

**The surface analysis of a brass plate**

**“LUDWIG LEICHHARDT 1848”**

**&**

**Assessment of authenticity**

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## Executive Summary

A brass plaque bearing the stamped impression “LUDWIG•LEICHHARDT 1848” was brought to the Western Australian Museum for non-destructive examination to see if there was sufficient information on its metallurgical structure and chemical composition to enable it to be characterised. Such characterisation should be able to attest to the history of the object, its manufacture, in service performance and provide guidance as to the likelihood that it was associated with the ill fated and last expedition of the famous Australian 19<sup>th</sup> century explorer Ludwig Leichhardt.

Examination was limited to non-destructive surface analysis methods and so the object was placed in an environmental cell utilising a low vacuum chamber of a scanning electron microscope (SEM) and examined using the backscattered secondary electron image mode. This mode provides not only topographical but also atomic number contrast images. Such images allow the observer to discern differences in morphology and mineralogy of the corroded surfaces and to discern the underlying nature of the structure of the object. Analysis of the emerging x-rays provides elemental analysis of the surface composition without any changes to the nature of the object under examination. Based on a combination of high resolution digital photographic images and the data from the SEM, the following conclusions have been made.

The object is made of brass and consists of approximately 62% copper, 34% zinc and 2% lead. The surface has been extensively scored in its manufacture with diagonal file markings that are readily apparent to the naked eye.

Analysis of the serrated lapped surfaces covering upper and lower areas of the plaque are consistent with cold working of another brass object, possibly a brass nail or spike, into the form of the rectangular plaque.

The distribution and form of the lead micro-droplets in the alloy are characteristic of that found in early to mid 19<sup>th</sup> century brass objects, commonly associated with ship building.

Corrosion analysis indicates that the source of sulphur is likely to have come from adsorption of smoke from spent black powder, following percussive discharge of a firearm.

The lettering has been heavily stamped into the plaque and was filled with a black shellac type of filler, which was characteristic of 19<sup>th</sup> -20<sup>th</sup> century memorial plaques.

At some stage in the history of the object, a modern titanium dioxide white pigment has been brushed across the lettering which has left behind a light-coloured deposit in some of the letters.

Corrosion products on the incised marks indicate that the damaged surface was created early in the history of the object.

**The surface composition, patination and structure of the plaque is entirely consistent with its purported provenance.**

# Analysis of the brass plate “LUDWIG LEICHHARDT 1848”

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September 2006

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## Background

A brass plaque measuring 146 x 20 x 1.6 -1.4 mm bearing the lettering “LUDWIG LEICHHARDT 1848” was examined at the CSIRO Australian Resources Research Centre in Bentley, Western Australia using an environmental Scanning Electron Microscope for elemental and morphological details to assess the likelihood that the plate was associated with the failed and final expedition of Ludwig LEICHHARDT across the continent from east to west. This form of analysis requires no sample preparation and leaves no residues on the surface. The analyses were conducted on 31 August 2006 by Michael Verrall, head of the Microscopy unit at CSIRO in the presence of David Hallam, Senior Conservator, National Museum of Australia and the author. The plaque is seen as a dark metal object lying on top of the aluminium stage in Figure 1, as it was being placed into the electron microscope.

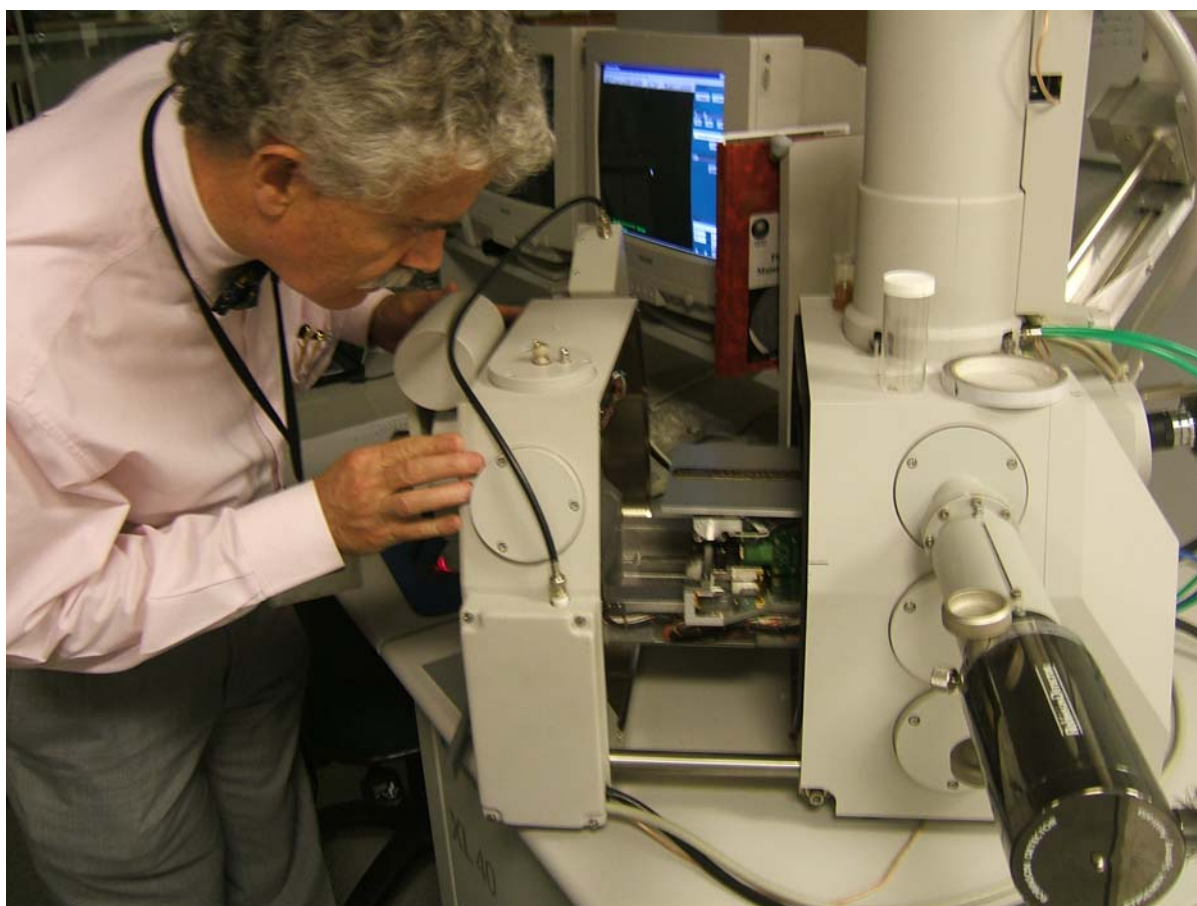


Figure 1: Placement of brass plate onto aluminium inspection plate in the SEM at CSIRO.

Once the sample was placed inside the chamber, the air was removed by a series of staged vacuum pumps to facilitate the passage of the electron beam that hits the surface and excites the x-rays which are used to characterise the nature of the surface being examined. A typical x-ray spectrum showing elemental analysis of the surface is shown in Figure 2 which relates to a surface near the letter “L” of LUDWIG on the left hand side of the plaque. The principal components of the brass are copper and zinc, along with a smaller percentage of lead, which is a typical impurity in 19<sup>th</sup> century brasses.

