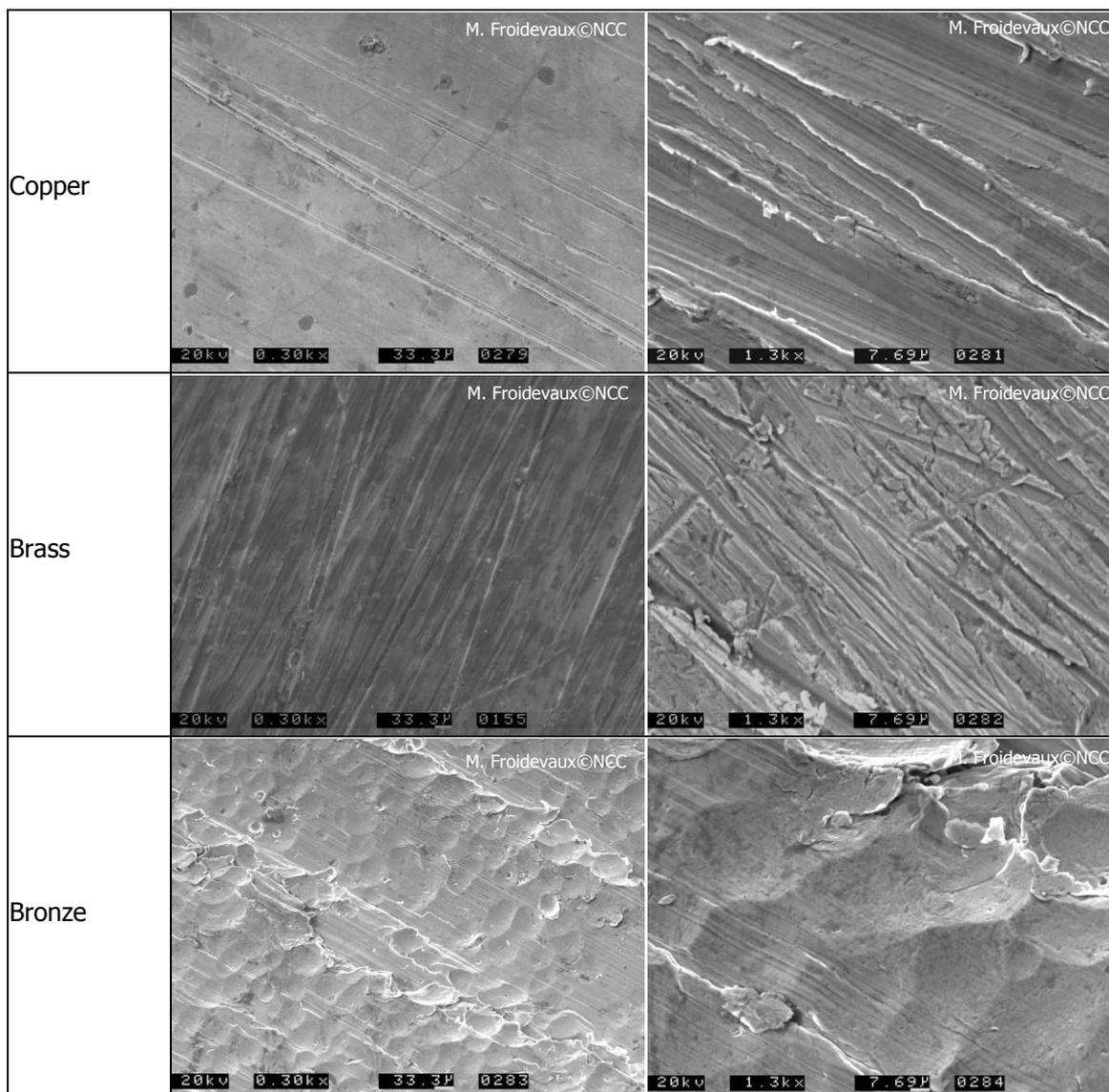
11.1.2. Laser cleaned

Magnification 1.3Kx
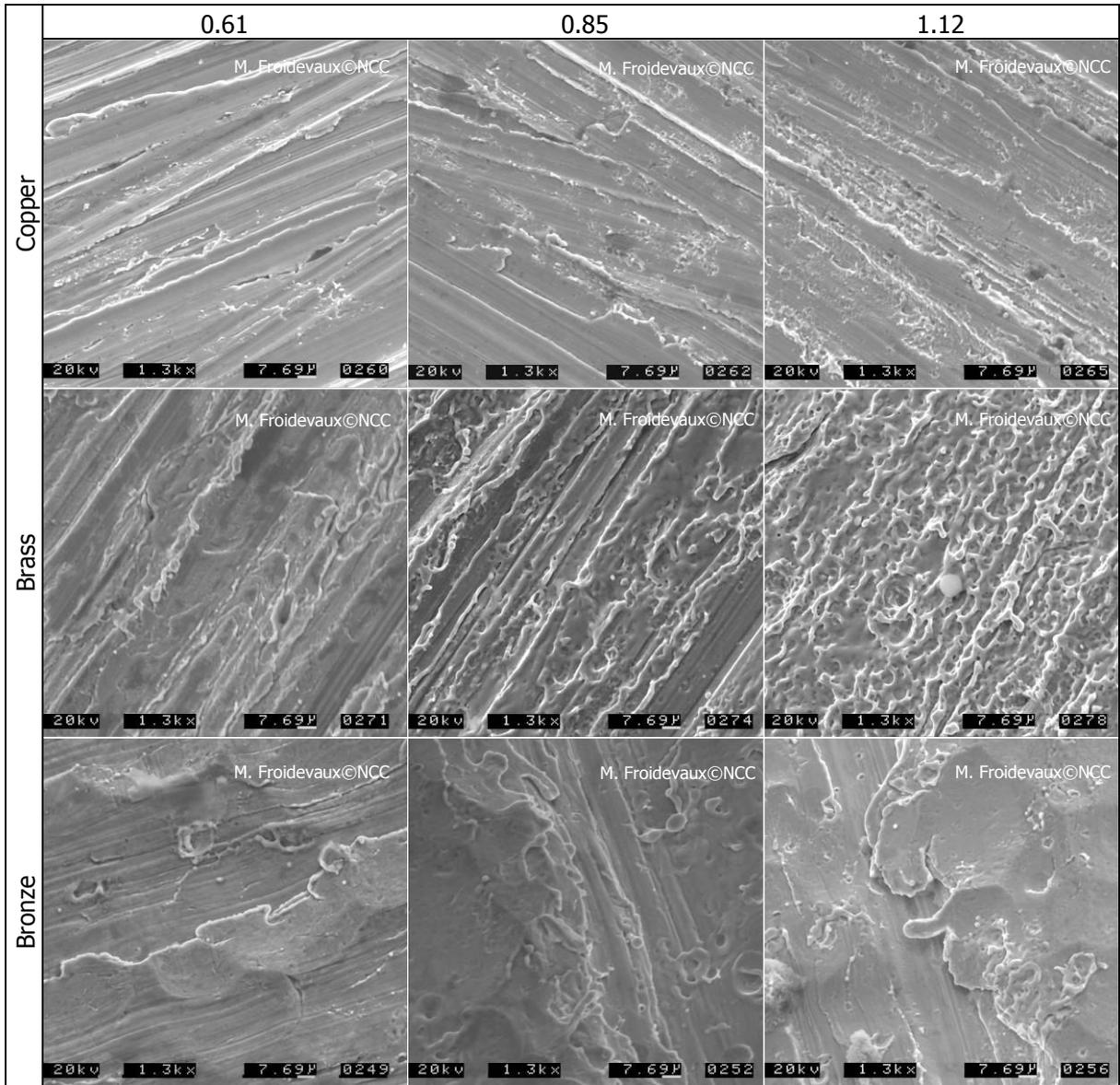
11.2. Cuprite samples

11.2.1. Un-cleaned

Magnification 0.3Kx (left) and 1.3KX (right).

Copper	
Brass	
Bronze	
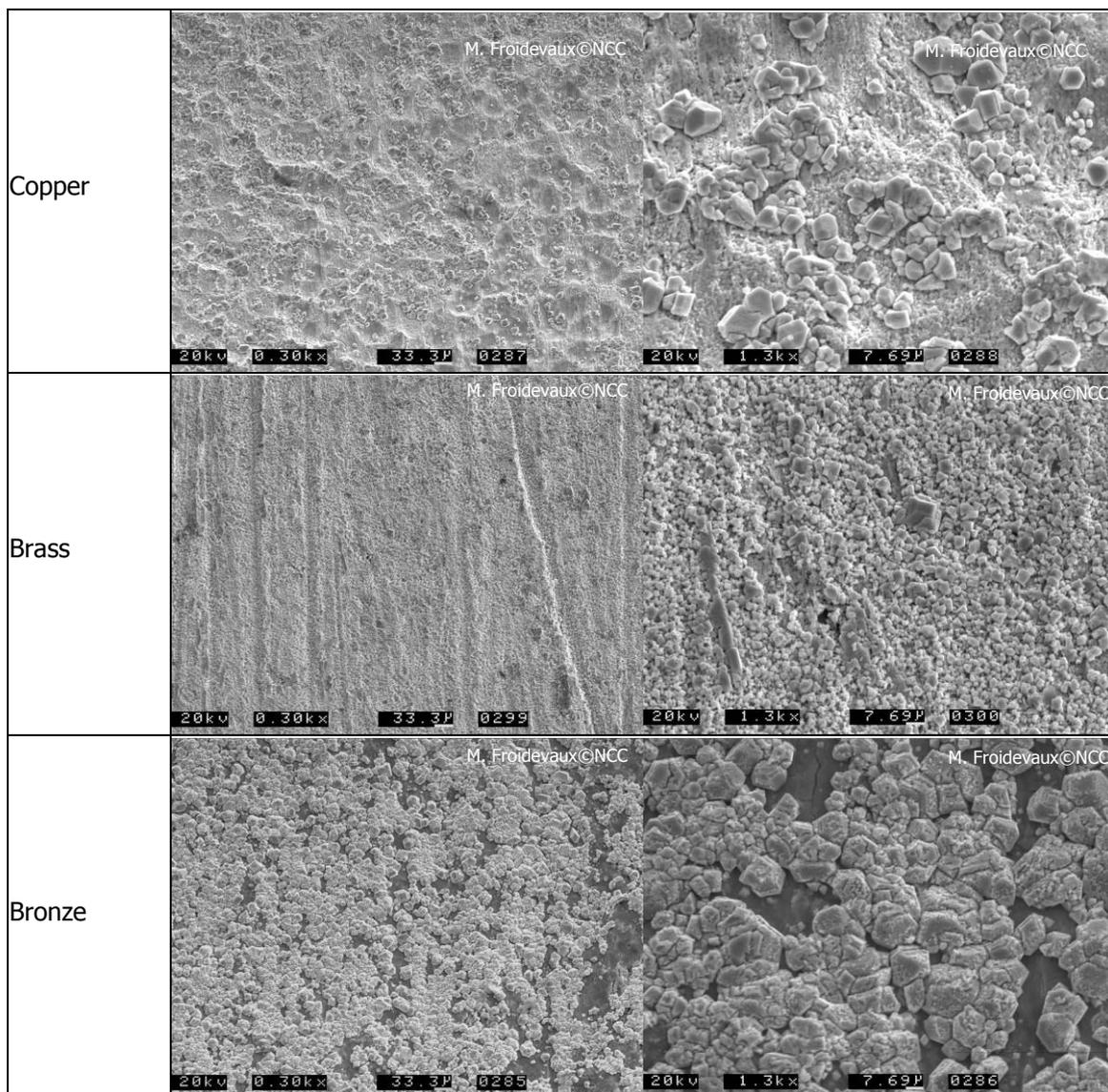
11.2.2. Laser cleaned

Magnification 1.3Kx.
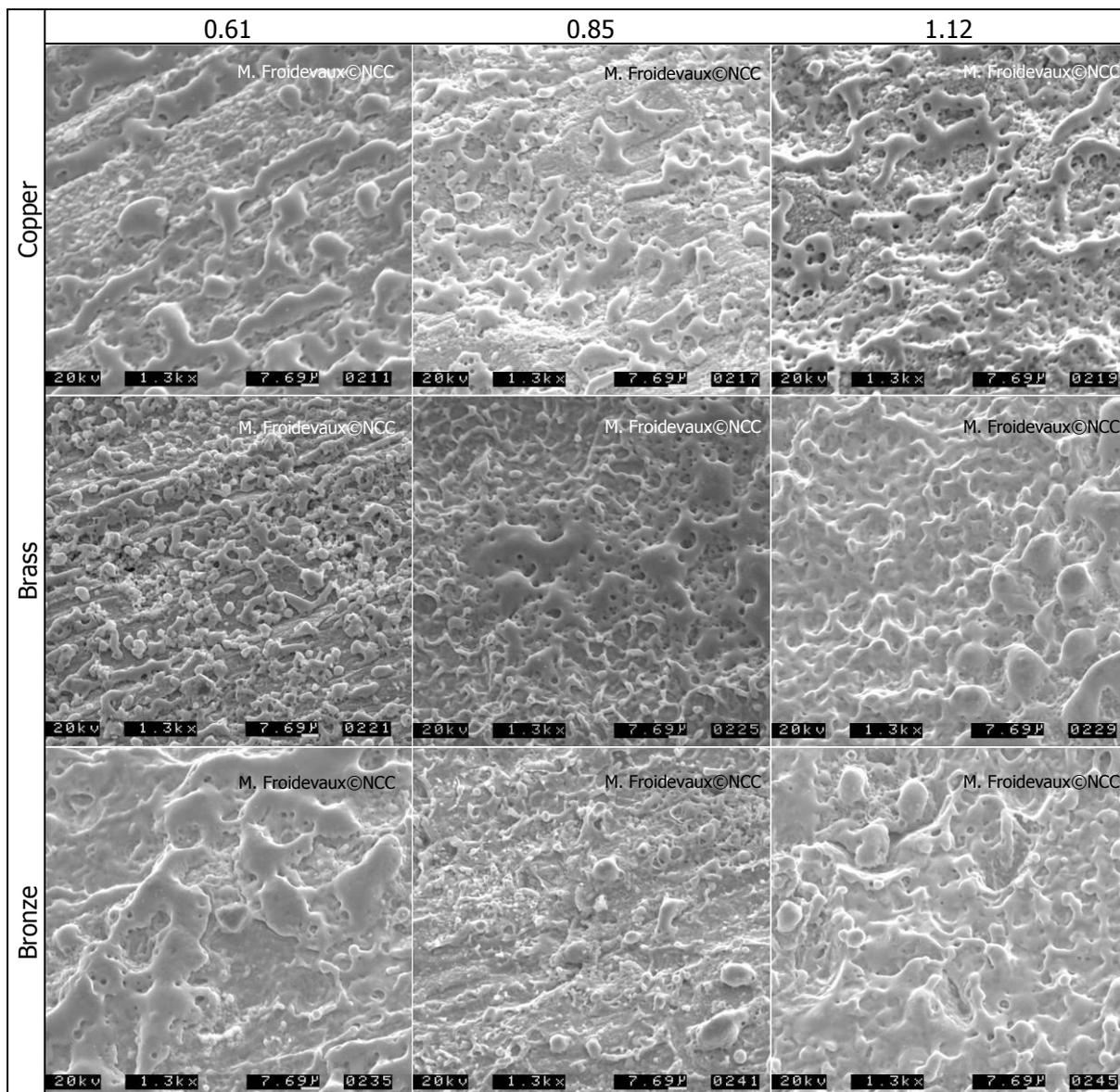
12. EDS spectra

12.1. Bare metal samples

12.1.1. Bare copper

Un-cleaned
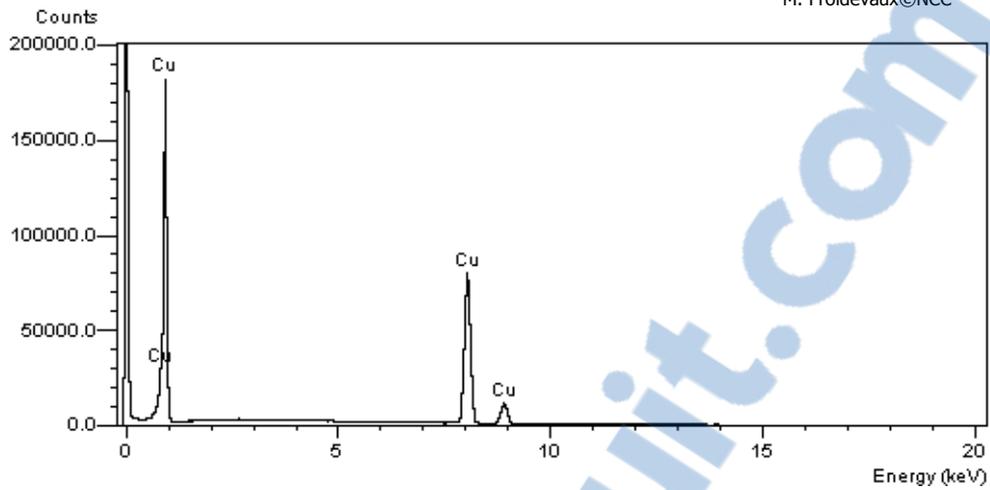
0.61 J/cm^2

0.85 J/cm^2

1.12 J/cm^2

12.1.2. Bare brass

Un-cleaned

0.61 J/cm²

M. Froidevaux©NCC
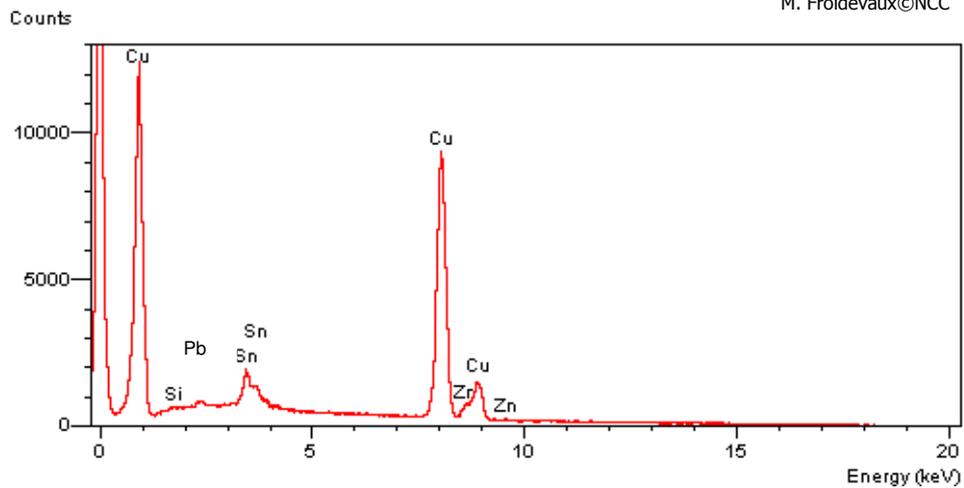
0.85 J/cm²

M. Froidevaux©NCC

1.12 J/cm²

M. Froidevaux©NCC

12.1.3. Bare bronze

Un-cleaned
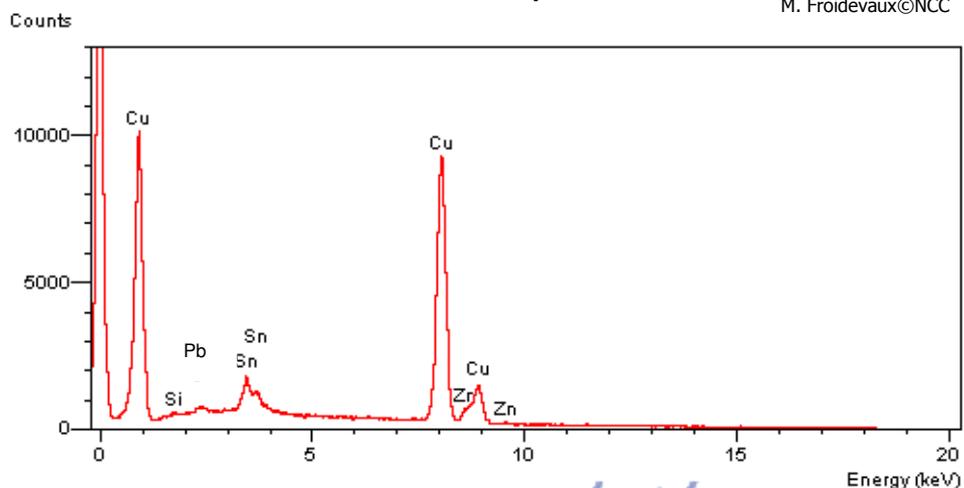
0.61 J/cm²

0.85 J/cm²

1.12 J/cm²
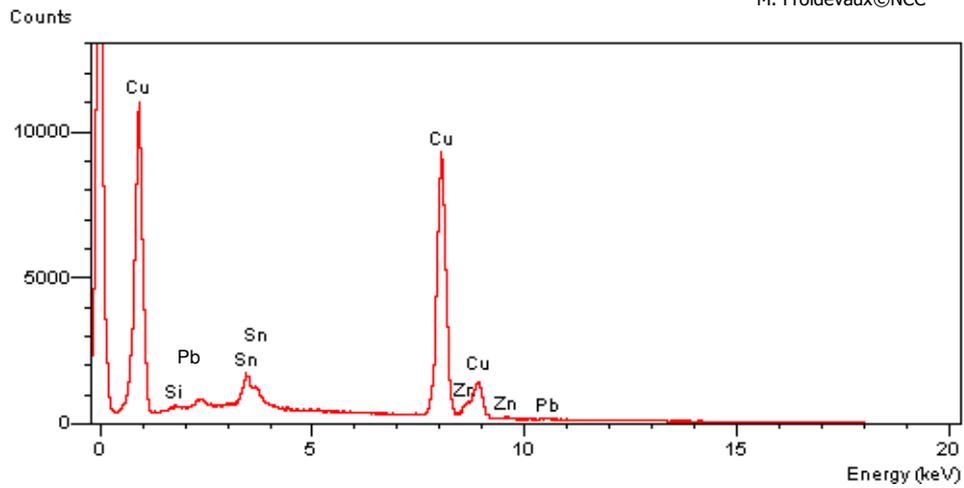