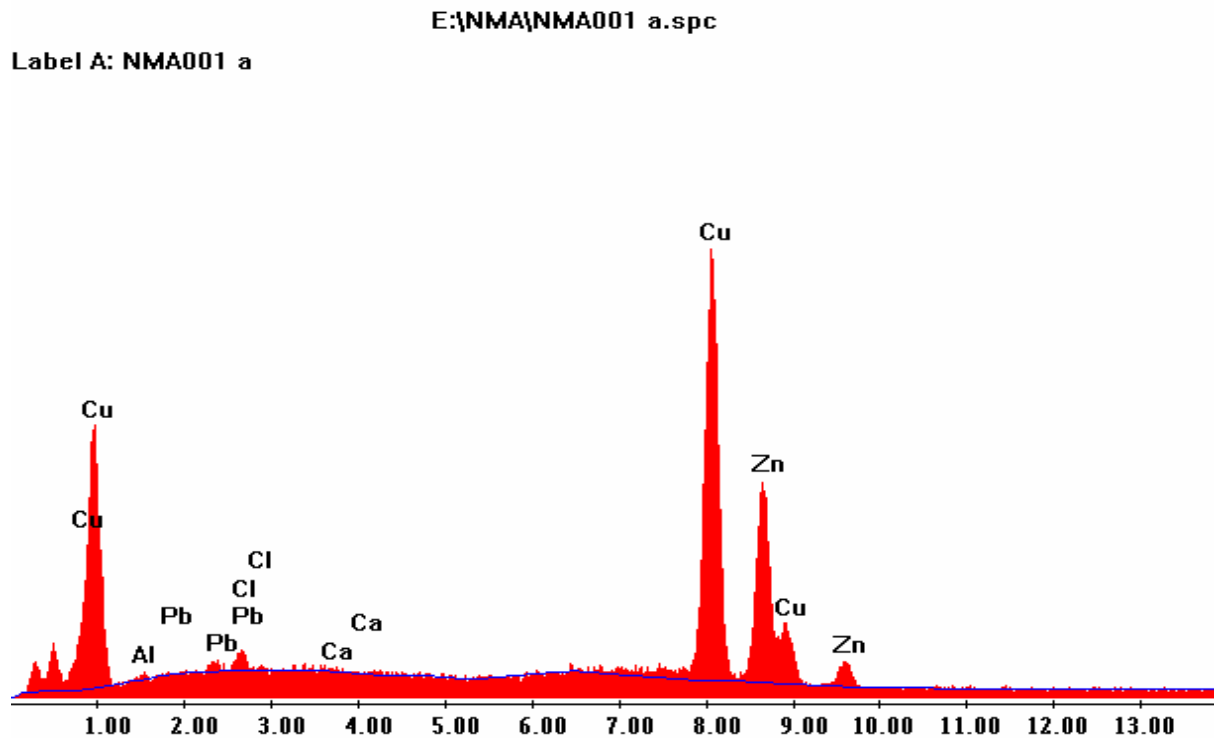


Figure 2: Typical x-ray analysis spectrum of the plate, showing the presence of the principal alloying elements of copper and zinc as well as a small percentage of lead and some chloride.

The SEM has an analysis program that converts the elements identified from the spectrum into a percentage elemental analysis, with results presented on a weight percent basis and on an atomic level. Whilst the differences between the two formats are small for the copper and zinc, since they are adjoining elements in the periodic table, the differences are more marked for the heavier elements of lead and lighter elements such as carbon, from organic surface deposits, where a small weight percent of carbon reflects a much greater molecular concentration on the surface of the object. The analytical data which forms the basis of this report and discussion are found in Appendix I.

In order to understand the complex nature of the surface of the object and how it has corroded it is important to review the nature of the alloys that are created when copper is melted with varying proportions of zinc, to create a wide range of brasses which were typically used in the 19<sup>th</sup> century for sheeting or sheathing of wooden ships, to prevent the attack of timbers by wood boring molluscs such as the “teredo worm” or the *Limnoria* species of wood gribble. The first analysis showed 60.69% copper (Cu), 33.7% zinc (Zn) 2.16% lead (Pb), 1.34% chlorine and 1.82% aluminium (Al). The amount of zinc places the alloy on the phase diagram, shown in Figure 3, at the point where the zinc-rich  $\beta$  phase will precipitate as the

liquid metal cools. The first phase to precipitate is the  $\alpha$ -phase which is a solid solution of zinc in copper which has more the chemical reactivity and characteristics of the principal component copper. As the copper rich phase solidifies, the remaining melt becomes richer in zinc and the composition line moves along the abscissa and the pink zone of a combination of the ( $\alpha + \beta$ ) phases are precipitated.

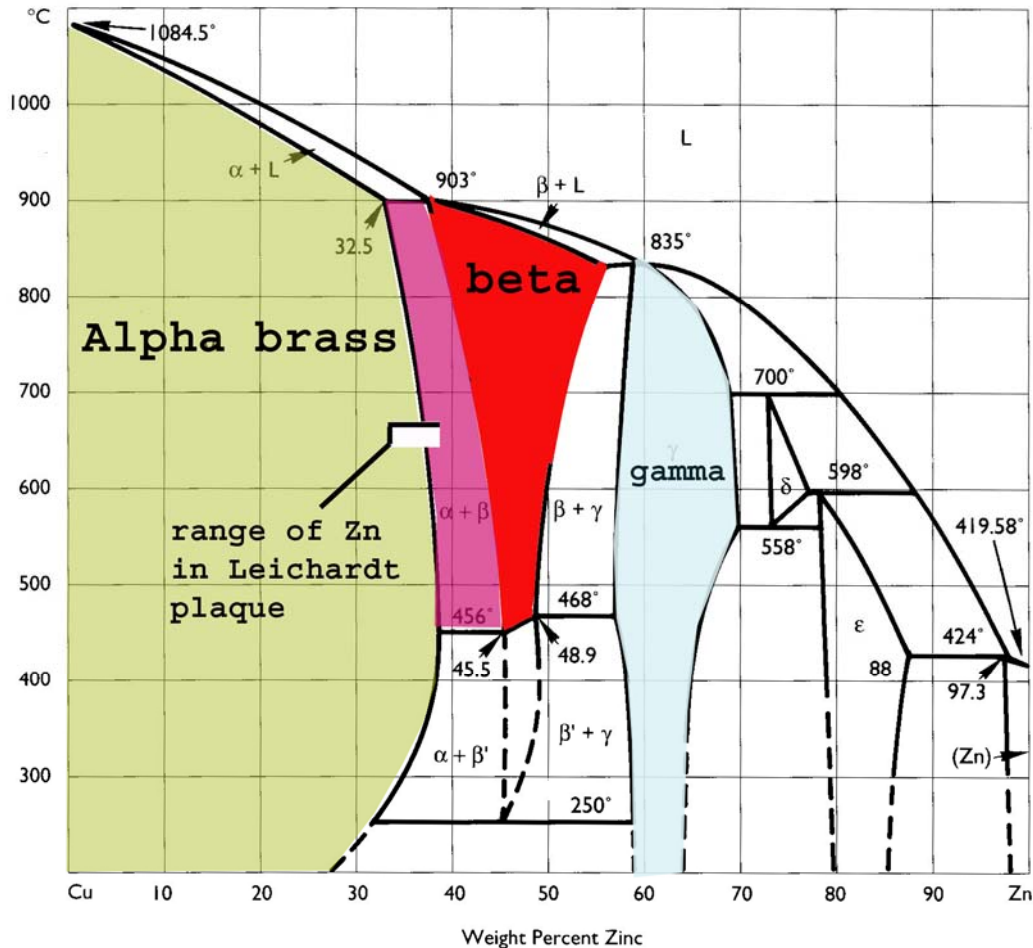


Figure 3: Phase diagram for copper and zinc. The bar illustrates the range of surface compositions found in the “LEICHHARDT” plaque

A second area closer to the worn edge had 61.89% Cu and 36.77% Zn, with only 0.35% Pb which reflects a zone that is richer in the  $\beta$ -phase than in the  $\alpha$ -phase which is richer in copper. The range of compositions that relate to the general distribution of metals in the alloy is shown in Figure 3. One of the chemical consequences of the presence of both alpha and beta phases are that there will be differential corrosion activity across the surface, with the zinc-rich  $\beta$ -phase generally being more reactive than the copper-rich  $\alpha$  phase. Lead in the alloy comes from typical impurities associated with the manufacture of zinc and copper since many mineral bodies are characterized by a mixture of copper, lead and zinc sulphides from which the parent metals are normally separated by a series of complex hydro- or pyrometallurgical processes. Because lead has a very low melting point it is the last element to freeze in the molten alloy and so it will tend to be present as micro-droplets which tend to

be evenly distributed throughout the object. However, owing to the higher solubility of lead in the zinc-rich  $\beta$  phase, the lead will tend to concentrate in this phase of the brass. Thus corrosion of the  $\beta$ -phase will tend to be richer in lead corrosion products than the  $\alpha$ -phase corrosion matrix. If the metal has been rolled during its manufacture, the lead inclusions will be present as elongated blobs of metal, with the lines of rolling being parallel to the longer axis of the inclusion.