M. Froidevaux©NCC

12.2. Cuprite samples

12.2.1. Cuprite copper

Un-cleaned

M. Froidevaux©NCC
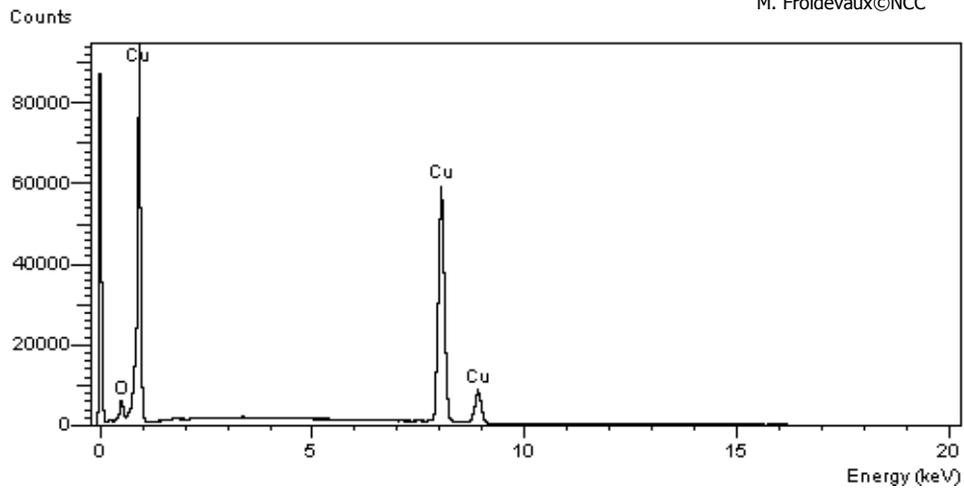
0.61 J/cm²
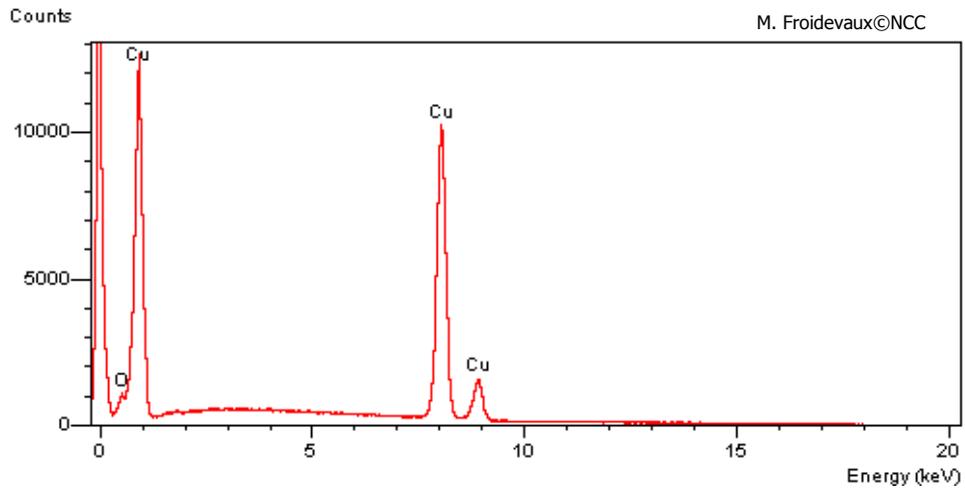
0.85 J/cm²
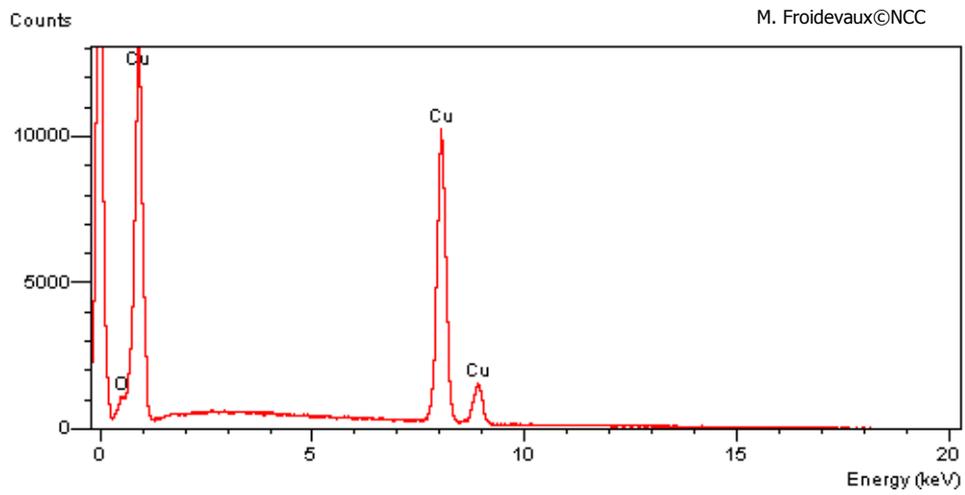
1.12 J/cm²
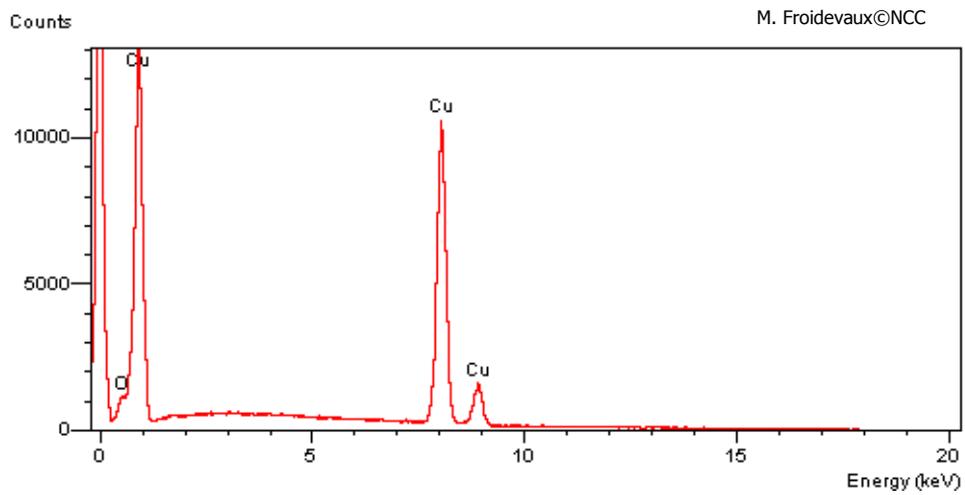
12.2.2. Cuprite brass

Un-cleaned
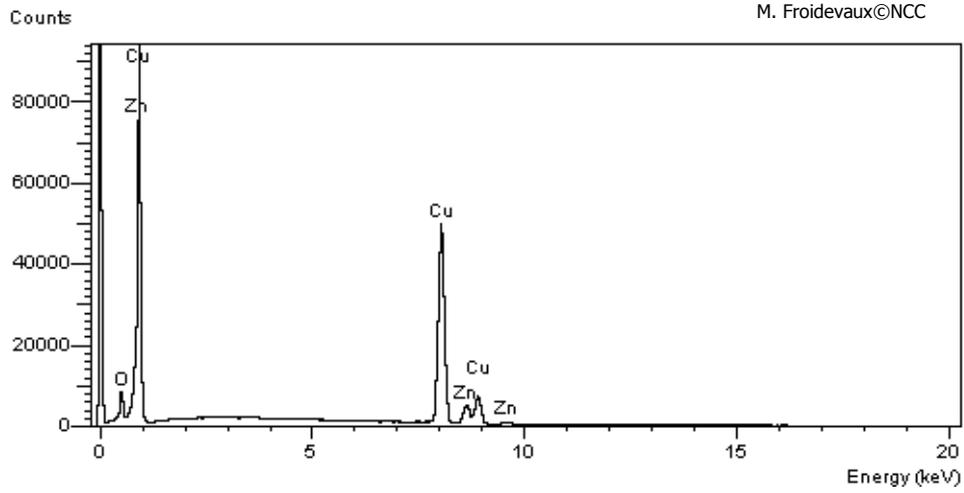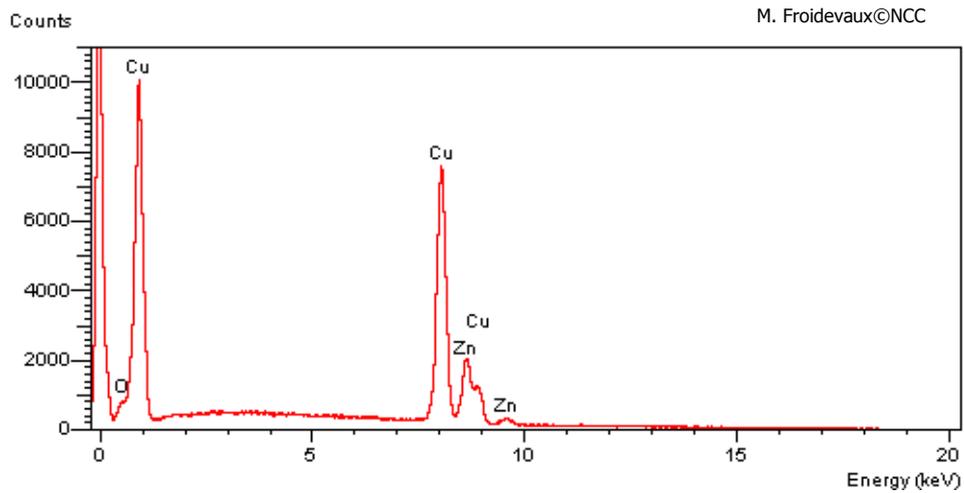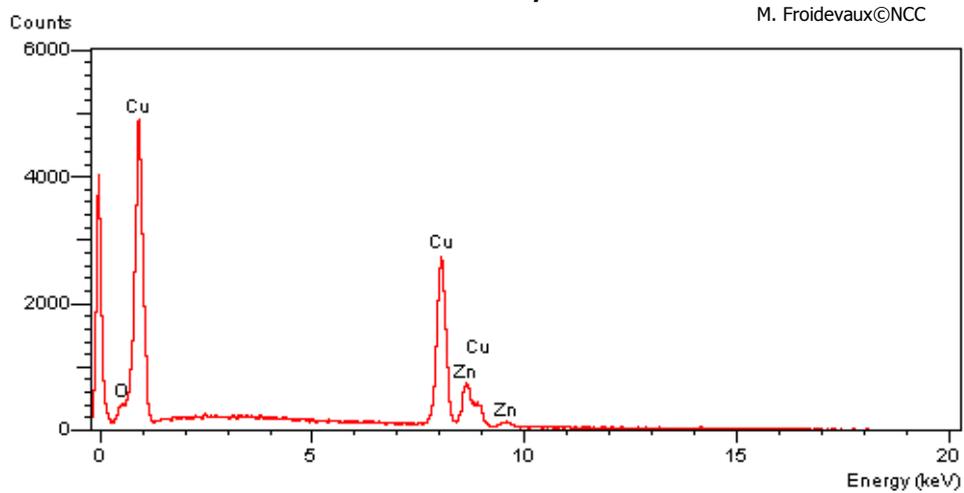
0.61 J/cm²
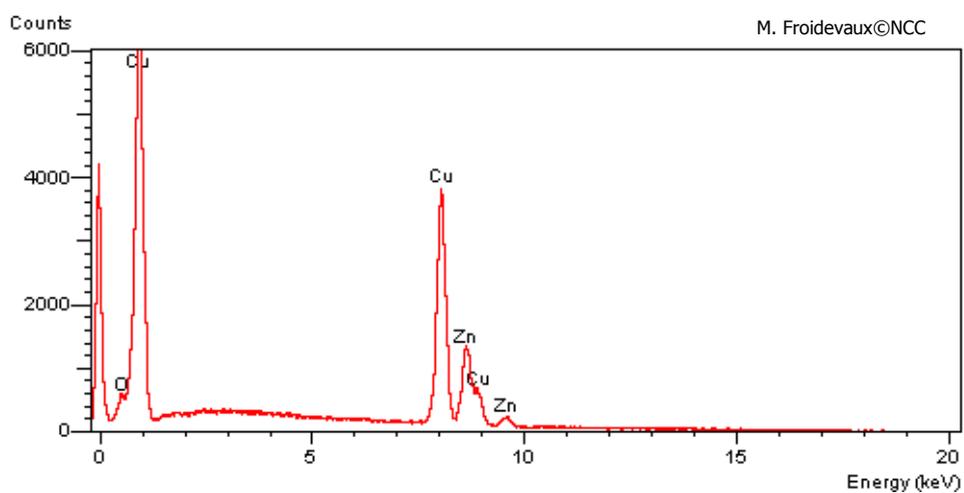
0.85 J/cm²

1.12 J/cm²

12.2.3. Cuprite bronze

Un-cleaned
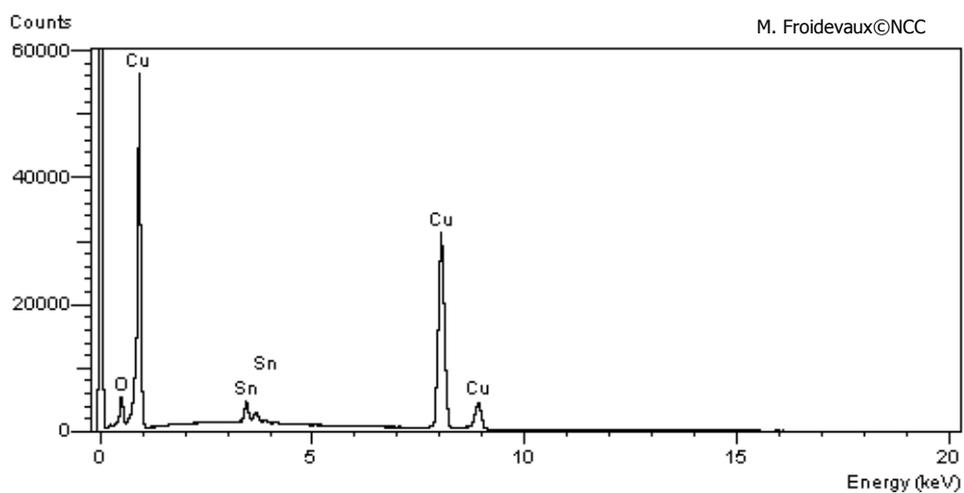
0.61 J/cm²
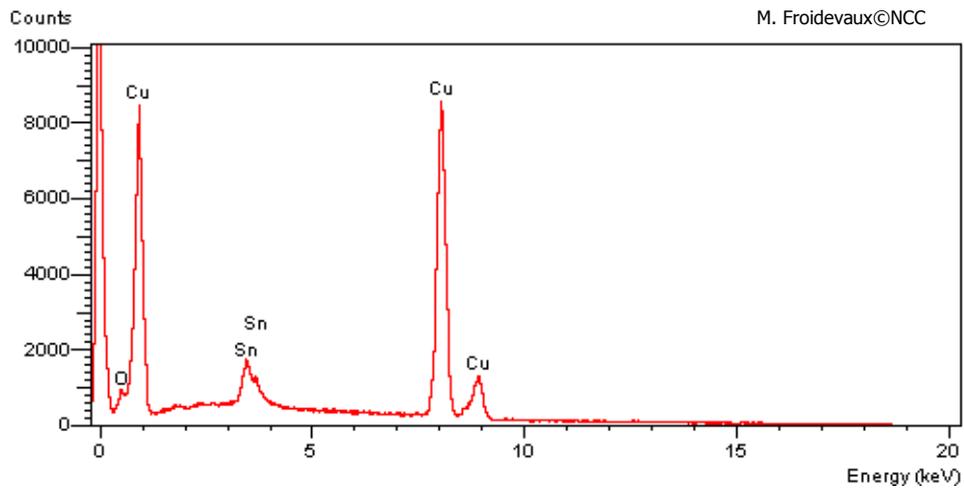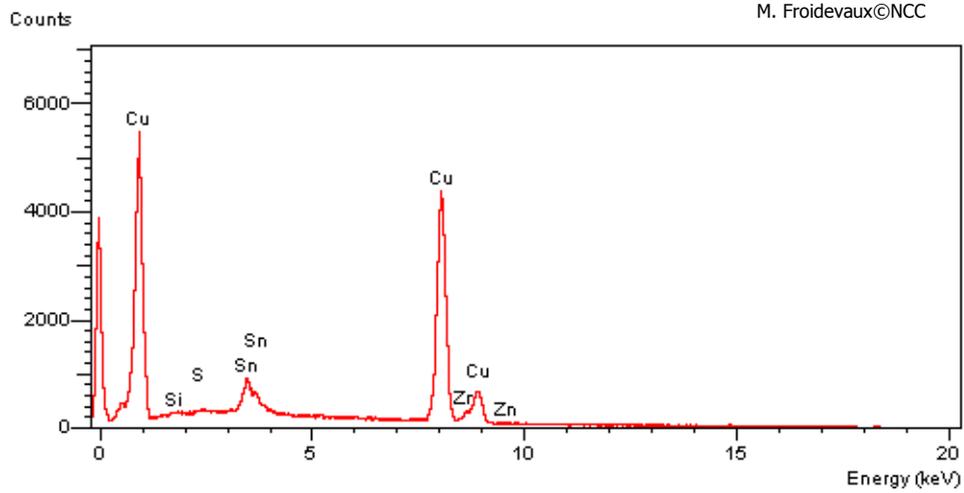
0.85 J/cm²

1.12 J/cm²
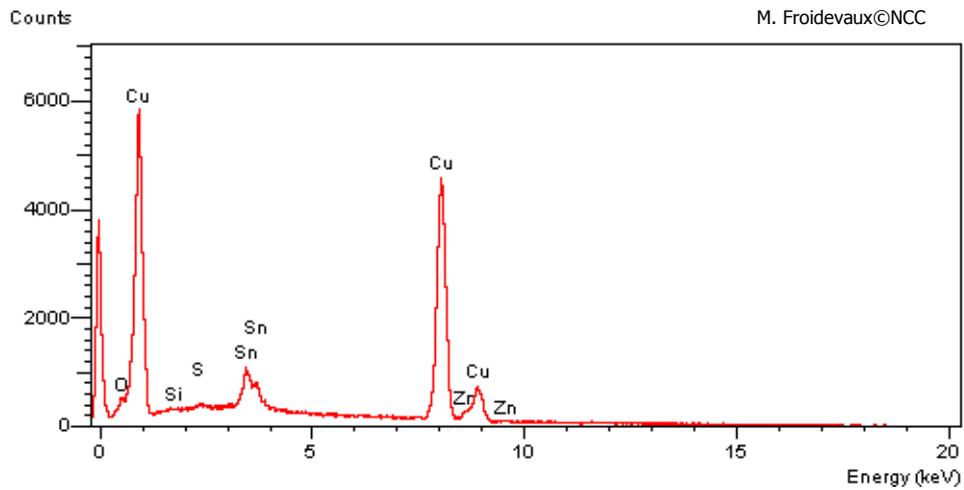
13. XRD spectra
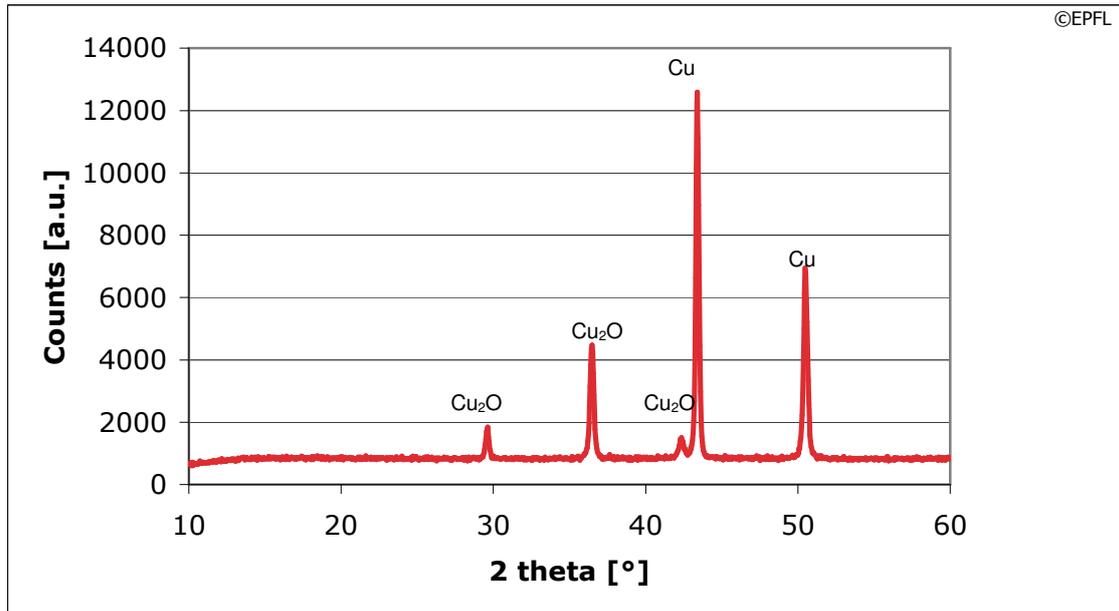
Figure 132 Before laser cleaning of cuprite copper.
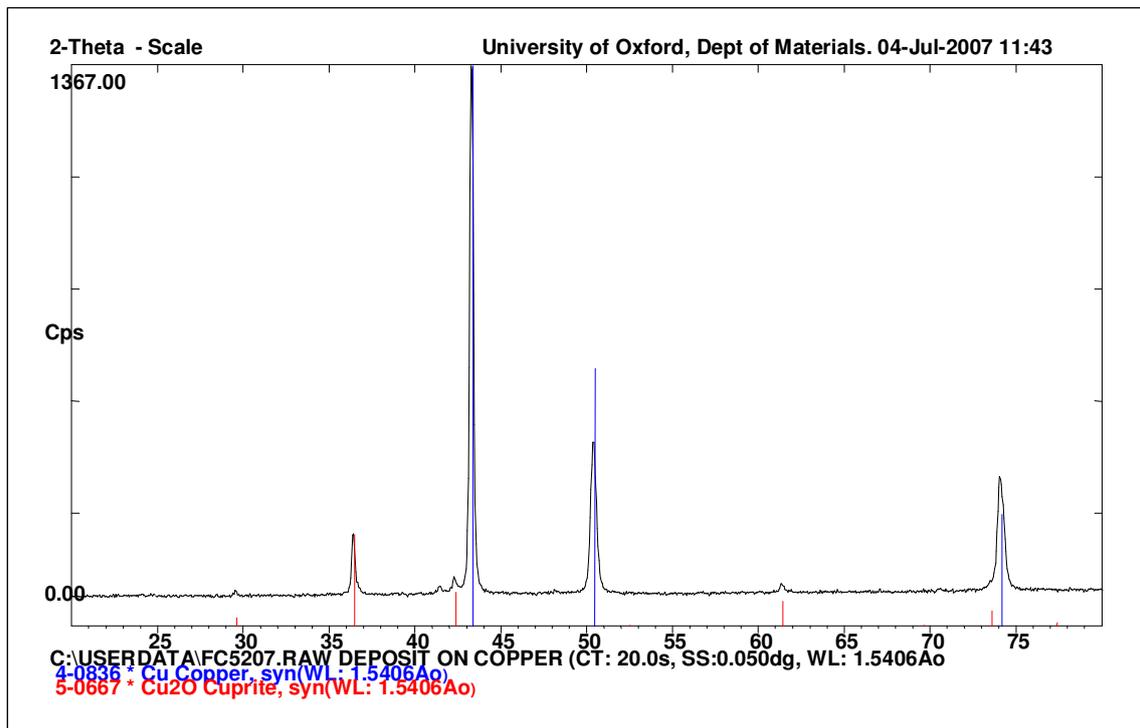
Figure 133 After laser cleaning (0.85 J/cm^2) of cuprite copper.