The electron microscope images in this report are based on the back scattered secondary electron mode of operation of the SEM which means that apart from presenting morphological or topographic features of the surface, the black and white image will have varying shades of grey. Bright areas are richer in elements of higher atomic number, like lead, while there is only a subtle “colour” difference between zinc and copper, since they are adjoining elements in the periodic table. Light weight elements such as calcium, silicon and aluminium appear dark grey while organic compounds, such as those associated with sweat and oils from human handling, will be very black. It is important to note that the presence of aluminium is not due to the background of the microscope stage but is due to the presence of small amounts of minerals such as the aluminosilicates kaolinite,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . This interpretation is supported by the presence of potassium which normally presents itself as potassium magnesium silicate hydroxide  $\text{KMg}_{2.5}\text{Si}_4\text{O}_{10}(\text{OH})_2$ , potassium aluminium silicate hydroxide  $\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$  in clay based minerals.

The first area to be analysed was located near the left hand edge of the plaque, as shown in Figure 4 and the SEM image of the upper midline of area is shown in Figure 5.



Figure 4: Photographic image of areas of spot analysis NMA001a and SEM image of area 1

The photographic image shown in Figure 4 illustrates the complex nature of the surface of the object, which has clearly defined transverse striations which are consistent with the metal



plaque having been somewhat crudely fashioned and finished with a flat file, with the scoring lines running approximately 45° to the horizontal plane. The detailed surface analysis was conducted at area NMA0001a since this zone seemed to be relatively free of corrosion products and the surface was relatively flat and was free from lettering impressions, and therefore free of localised stress associated with the manufacture of the plate. The area covered in the SEM image of this plate, area 1, was chosen to illustrate the general properties of this section of the plate which is characterised by an apparent upper surface layer on top of the lower section of brass. This area may represent a “lapping layer” which is characteristic of poor workmanship in the manufacture of brass and copper fastenings in the 19<sup>th</sup> century (MacLeod and Beng 2000, MacLeod and Pitrun 1988). The layering of the surface of the plaque is consistent with the metal having been produced by cold working and hammering of a different object, such as a brass sheathing nail or bolt, into a flat form. Evidence of the lack of a suitable heat treatment is seen in the ragged edges of the upper zones which overlie the underneath areas which have the lettering stamped into them. If the original form of the brass object was a square shank nail and if the maker of the plaque had hammered a square edge flat, the irregular edged layers would be consistent with what is seen on the surface of the plaque. Many of the defects seen on the plaque would not have been apparent to the fabricator or to the owner. The subtle surface differences would have become increasingly apparent as the impact of corrosion along the stress lines associated with the cold working became more pronounced.

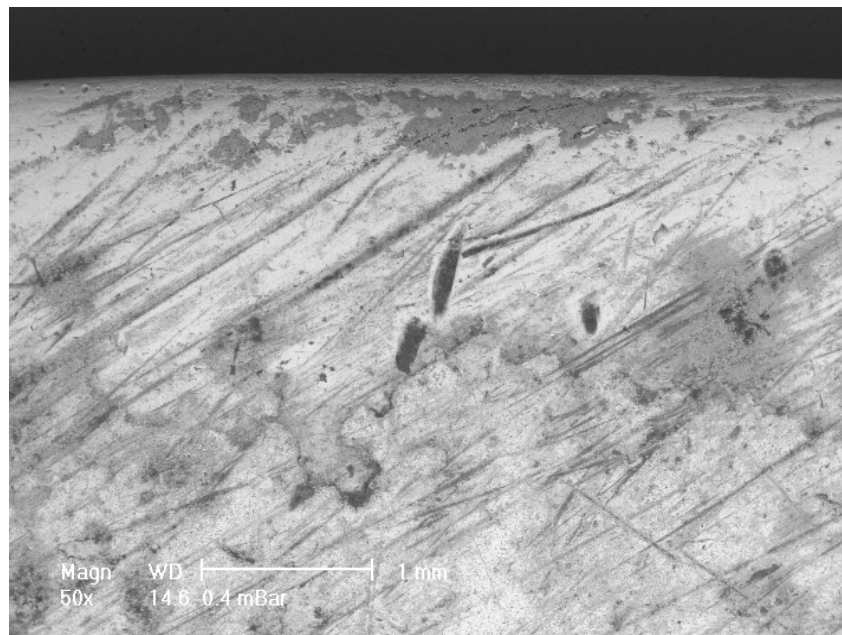


Figure 5: Backscattered SEM x 50 image of upper section of plaque at “LU” area 1 showing the morphological differences between the upper and lower section at the “join” between the two layers of metal.

The crusty deposit on top of the SEM image in Figure 5 is a layer of corrosion debris which also incorporates some elements of the archaeological deposit. The fact that the deposit has the same morphology as the gouges and scratch marks on the surface is consistent with the material having been naturally deposited on the surface i.e. not artificially formed. The next zone of the plaque that was examined was located above the letter “D”, area 2, and was characterized by an almost total lack of zinc; see Appendix I spot 3 for details, and was rich in copper, chloride and oxygen.

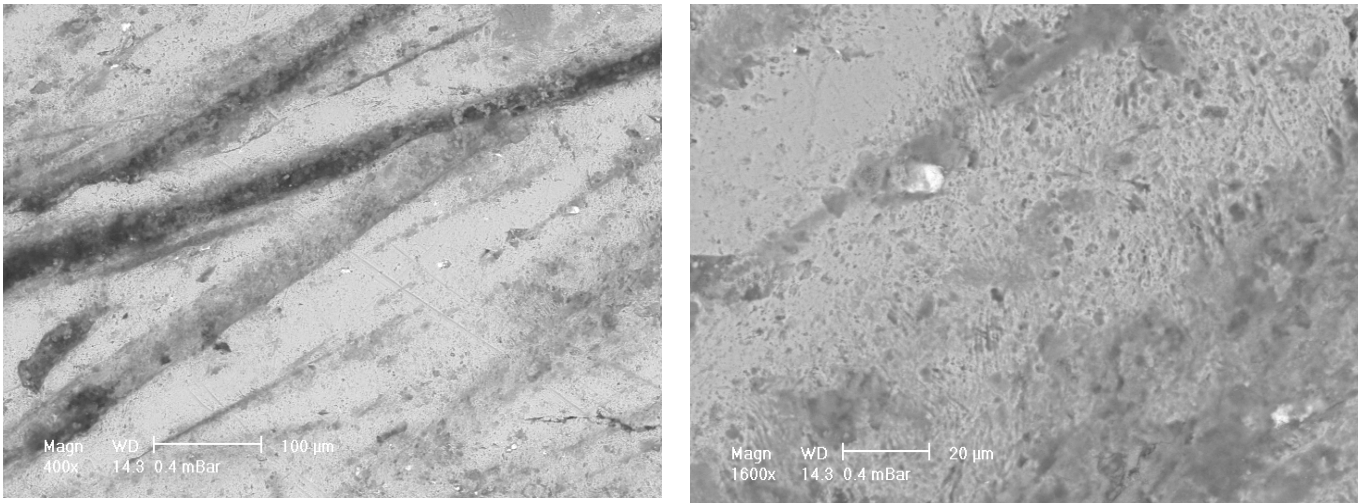


Figure 6: Left hand SEM image x 400 image of upper section of “LU” area showing elongated lead (bright grey) micro-droplets of lead and light weight mineral deposits in the grooved surfaces. Right hand image of the same object but at x 1600 showing a distorted lead inclusion and apparent sweat-induced corrosion in the middle of the image.