14. XPS spectra
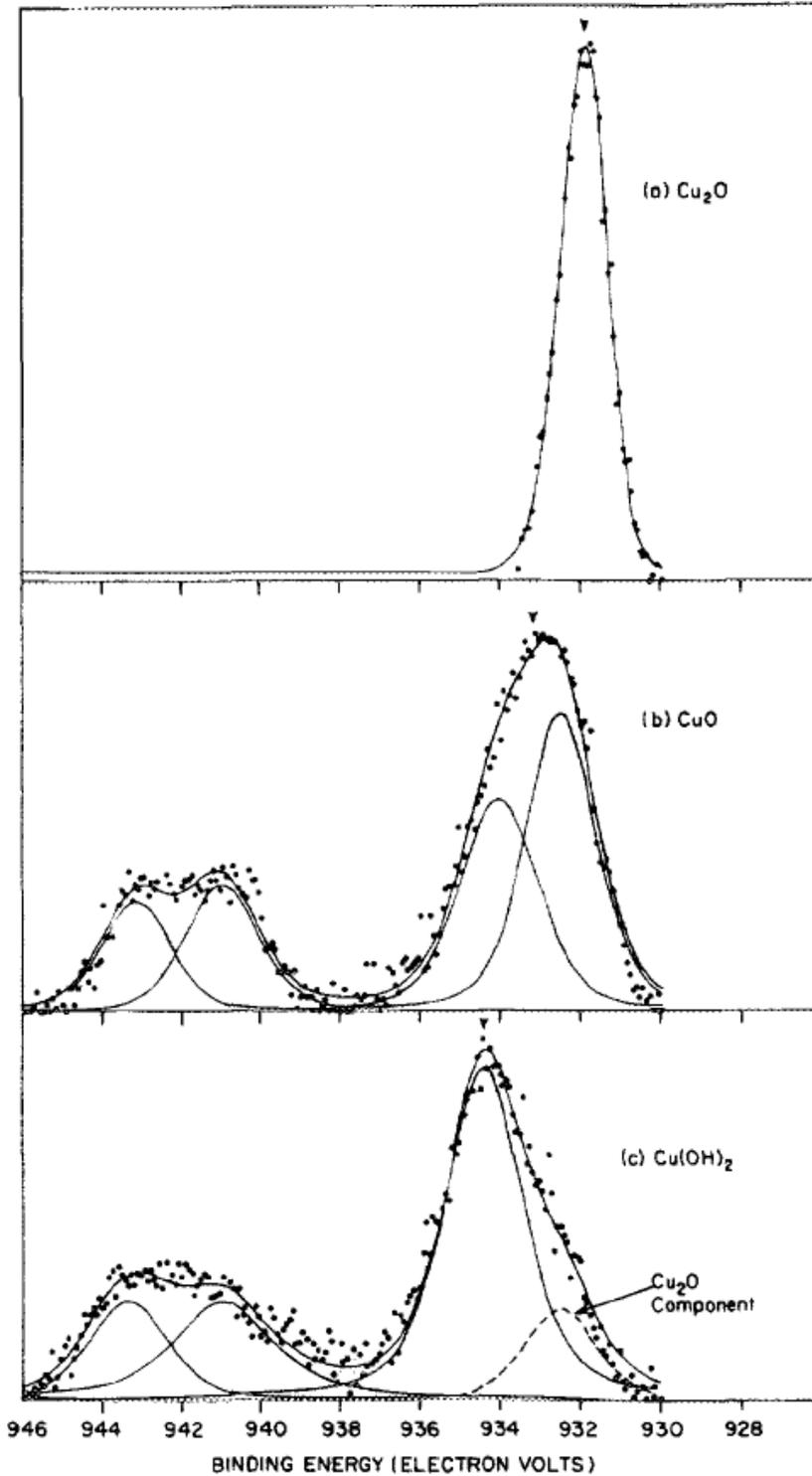
Figure 134 Cu(*2p* 3/2) photoelectron spectra for (a) Cu2O, (b) CuO, and (c) Cu(OH)2. The line through the experimental points represents a summation of the fitted peaks. The arrows indicate the mean peak position (From McIntyre *et al.*, 1981, p.714).
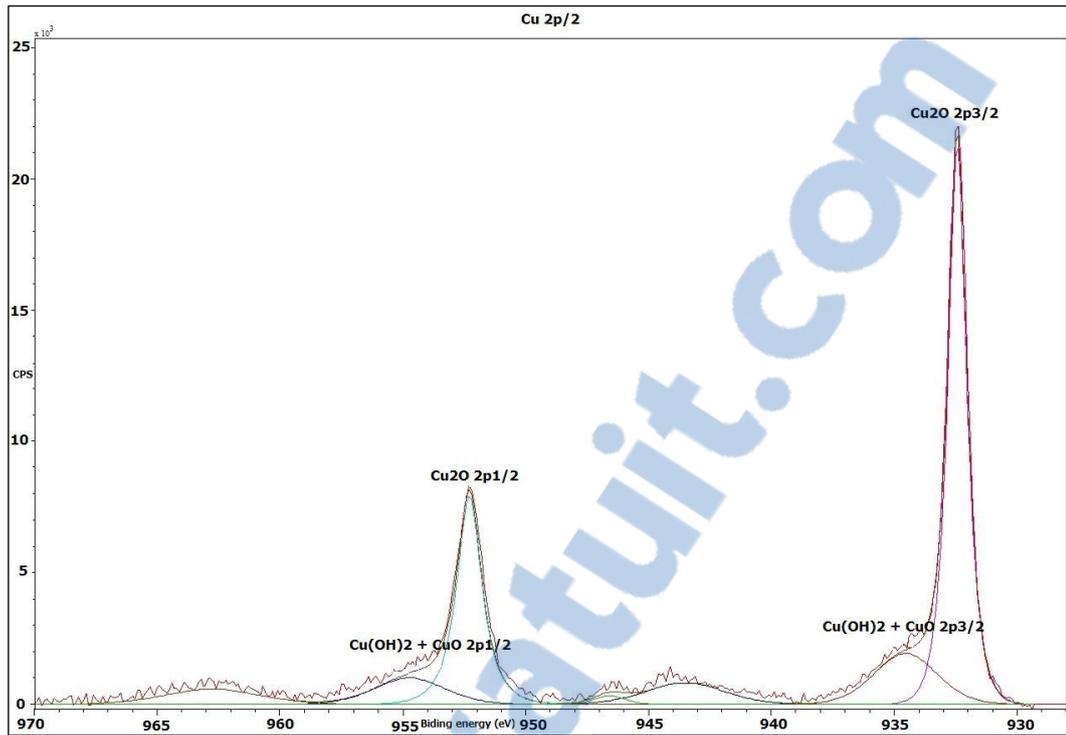
Figure 135 XPS spectrum of Cu 2p in the laser cleaned area of the copper oxide layer.
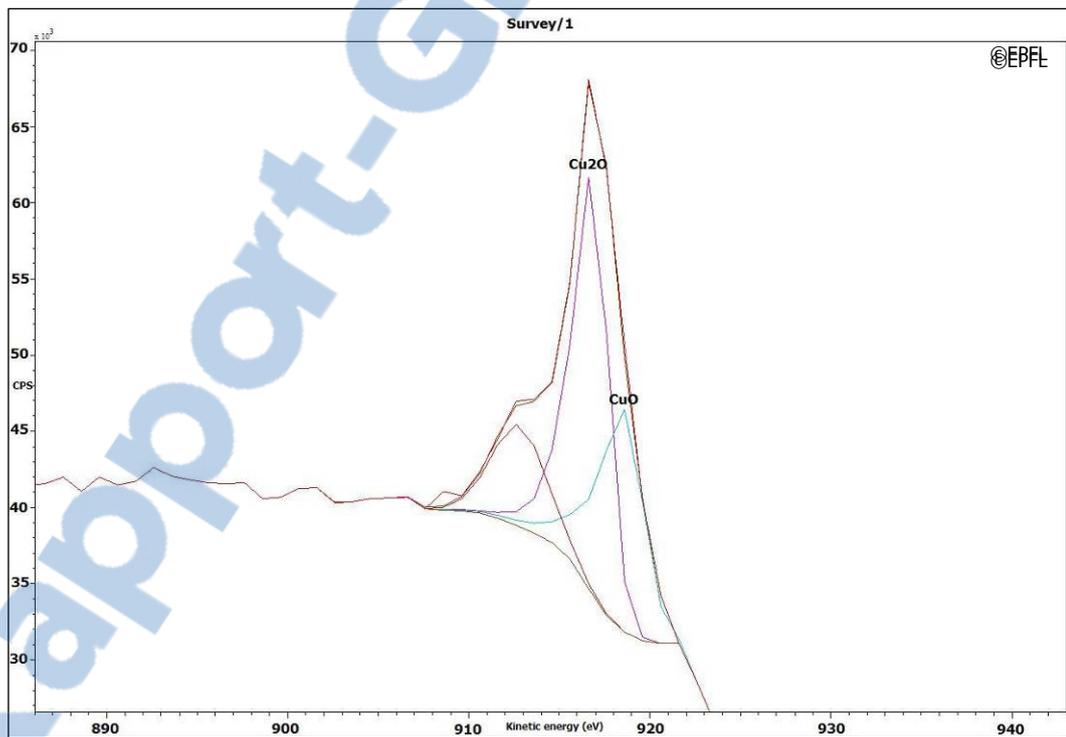
Figure 136 Auger spectrum of the laser cleaned area of the copper sample. The mixture of Cu_2O (major) and CuO (minor) is evidenced. $Cu(OH)_2$ may be hidden in the Cu_2O peak.
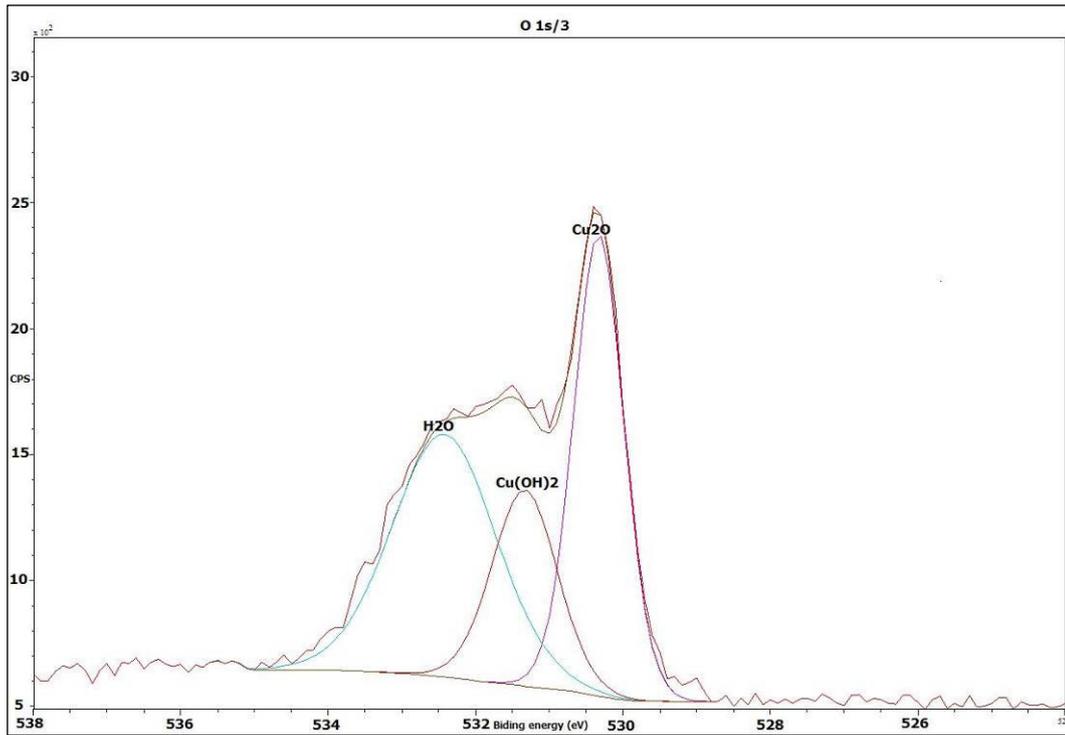
Figure 137 XPS spectrum of O 1s before laser cleaning of the copper oxide layer, indicating the presence of Cu_2O as a major component, $Cu(OH)_2$, and H_2O. No CuO is detected.
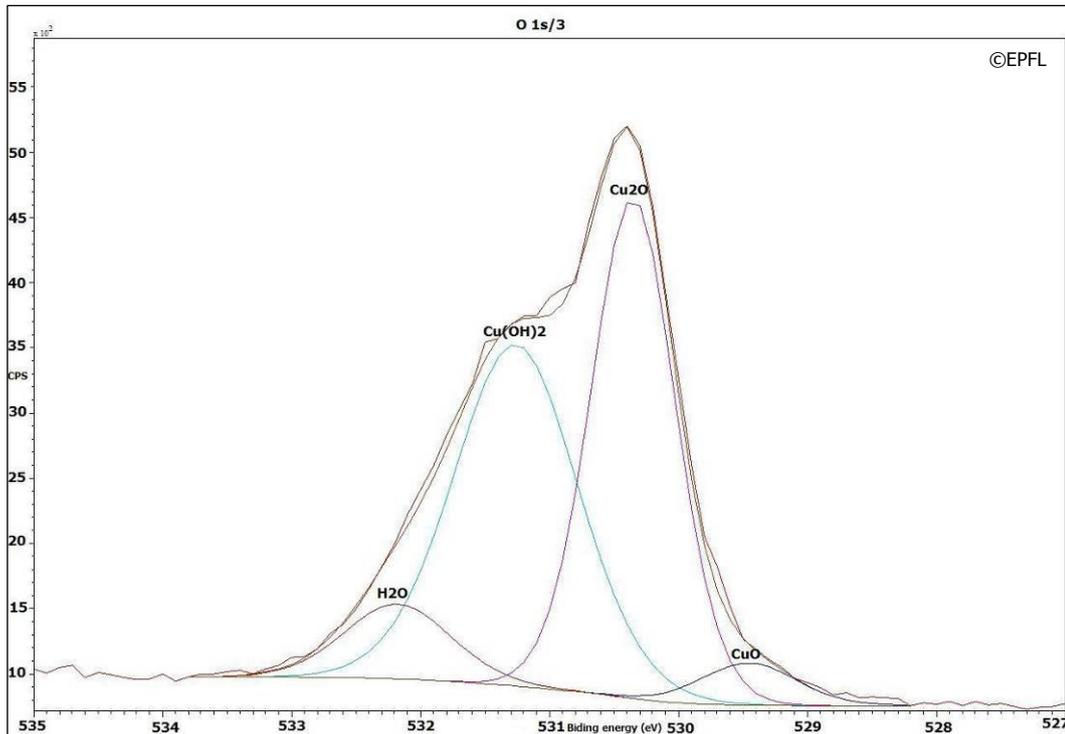
Figure 138 XPS oxygen spectrum of O 1s in the laser cleaned area of the copper oxide layer, before sputtering, showing the presence of Cu_2O as a major component, $Cu(OH)_2$, CuO and H_2O.
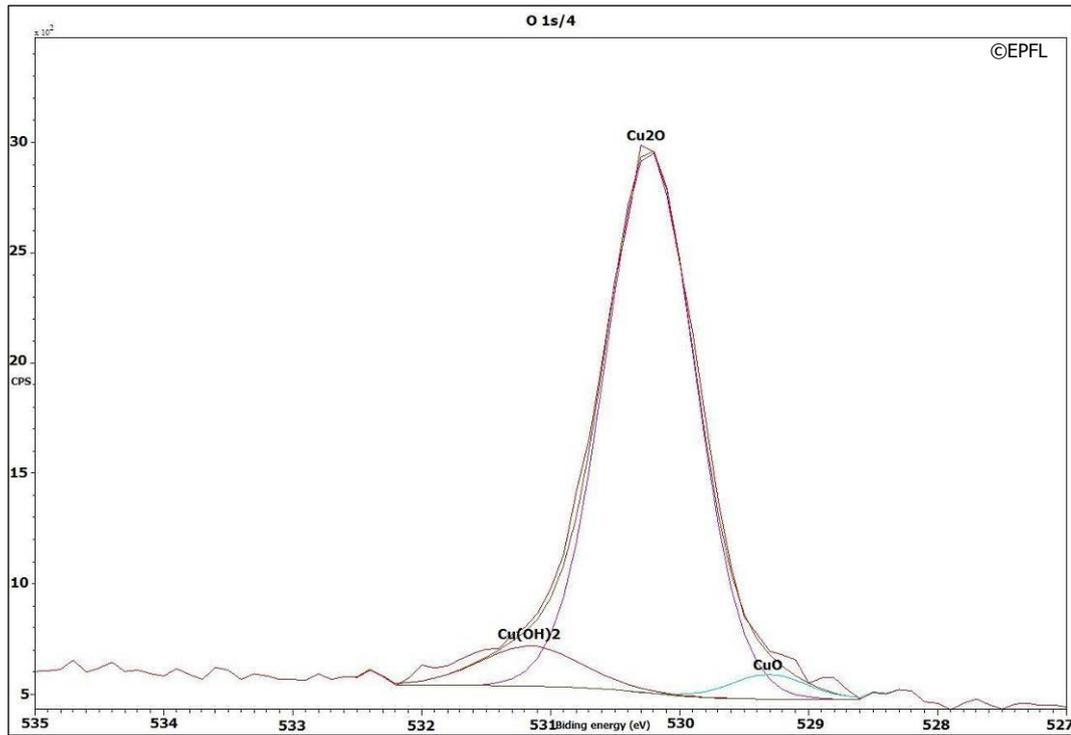
Figure 139 XPS oxygen spectrum of O 1s in the laser cleaned area of the oxide layer, after sputtering, with removal of nearly all the minor components (Cu(OH)$_2$ and CuO) and complete removal of water.
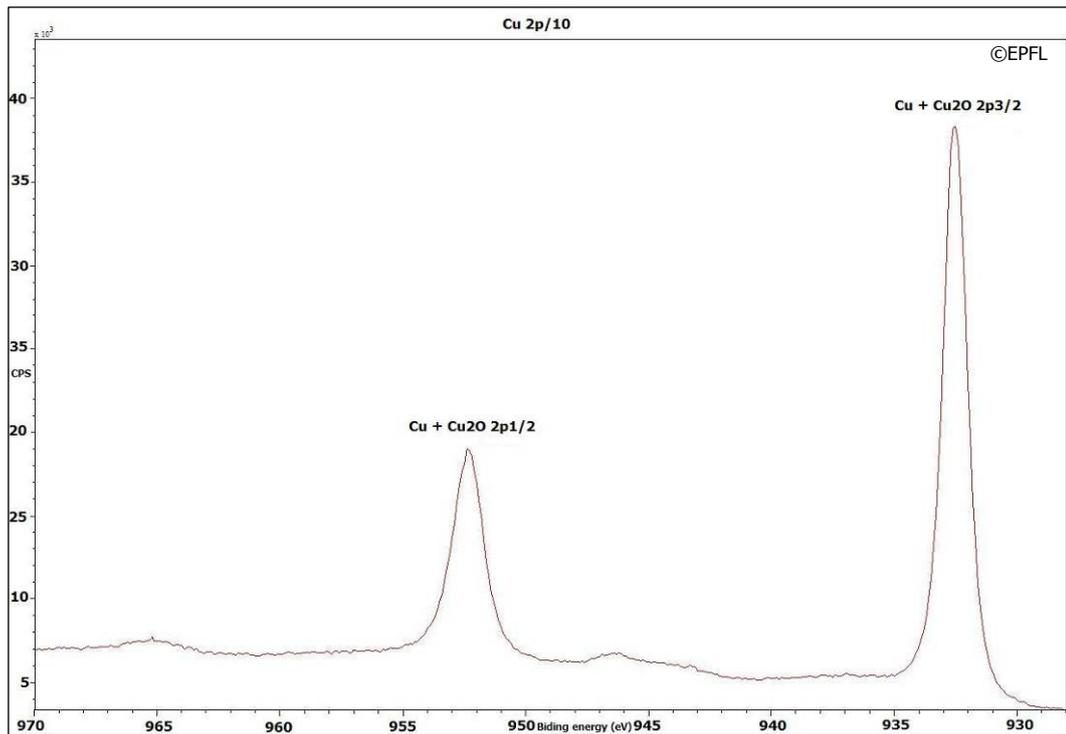
Figure 140 XPS spectrum of Cu 2p in the laser cleaned area of the oxide layer after sputtering. This shows the presence of metallic Cu mixed with the Cu$_2$O peak.

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15. Spectrometry graphs
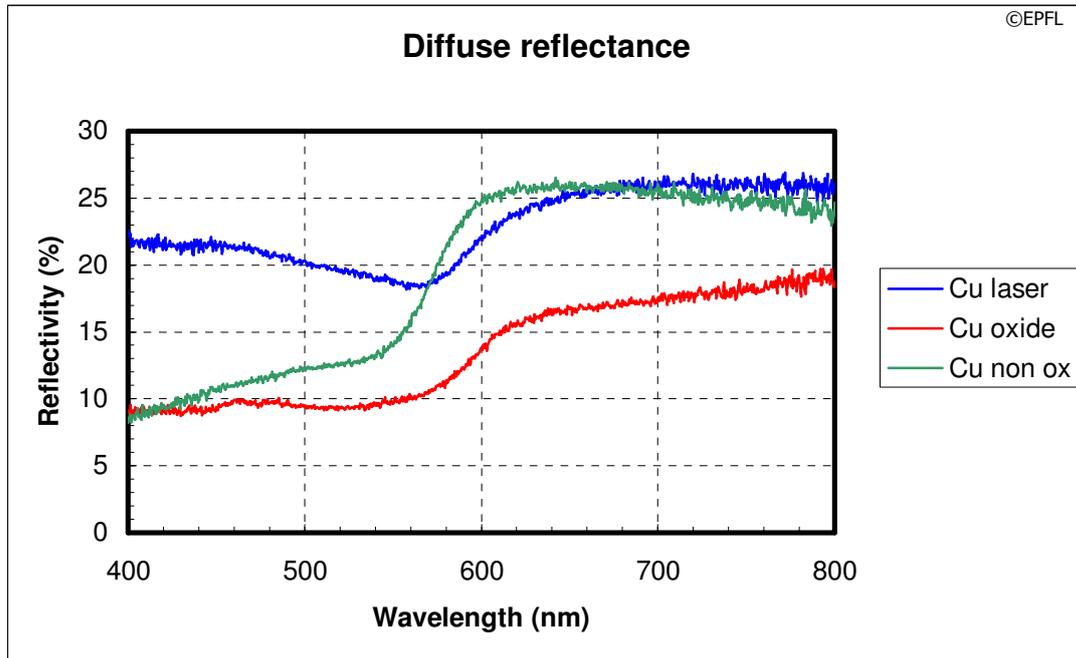
Figure 141 Diffuse reflectance.
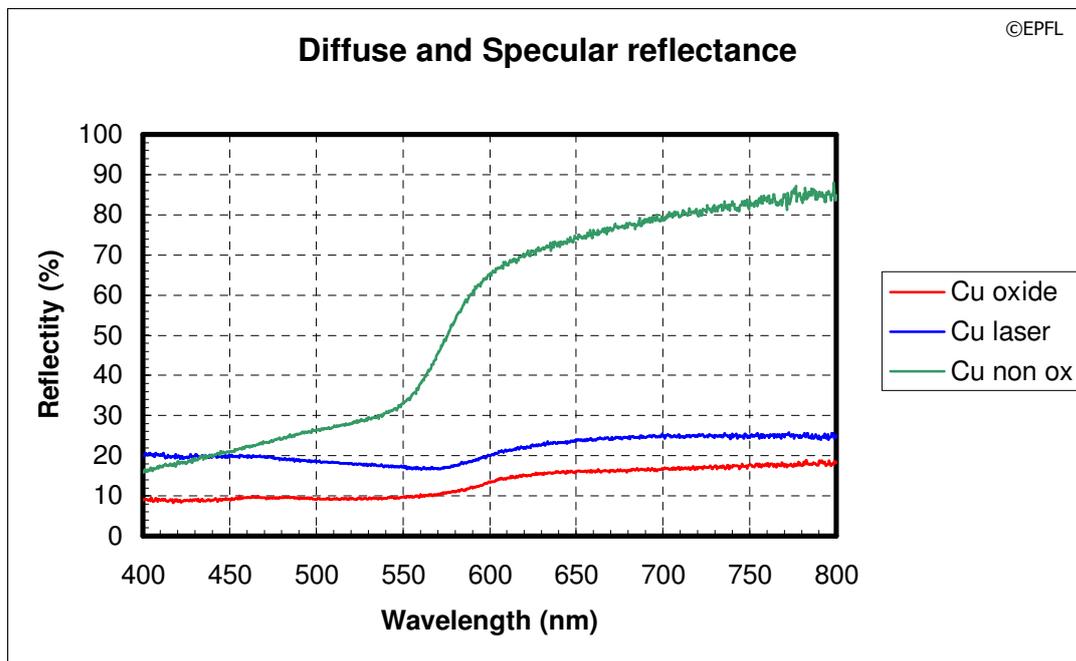
Figure 142 Diffuse and specular reflectance.
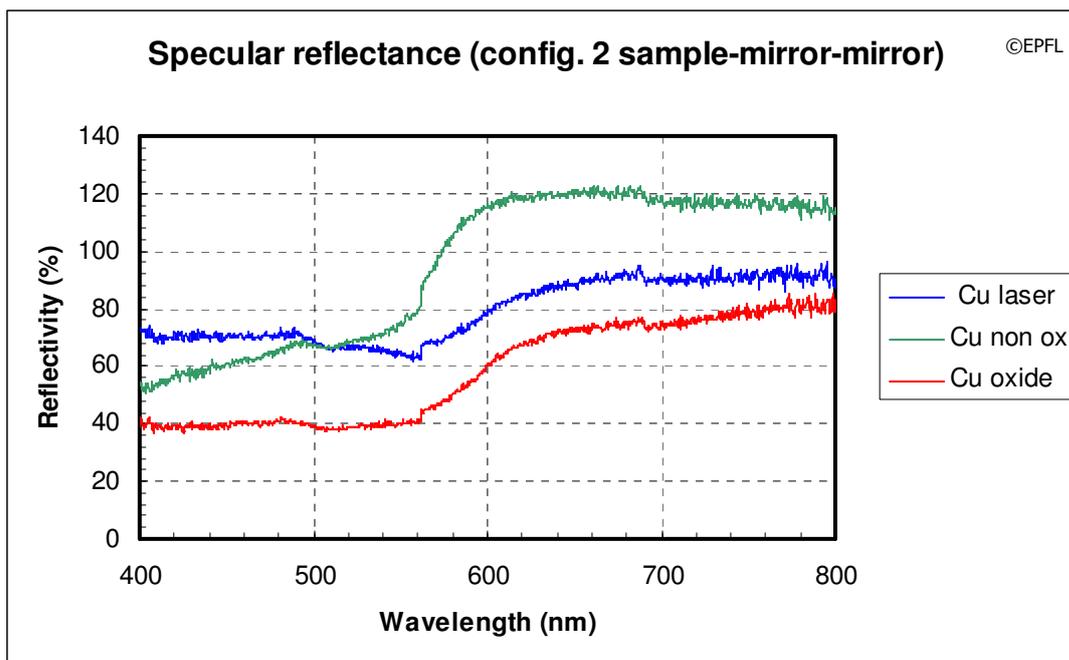
Figure 143 Specular reflectance.