Support for the supposition that the plaque was manufactured from a square shank nail was obtained by experimenting with a 4 x 4 mm copper planking nail from an unidentified Western Australian shipwreck dated circa 1860. Repeated striking of the square edge with a 3 cm diameter head of an 800 g claw-hammer reduced the thickness to 2mm and the width increased to 10 mm. This reduction is very similar to that which would have produced the dimensional change in the lead micro-droplets in the plaque. After 40 blows the nail cracked and the hammered section fractured. Optical examination of the cold-worked surface showed the same characteristic ragged edge at the fold line that mimics the forms observed on the plaque and a 240 µm wide zone above it where the hammering did not effect fusion (see Figure 7).

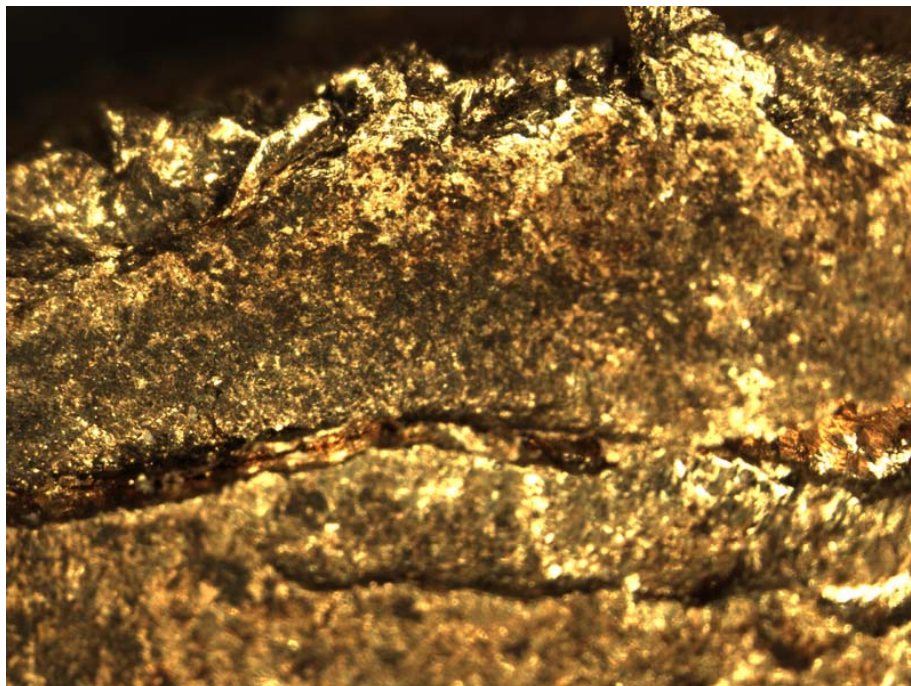


Figure 7: Optical micrograph of cold worked 19<sup>th</sup> century copper nail full width 4.4 mm



Since brass is more ductile than the copper used in this experiment, the formation of the plaque through a similar hammering process is confirmed as being the most likely form of fabrication. The apparent loss of zinc from some surfaces is simply a reflection of localised corrosion processes. The formation of corrosion products on the surface means that minerals such as copper (II) hydroxy chlorides of the form  $\text{Cu}_2(\text{OH})_3\text{Cl}$  as well as the normal dominant copper (I) oxide cuprite,  $\text{Cu}_2\text{O}$  would provide a reasonable explanation for the lack of zinc in the surface analysis. The surface analysis of the oxygen and chloride shows an atomic ratio of 3:1 which is consistent with the suggested chloride containing mineral (MacLeod, 1991).

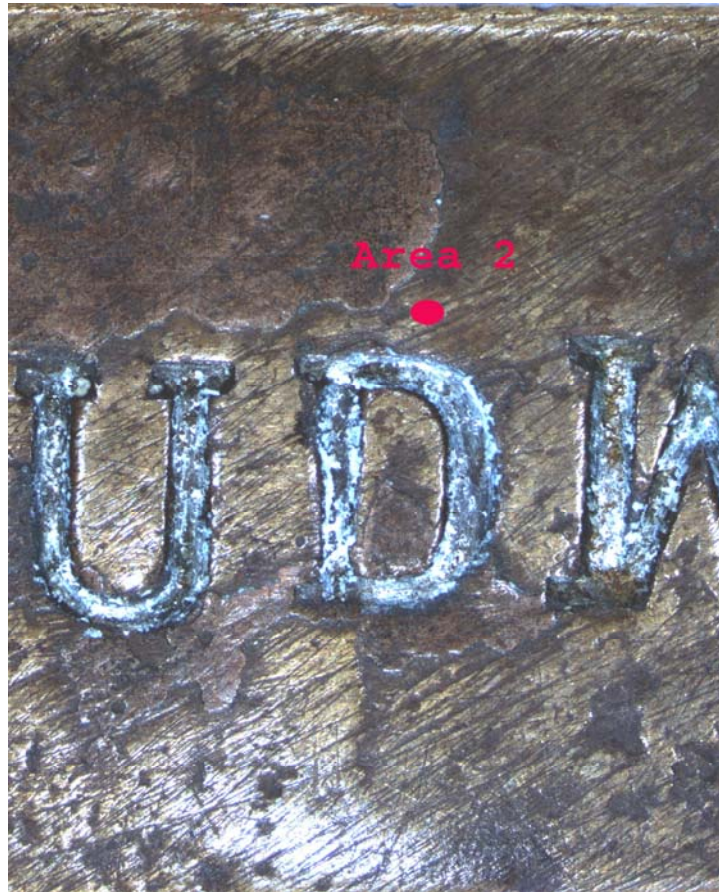


Figure 8: Optical image of the plaque at “UDW” area 2 of “LUDWIG • LEICHHARDT”

Spot analysis of the “lapped” area above the letter “D” shown in figure 8 is consistent with a primary oxidation layer of  $\text{Cu}_2\text{O}$  being on the surface which has a very low zinc content of 1.25 wt% - see Appendix 1 spot 4a. An area of localised corrosion near the letter “D” is shown in Figure 9 at x 50 and x 200 magnification. The dark spot is rich in low atomic weight elements such as carbon, which represents 49.2 wt% of the material, with a small amount of copper and less zinc. This is consistent with the corrosion matrix being a “copper spew” or a corrosion matrix that consists primarily of reaction products where copper has reacted with organic oils from fatty acids, such as found from repeated handling of an object. Since the copper (II) organic salts have a very different density and crystal structure to the underlying metal, they do not form a coherent coating on the surface and corrosion continues in the presence of moist air. The presence of chloride ions is consistent with the object being repeatedly handled and the earth elements of magnesium, calcium, silicon, potassium, iron and phosphorus are commonly associated with dirt and clay- see spot 004a in Appendix I.

In the same area of the metal plate, there were also some very clearly defined sections of the surface where the main corrosion products were copper sulphides, with almost 12 wt% sulphur found at spot 004c, along with some chloride and only copper (no zinc) was present on the surface layers. The area of discussion is located in the lower right hand side of the higher resolution image in Figure 9 and is seen as a crusty mid grey crystalline deposit. The organic copper corrosion products are the dark grey phases at the edge of the interface between the lapped area, upper left side of the higher resolution image in Figure 9, and the body of the plaque.

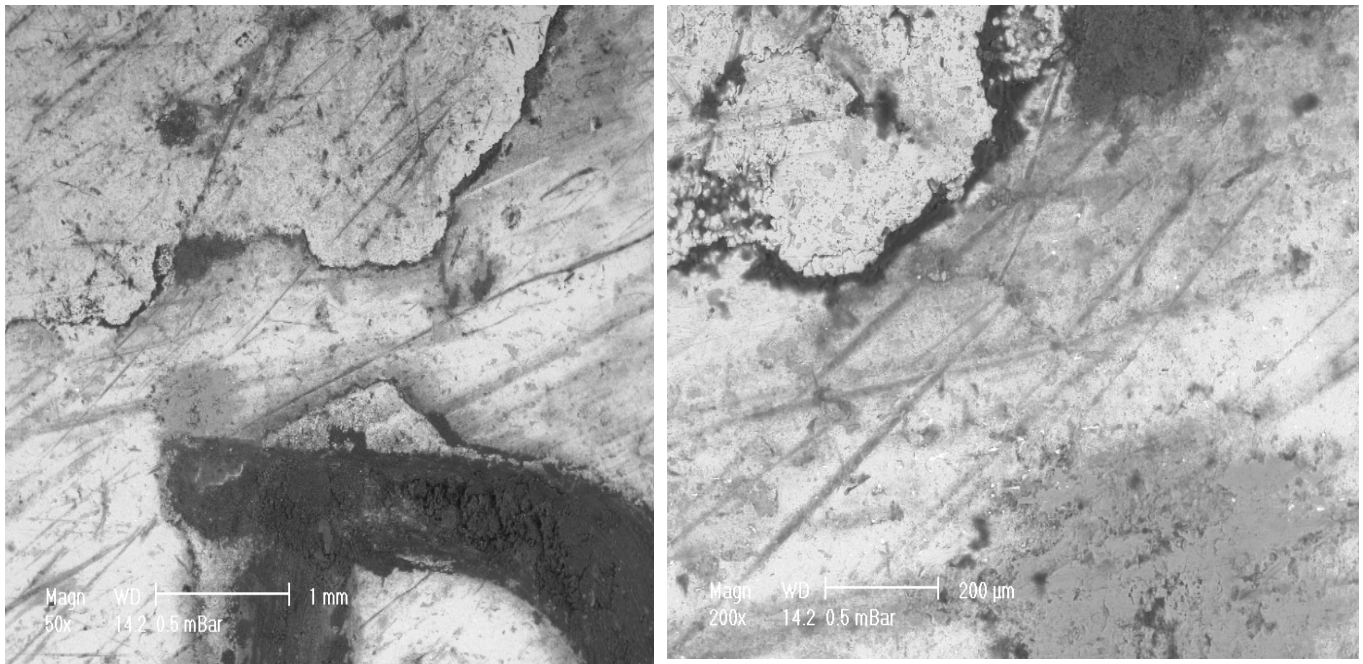


Figure 9: SEM image x 50 (LHS) and x 200 (RHS) including the letter “D” on the plate.

It should be noted that there is a clearly defined crusty infill in the letter “D” which is characteristic of the use of a black shellac (carbon black mixed in with normal shellac or French Polish) which has suffered degradation from the effects of ultraviolet light and general exposure to humidity cycling. The clear separation of the copper sulphide phases from the general corrosion is seen in Figure 10, which shows the discrete corrosion areas at high magnification. The size of the corrosion zones is  $20\pm 10\ \mu\text{m}$  and this is typical of the response of copper to the presence of small particles of sulphur, since bacterial colonies associated with production of sulphide ions from sulphate tend to be of the order  $300\pm 150\ \mu\text{m}$  which are typical by-products of sulphate reducing bacteria. This form of localised corrosion is a characteristic of anaerobic bacterial metabolites reacting with copper based alloys or of direct chemical reaction of copper with sulphur (MacLeod 1993). The nature of the copper sulphide deposits, in terms of their distribution, morphology and size, supports an alternative source of sulphur than that coming from the metabolites of sulphate reducing bacteria, which reduce sulphate ions to sulphide ions.

It is not possible to determine the precise nature of the patina without resource to x-ray diffraction analysis of the corrosion products on the surface. However, the mixed dark brown and black surface is consistent with the plaque being covered by a mixture of the dark brown  $\text{Cu}_2\text{O}$  resulting from normal atmospheric corrosion and the black of  $\text{CuO}$  or tenorite, which is

typically formed with high temperature oxidation of the metal, such as can occur in a wood fire or heating a copper alloy with a blow-torch.

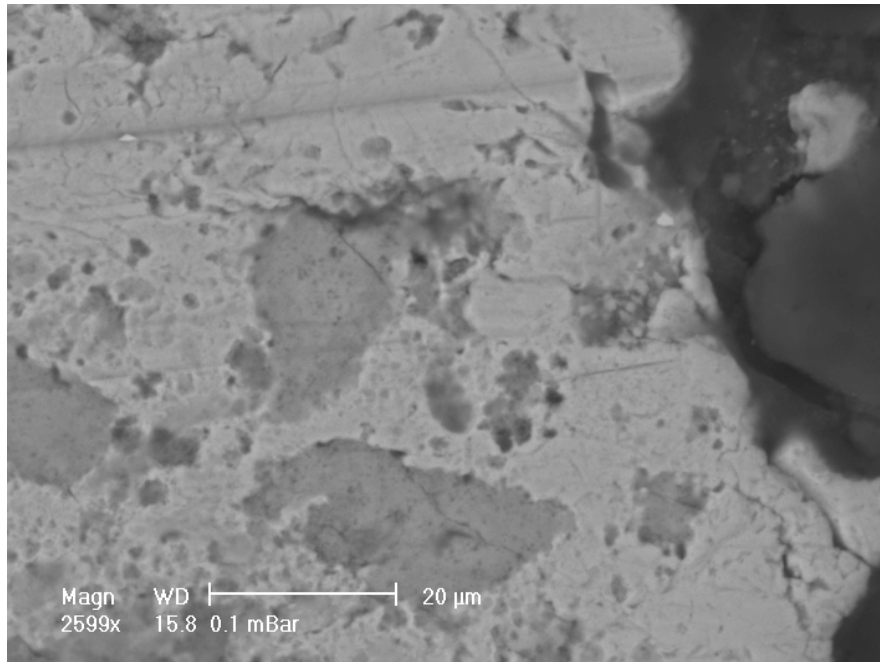


Figure 10: SEM x 2599 image of copper sulphide corrosion zones (mid grey) near letter “D”

The presence of chlorides and sulphides in spot 004d means that it is also possible that a salty object became buried in an archaeological context where there was a ready supply of organic materials. Experience with copper alloy objects resting for several months against the floor of a treatment container shows that this form of “burial” is sufficient to allow anaerobic bacteria to produce sulphide ions at the metal-water interface. The sulphide ions react with the copper alloys to produce a range of copper sulphides. Sulphate ions, which are prevalent in the salty margins of all soaks and water courses in the interior of the Australian continent, will have provided the source of sulphur and anaerobic conditions can develop in very shallow deposits if there is some physical barrier that prevents the ready diffusion of oxygen to the corrosion zone. The high resolution image also shows up the granular nature of the brass plate in that intergranular corrosion lines can be seen in the upper section of Figure 10 that give a grain size of approximately 5  $\mu\text{m}$  in diameter. Further evidence as to the nature of the source of the sulphide ions became apparent with subsequent analysis further towards the right hand edge of the plaque.