16. Glossary

Absorptivity	Fraction of incident energy absorbed by a surface.
Coherence	Property of two waves perfectly superposed to each other.
Collimated	Means parallel.
Density	Mass per unit volume. In g/cm^3.
Directionality	Property of a highly parallel laser beam.
Energy	Measure of the ability of a system to do work (produce heat, light, motion). In Joules (J).
Energy density	Also named fluence, it is the concentration of the energy contained in a laser pulse for a given surface (or per unit area). In J/cm^2. It is obtained by dividing energy in Joules by beam size in cm^2.
Excimer laser	Gas laser which lasing medium is made of a rare gas halide such as ArF, KrF, KrCl, XeF or XeCl and emitting in the ultra-violet part of the spectrum.
Excited state	On the energy level system, when the atoms/molecules have a higher energy than on the ground state.
Fluence	See energy density.
Frequency	Number of waves passing at a fixed point in one second. In Hertz (Hz).
Ground state energy	The lowest energy on the energy level system.
Harmonic	Different wavelengths obtained by multiplying the fundamental frequency, respectively dividing the wavelength.
Hot spot	Area of a higher energy inside a single spot, appearing with a multimode laser beam.
Infrared	The invisible part of the electromagnetic spectrum which wavelength is between 700 nm and 12 µm.
Intensity	Power per unit area. In W/cm^2.
Irradiation	Exposure of a substance to electromagnetic radiations.
Laser ablation	Ejection of material from a solid surface resulting from the irradiation by a laser beam.

Lasing medium	Medium in a laser system emitting the beam by providing the appropriate energy levels for stimulated emission. It can be a gas, a solid or a liquid.
Light	Part of the electromagnetic spectrum from the ultraviolet to the infrared, including visible and invisible radiations.
Monochromaticity	Radiation of a single wavelength.
Multimode	Laser producing intensity variations inside a single spot.
Nd:YAG	Solid state laser composed of an Yttrium Aluminium Garnet ($Y_3Al_5O_{12}$) rod and doped with Neodimium ions, which fundamental wavelength emits in the infrared part of the spectrum.
Optical cavity	See resonator.
Optical penetration depth	Depth into which photons penetrate a material.
Oscillation	Excitation above the laser threshold, resulting in photons oscillating between the mirrors located at the ends of the laser cavity.
Photon	Light particle.
Plasma	Fourth state of the material, it is a highly ionized gas.
Population inversion	A condition necessary for laser amplification, achieved by the pumping source, where the particles (atoms/molecules) in the lasing medium are more numerous on the excited state than on lower levels, which is contrary to the natural equilibrium.
Power	The rate at which energy is emitted. In Joules/second / Watts (W).
Pulse energy	Amount of energy contained in a single laser pulse, in Joules.
Pulse length	Duration of a single laser pulse, in seconds.
Pumping source	Source (often a flashlamp for pulsed lasers) providing enough power to the lasing medium to obtain a population inversion.
Q-switched	A laser emitting energy in pulses of very short duration (typically ns).
Reflection	Reflected part of the light when it hits a boundary between two media.
Reflectivity	Fraction of incident energy reflected by a surface.
Repetition rate	Number of pulses emitted in a second. In Hertz (Hz).
Resonator	Optical cavity containing the lasing medium and the mirrors.