The grain boundaries of the brass crystals can be seen in main copper sulphide deposit (see Figure 10 bottom midfield view) which seems to span three grains. It is possible that elemental sulphur fumes, thus very small particle size, resulting from the use of black powder as the rifle was fired, could have been absorbed from gun smoke. Typical composition of black powder had 10% charcoal, 10% sulphur and 80% potassium nitrate. In the event of such adsorption, the subsequent formation of copper sulphides is not unexpected and it is likely that sulphur fumes from spent black powder are the most likely source of sulphur on the brass plaque. Typical sizes of finely divided elemental sulphur used in the manufacture of gun powder are in the range of 10-6  $\mu\text{m}$ , which is the same size as the primary copper sulphide corrosion products seen on the plaque.





Figure 11: Optical image of the plaque at the separation of LUDWIG•LEICHHARDT showing overlapping layers of metal near the foot of the image and areas shown in the SEM Figure 12.

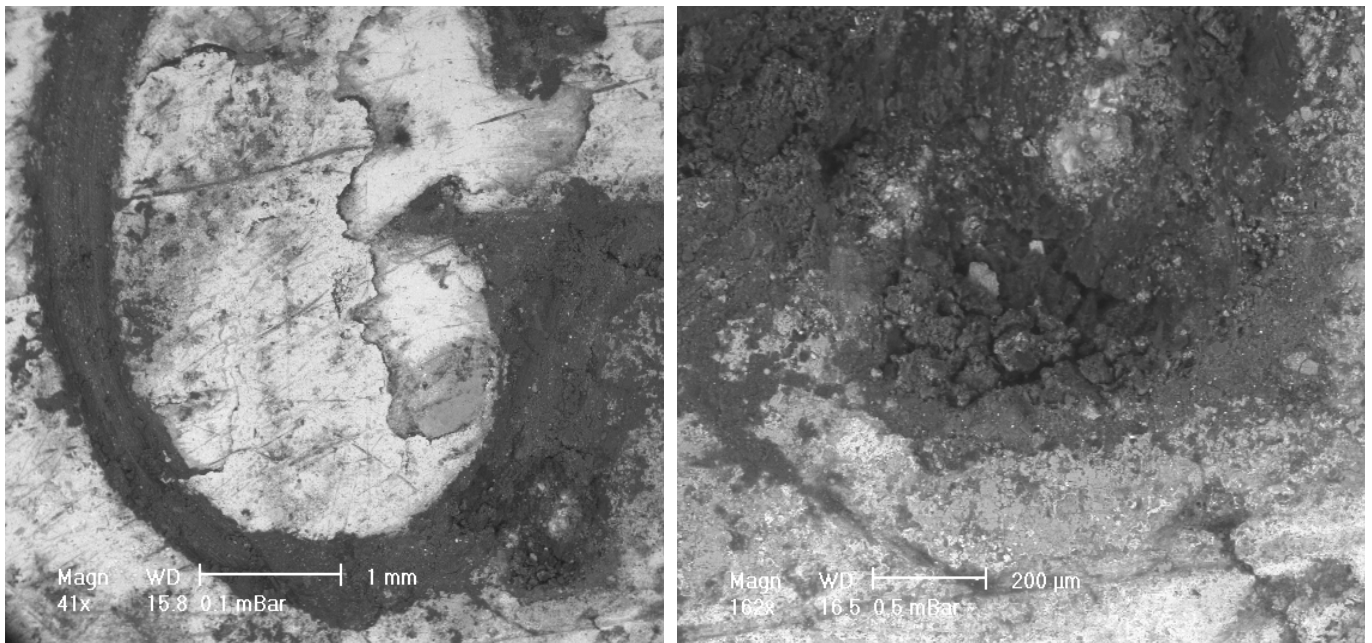


Figure 12: SEM surface details x 41 of the letter “G”. The right hand image x 162 is located near the bottom of the letter.



Four spot analyses of the dark deposits at the right hand side of the letter “G”, as shown in figure 12, showed that the corrosion deposits are dominated by organic copper corrosion products, see spot 006b in Appendix I. The content of the infill of “G” is essentially pure organic materials as shown in analyses 006a, 006c and 006d where the atomic ratios of carbon to copper are 52, 82 and 41 respectively. This is consistent with the material that produced the very dark grey SEM images being black shellac. Some intergranular corrosion below the letter “G” can be seen in the lower right hand side of the x 162 image in Figure 12. It should be noted that these surfaces also have high amounts of sulphur in them, with the maximum value of 8.57 wt % in sample 006c which has only 2.96 wt% copper and so there must be another source of sulphur other than copper sulphides. This sample area is also characterised by a high calcium content of 9.44 wt% which is consistent with some of the sulphur being present as gypsum or  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . It is likely that calcium carbonate,  $\text{CaCO}_3$ , is the most probable source of the additional calcium content of this area since evaporation of inland waters around lakes and soaks leads to precipitation of calcareous deposits.

Selective corrosion of brasses can result in the “dezincification” of a surface where there has been mobilisation of zinc corrosion products away from the metal, which leaves the surface selectively enriched with copper i.e. the surface is depleted with regard to the underlying amount of zinc in the parent alloy. One of the underlying reasons why it is difficult to find large deposits of zinc corrosion products is that most zinc minerals, other than zinc sulphide, are quite soluble and will normally not be found on the surface of corroded brasses, certainly those found in a chloride rich environment. Although many areas of the plate have a copper enriched surface, some of the areas such as around the letter “C” near the hole, as shown in Figure 13, are characterised by a relatively high abundance of zinc and chloride.

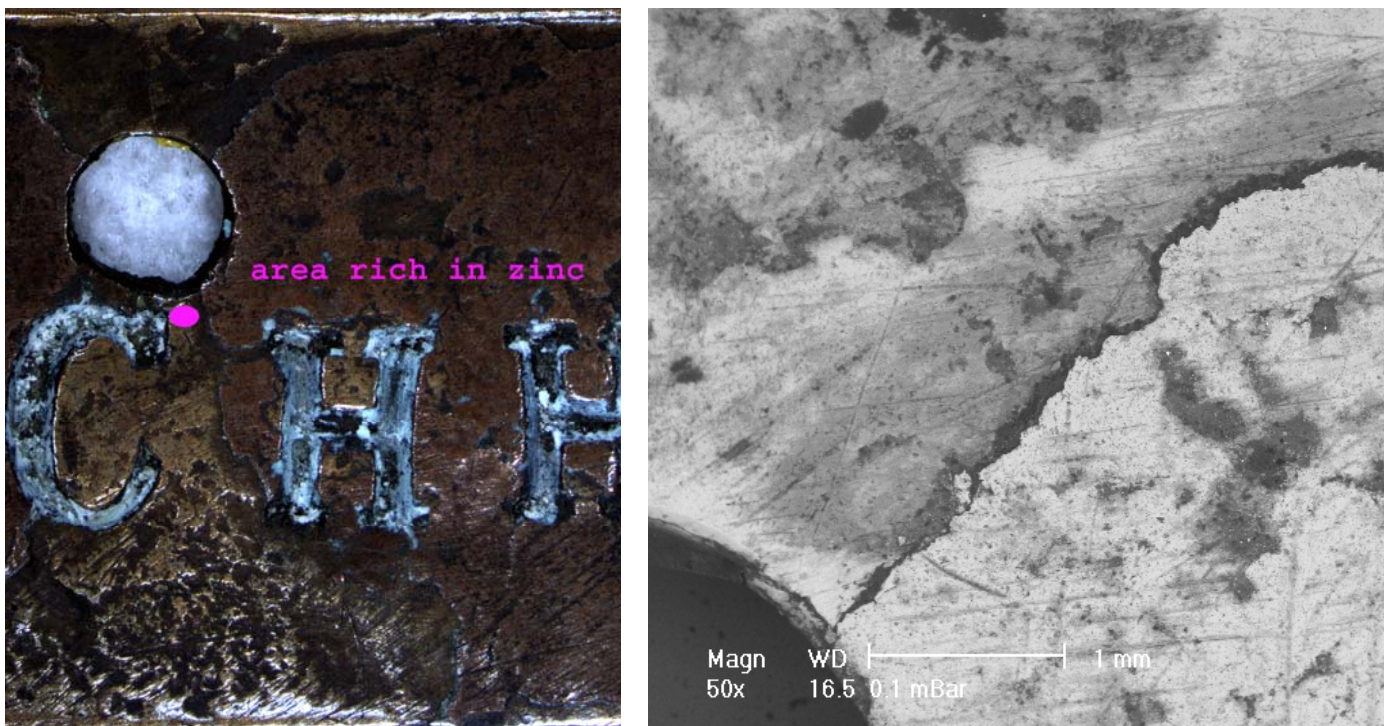


Figure 13: Photograph of the plate showing the attachment hole and letters “CHH” and SEM images x 50 of zinc chloride rich corrosion near “C”

Although no X-ray diffraction was done on the surface, since no sampling was permitted, it is likely that the zinc chloride compounds on the surface could have included species such as simonkolleite,  $Zn_5Cl_2(OH)_8 \cdot H_2O$  (Selwyn 2004). The presence of zinc hydroxy chlorides attests to the arid nature of the environment from which the object has presumably been sourced.

A more detailed examination of the surface area adjacent to the letter “C” of LEICHHARDT is shown in Figure 13 as the x 50 image, seen in the right hand side of the figure. The fissure relates to the lapping of the surfaces which relate to defects associated with the manufacture of the brass plaque, as previously noted. If the plaque had been formed by hot working of the original brass it is likely that the fusion bonding caused by hot hammering of the metal would have been disguised. Brass sections from infill a steam pipe from the wreck of the *Xantho* (1872), where inserts were formed by hot working, it was noted that the brass resisted any form of selective corrosion on the joining lines even after 130 years in seawater. The right hand side of the Figure 13 relates to an area of the plaque that is relatively uncorroded while the zone immediately to the left and lying above the fissure line has essentially no copper in it and is the zone where zinc chloride corrosion products dominate the EDAX analysis.

The lettering in the middle of the plaque, as seen in Figure 14, as the three leading letters of “LEICHHARDT” has little of the original infilling material present and the greatest amount of the white coloured infill material, which was originally thought to be polish residues. The greatest concentration of infill is seen in the foot of the letter “L” and in the lower right margins of the letter “E”, with a patch of the paint near the top of the letter.



Figure 14: Photographic image of the letters “LEI” showing presence of the white titanium based pigment inside the lettering, where the original black shellac has been lost.

The last detailed analysis was conducted on the letter A of “LEICHHARDT” which still retained significant amounts of the original infilling of the lettering. The analysis of the infill was conducted in association with a mixture of phases present in the lettering. The analysis in spot 010b in Appendix I is consistent with the nature of oxidized black shellac. The nature of the white deposit alluded to in Figure 14 was determined by the EDAX analysis where there was a significant amount of titanium (3.91 wt %) present on the surface of the deposit. The most likely compound that is consistent with the nature of the analysis is a pigment based on titanium dioxide,  $\text{TiO}_2$ , which is consistent with the highlighting the lettering with modern white paint – see Figure 15. Other elements present in this area of the lettering and associated with the materials deposited in the scoring associated with the coarse filing of the surface were significant amount of aluminium, silicon, potassium, calcium and some sulphur.

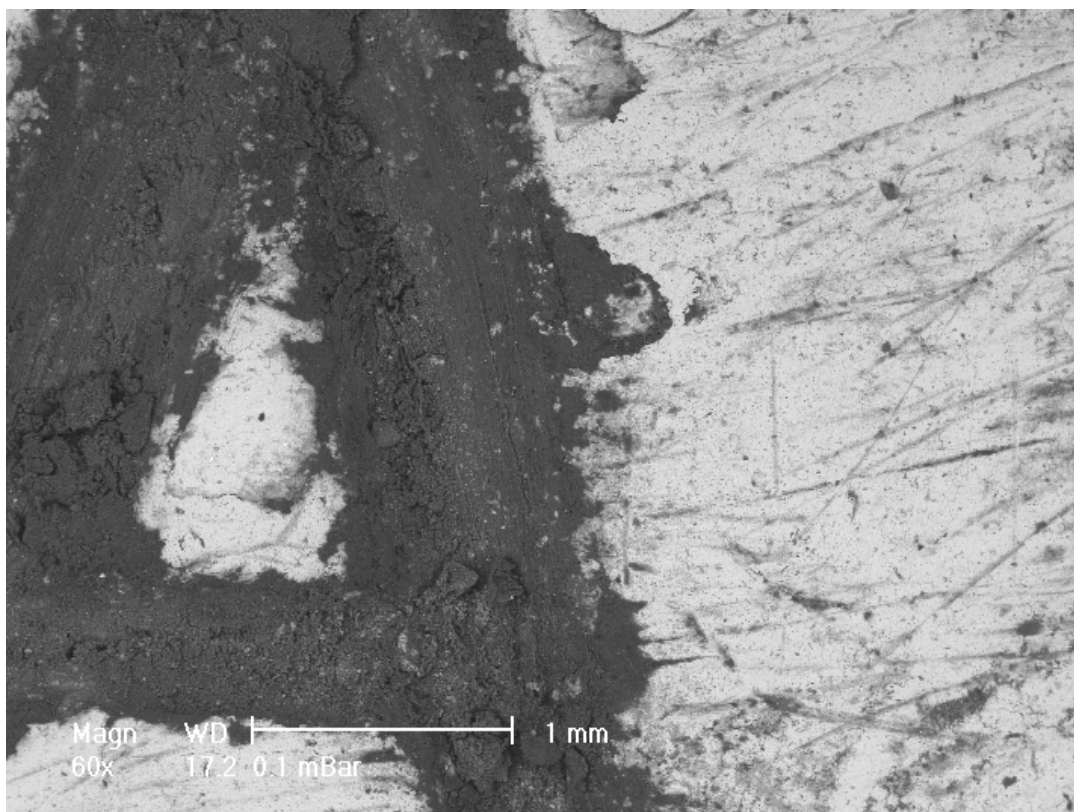


Figure 15: and x 60 letter “A” with in-filled lettering.

The origin of the sulphur is most likely associated with remnants of the use of black powder in the firing of the rifle while the presence of potassium, aluminium and silicon indicates clay like aluminosilicate minerals such as kaolinite. The calcium would normally be associated with gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  or some calcareous deposit such as calcite  $\text{CaCO}_3$ . Rubbing the plaque with the earth and ash deposits from a bush campfire would leave behind residues which would be essentially identical to the materials that were observed on the plaque.

Inspection of the letters and numbers on the plaque indicates that there appears to have been some degree of difficulty associated with manufacturing the lettered plaque. Apart from the use of the upside down “M” instead of a “W” in “LUDWIG” and the number “4” is clearly a composite of the letter “I” and crossed tails of smaller letters to finish off the formation of the number.