Self-limiting	Laser cleaning is said to be self-limiting if the removal of material form the surface stops as soon as the underlying surface has been reached and the dirt layer removed, even if irradiation of the surface goes on.
Shock wave	Intense sound wave.
Singlemode (monomode)	Laser producing a beam of very regular energy.
Spontaneous emission	When atoms/molecules return to a lower energy level after a natural decay time without any external intervention
Stimulated emission	When any initial photon of adequate energy stimulates the emission of other photons, leading to a cascade of stimulated photons.
Thermal conductivity	Measure of the ability of a material to conduct heat. In W/cmK or J/scmK.
Thermal diffusivity	Measure of the velocity of a material to accept and conduct heat. In m^2/s.
Heat diffusion length	Depth into which heat penetrates a material.
Ultraviolet	The invisible part of the electromagnetic spectrum which wavelength is between 30 and 400 nm.
Wavelength	The distance between repeating units of a propagating wave of a given frequency. Commonly designated by λ.

17. Suppliers list

Items category	Product	Trademark & model	Address for UK	Address for Switzerland
Analytical techniques	Camera	JVC®KY-F1030	**Cecil Jacobs Ltd.** 54 Bold Street Liverpool L1 4EA, UK Phone +44 151-7093733 Fax +44 151-7093440 www.jacobs-photo.co.uk www.jvc.co.uk	**JVC Suisse SA** Sternenhofstrasse 15a 4153 Reinach Phone +41 (0)61 405 15 00 Fax +41 (0)61 405 15 03 info@jvc.ch
	EDS analyser	Oxford Instruments Software Link ISIS 300	**Oxford Instruments** Halifax Road High Wycombe Buckinghamshire HP12 3SE UK Phone +44 (0)1494 442255 Fax +44 (0)1494 524129 nanoanalysis@oxinst.co.uk	**Oxford Instruments** Bâtiment Ariane Domaine Technologique de Saclay 4, Rue René Razel, 91892 Saclay, France Phone +33 1 69 85 25 25 Fax +33 1 69 41 86 80 info@oxford-instruments.fr
	Fibre optic light	SCHOTT®KL 1500 LCD	**Schott Industrial Glass Ltd.** Ketton Way Aycliffe Business Park Newton Aycliffe County Durham DL5 6SR, UK Phone +44(0)1325 300 111 Fax +44(0)1325 300 354 www.schott.com gbnay.info@schott.com	**Schott Schweiz AG** St. Josefen-Str. 20 Postfach 9001 St. Gallen, Schweiz Phone +41 (0)71 274 42 42 Fax +41 71 (0)274 42 43 info.schweiz@schott.com
	Grinder / Polisher	LECO®GP20	**LECO Instruments Ltd**. Newby Road Industrial Est Newby Rd, Hazel Grove, Stockport Cheshire SK7 5DA, UK Phone 044 161 487 5900 Fax 044 161 456 0969 www.lecouk.com uk@leco.com general@lecouk.com	**LECO Instrumente GmbH** Mönchengladbach Germany Phone 49-2166-687-0 Fax 49-2166-687-100 www.leco.de marketing@leco.de

Optical Microscope (used at NCC)	LEICA®LEITZ DMR	**Leica Microsystems Ltd** Davy Avenue, Knowlhill Milton Keynes, MK5 8LB Bucks, UK Phone +44 1 908 246 246 PhoneII +44 1 908 666 663 Fax +44 1 908 609992 http://www.leica-microsystems.com/eu/uk	**Leica Microsystems (Schweiz) AG** Verkaufsgesellschaft Max Schmidheinystrasse 201 9435 Heerbrugg Switzerland Tel +41 71 726 34 34 Fax +41 71 726 34 44 http://www.leica-microsystems.com/eu/ch	
Optical Microscope for metallurgy (used at the University of Oxford)	Reichert-Jung	**Leica Microsystems Ltd** Davy Avenue Knowlhill Milton Keynes, MK5 8LB Bucks, UK Phone +44 1 908 246 246 PhoneII +44 1 908 666 663 Fax +44 1 908 609992 http://www.leica-microsystems.com/eu/uk	**Leica Microsystems (Schweiz) AG** Verkaufsgesellschaft Max Schmidheinystrasse 201 9435 Heerbrugg Switzerland Tel +41 71 726 34 34 Fax +41 71 726 34 44 http://www.leica-microsystems.com/eu/ch	
Microscope low magnification (used at NCC)	OPTIVISION (Yorkshire) Ltd.	**OPTIVISION (Yorkshire) Ltd.** 12, Leeds Road, Ossett West Yorkshire WF5 9QA, UK Phone +44(0)1924 277 727 Fax +44 (0) 1924 280 016 www.optivision.co.uk	Idem	
SEM	ABT®-55 Software IScan 2000	**Akashi Seisakusho Ltd. GmbH** Siegmund-Hiepe Str. 24 2330 Wetzlar- Germany Phone 06441 22002, 22003	Idem	
Spectrophotometer (Used at NCC)	X-Rite® Digital Swatchbook Software ColorShop®	**X-Rite Ltd.** Poynton Cheshire, UK Phone +44 1625 871 100 Fax +44 1625 871 444 www.xrite.com	**GretagMacbeth AG** Althardstrasse 70 8105 Regensdorf Switzerland Phone+41 (0)44 842 24 00 Fax +41 (0)44 842 22 22	

	Spectrometer (Used at EPFL)	Perkin Elmer Lambda 19 DM	**PerkinElmer LAS (UK) Ltd** Customer Care Phone 0800-89 60 46 Fax 0800-89 17 14 www.perkinelmer.com	**PerkinElmer (Schweiz) AG** Bahnstrasse 8 8603 Schwerzenbach, Switzerland Phone Sales 0800 000 015 Phone Service 0800 001125 Fax 0800 000 016 www.perkinelmer.com cc.switzerland@perkinelmer.com
	Sputter – coating	EMITECH®K550 (gold) and K250 (carbon)	**EM Technologies Ltd.** South Stour Avenue Ashford Kent TN23 7RS Phone +44 (0)1233 646332 Fax +44 (0)1233 640744 sales@emitech.co.uk techonline@emitech.co.uk	**Nano-Physics** 95, Av. des Monts Auréliens ZA Saint-Charles 13710 Fuveau, France Phone +33 4 425 38 035 Fax +33 4 425 38 091 www.orsayphysics.com nano@orsayphysics.com
Artificial corrosion	Chemicals for brochantite	Copper sulphate pentahydrate $CuSO_4.5H_2O$	**Sigma-Aldirch Company Ltd.** The Old Brickyard New Road Gillingham SP8 4XT, UK Tel +44 (0) 1747 833 000 Fax +44 (0) 1747 833 313 www.sigmaaldrich.com/ ukorders@europe.sial.com	**Sigma-Aldrich Chemie GmbH** Industriestrasse 25 Postfach 9471 Buchs SG Phone +41 (0)81 755 25 11 Fax +41 (0)81 755 28 15 fluka@sial.com cheorders@europe.sial.com
		Potassium chlorate $KClO_3$	**Sigma-Aldirch Company Ltd.** The Old Brickyard New Road Gillingham SP8 4XT, UK Tel +44 (0) 1747 833 000 Fax +44 (0) 1747 833 313 www.sigmaaldrich.com/ ukorders@europe.sial.com	**Sigma-Aldrich Chemie GmbH** Industriestrasse 25 Postfach 9471 Buchs SG Phone +41 (0)81 755 25 11 Fax +41 (0)081 755 28 15 fluka@sial.com cheorders@europe.sial.com

			Sigma-Aldirch Company Ltd. The Old Brickyard New Road Gillingham SP8 4XT, UK Tel +44 (0) 1747 833 000 Fax +44 (0) 1747 833 313 www.sigmaaldrich.com/ukorders@europe.sial.com	**Sigma-Aldrich Chemie GmbH** Industriestrasse 25 Postfach 9471 Buchs SG Phone +41 (0)81 755 25 11 Fax +41 (0)81 755 28 15 fluka@sial.com cheorders@europe.sial.com
		Sodium sulphate decahydrate $Na_2SO_4.10H_2O$		
	Chemicals for cuprite	Copper (II) nitrate $Cu(NO_3)_2.xH_2O$	**Sigma-Aldirch Company Ltd.** The Old Brickyard New Road Gillingham SP8 4XT, UK Tel +44 (0) 1747 833 000 Fax +44 (0) 1747 833 313 www.sigmaaldrich.com/ukorders@europe.sial.com	**Sigma-Aldrich Chemie GmbH** Industriestrasse 25 Postfach 9471 Buchs SG Phone +41 (0)81 755 25 11 Fax +41 (0)81 755 28 15 fluka@sial.com cheorders@europe.sial.com
Laser cleaning	Energymeter	OPHIR Nova®	**BFI OPTILAS Ltd.** Mill Square Wolverton Hill South Milton Keynes MK 12 5ZY, UK Tel 044 1908 326 313 Fax 0044 1908, 221 110 www.bfioptilas.com ross.hoder@bfioptilas.com	**BFI OPTILAS SAS** 4, Allée du Cantal Z.I. La Petite Montagne Sud CE 1834 – 91018 EVRY Cedex, France Phone +33(0)1 60 79 59 00 Fax +33(0)1 60 79 89 01 www.bfioptilas.fr info.fr@bfioptilas.com
	Laser system	Lynton Lasers Ltd. pulsed Nd:YAG Phoenix®2(+)	**Lynton Lasers Ltd.** Lindow House, Beech Lane Wilmslow Cheshire, SK9 5ER, UK Phone +44(0)1625 536 646 Fax +44(0)1625 530 633 www.lynton.co.uk	Idem

	X-Y Table system Copper and brass plates	ISEL® Step motor controller	**ISEL UK Ltd.** Granville Road 130 NW2 2LN London, UK Tel +44 2089 221 044 Fax +44 2089 221 1066 www.isel.com	**ISEL France** 4, Rue des Côtes d'Orval BP 41 ZAC de la Prévauté 78550 HOUDAN / France Phone +33 (0) 130 461 201 Fax +33 (0) 130 596 932 www.isel.fr info@isel.fr
Metal samples	Copper and brass plates			**Kauffmann & Fils SA** Av. Léopold-Robert 77A 2302 La Chaux-de-Fonds Phone 032 911 10 50 www.kaufmann-fils.ch info@kaufmann-fils.ch Order: M. Prestinari (032 911 10 52); Work: M. Velti
	Gunmetal ingot		**Castle Fine Arts Foudry** Sculpture Workshop, Llanrhaedr Powys SY10 0AA Phone +44(0)1691 780 261	