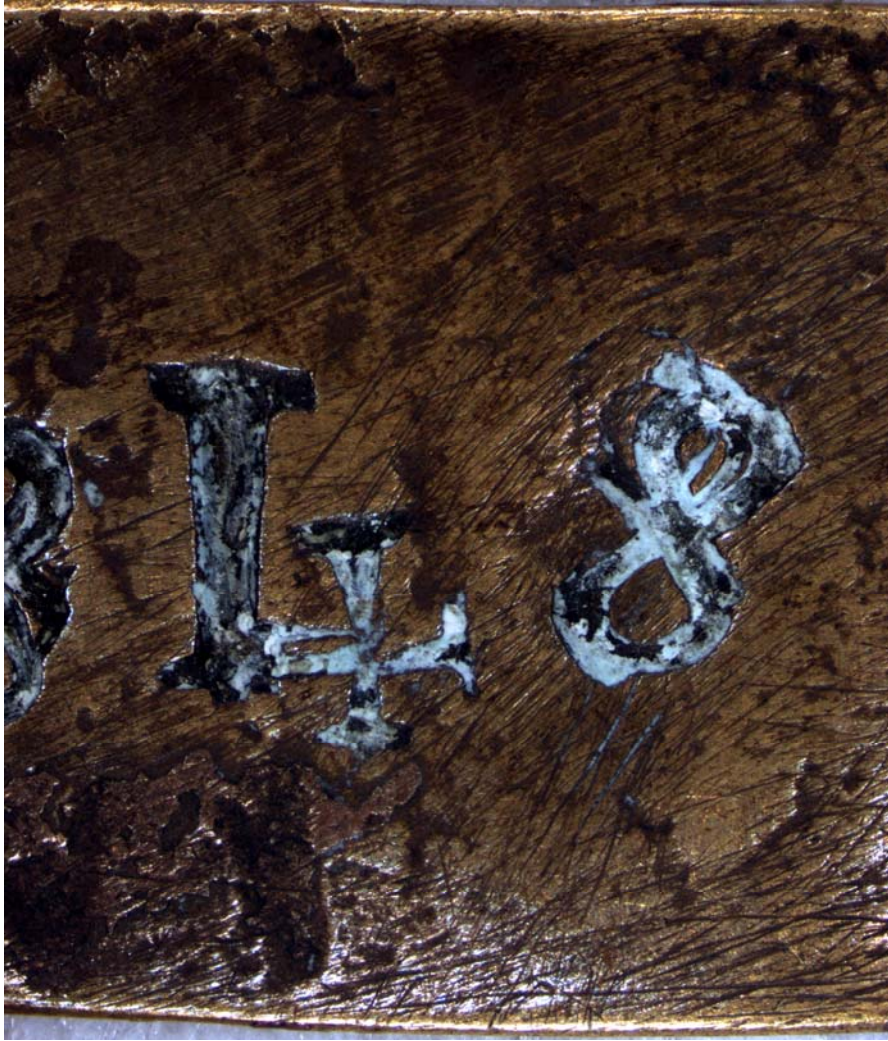


Figure 16: Photographic image of the final date stamps “48” showing poorly formed “4” and a double strike on “8”.

Close to the right hand edge the final “8” of the “1848” date shows evidence in the upper section of the number of at least two attempts to successfully imprint the last number. The difficulty of punching the numbers close to the end of the plaque may well be a reflection of the cold working having produced a much harder brass that resisted the impact of the striking punch (MacLeod and Pitrun, 1988).

### **Potential sources of metal for the plaque**

The assertion that the brass used in the manufacture of the plaque is likely to have come from re-use of a piece of metal from a ship, is based on experience with detailed examination of scores of fittings combined with a number of metallurgical examinations. Analyses of the relevant brass objects are reported in Table 1, along with their date of manufacture. The earliest brass fitting was a nail from the wreck of the American spice trader *Rapid* which was built in Braintree in the USA in 1807. Although the *Rapid* nail has significantly lower zinc content than the LIECHHARDT plate it does have an essentially the same amount of lead in it. The brass bolt from the wreck of the *Gem*, which was built in 1835, had a lead content of 1.2%. The plaque under examination had an average lead content of 1.5%. Between the period of 1835 and 1857, the date of construction of the *Mary Hamilton*, significant improvements in the technology of manufacturing non-ferrous alloys for shipbuilding took



place. Thus the brass bolt from the wreck of the *Mary Hamilton* that was recovered along with materials from the wreck of HMS Sirius had a lead content of 0.67% which represents a turning point in quality control of impurities in brass fittings. The plaque appears to have been manufactured from fittings that were created in the first 45 -50 years of the 19<sup>th</sup> century. It is only with the development of metallurgical science that the properties of brass and bronze fittings were able to be tailor made to suit specific performance issues.

Table 1: Composition of brass fittings recovered from 19<sup>th</sup> century Australian shipwrecks.

Source	Date	Cu	Zn	Pb	Sn
<i>Rapid</i> brass nail RP 0000	1807	70.40	26.39	1.90	0.32
<i>Gem</i> brass bolt no GE 2366	1835	65.60	32.40	1.20	0.10
<i>Leichhardt</i> plate average	1848	59.71	36.68	1.51	0.00
<i>Mary Hamilton</i> bolt SI 15	1857	67.70	31.50	0.67	0.04

When the “LUDWIG • LEICHHARDT” plaque is compared with the other listed shipwreck objects that were analysed by wet solution chemistry, as distinct from surface analysis by Scanning Electron Microscopy, it is seen that the composition is typically that of an early 19<sup>th</sup> century brass spike or nail. If a microscopic sample of the plaque was analysed by spark spectrophotometric techniques it would be possible to obtain the trace element analyses for arsenic, antimony, silver which may assist further curatorial work in establishing the origin of the metal.

The presence of the lapping joins clearly shows that the plaque has been manufactured by cold working of an existing brass object. It is not possible to metallurgically differentiate between the effects of heating from events such as the rifle being burnt and from deliberate heating of the object to remove residual mechanical stress. If the object had been made from a cut section from a sheet of rolled brass, which was readily available in 1844 (McCarthy 2005) the surface texture would have been very different and there would have been little or no need to remove the surface imperfections by filing the plaque. If the plaque had been made of brass sheathing it would have been thinner and would also have had a higher zinc content that was reflecting the formulation of the classical 60% copper 40% zinc of Muntz metal which had become commercially significant by 1840.

## CONCLUSION

The plaque appears to have been manufactured from an existing brass object, rather than having been cut from a sheet of rolled brass. The structural details revealed by the surface analysis indicate that the plaque was likely to have been originally a square-section cast nail. Such objects were readily available in the middle of the 19<sup>th</sup> century from ships’ chandlers or from debris recovered from contemporary shipwrecks. The amount of lead in the brass plaque is more consistent with marine brasses from the first half of the 19<sup>th</sup> century i.e. pre- 1850 rather than in the second half of the century. The lead inclusions show extensive distortion, their length being twice the width, which is an indicator of mechanical cold working. The “lapping” or apparent seams in the metal surface along the upper and lower portions of the plaque are indicative of the object having been made by cold working i.e. hammering of a different object into a flat form. If there had been any significant annealing of the cold worked object the lap lines would have been much less distinct. Cold working leaves significant stress in the metal, which is consistent with extensive corrosion found on the surface.

The lettering of the plaque has obvious errors, such as the use of an upside down “M” for the “W” in the forename of the explorer. It is likely that this “error” is a simple response to there being no appropriate “W” stamp and so an upside down “M” sufficed. Inspection of the plaque shows that the manufacturer was not content with the original strike of the number “8” and there is clear evidence of multiple strikes of this digit. Increased hardness from cold working of the plaque would have made it much more resistant to the impression of the struck letter and digit dies or stamps.

Corrosion analysis of the deposits on the surface shows that the object has been exposed to a number of episodes where different microenvironments have resulted in a mixed patination that has typical aerobic and anaerobic deposits on the brass. Although it is possible that the copper sulphides on the surface could have arisen from the object having been buried and bacterial metabolites having been the source of sulphide ions, it is much more likely that the distribution and amount of sulphur on the surface of the plaque is consistent with initial adsorption of sulphur from the smoke of expended black powder. Following adsorption onto copper-rich phases of the brass, the subsequent chemical changes resulted in reduction of the elemental sulphur to sulphide with concomitant oxidation of metallic copper and formation of insoluble copper sulphides on the surface of the plaque.

The extensive deposits of chloride ions and areas of where there has been selective corrosion and formation of organic copper salts is consistent with either repeated handling of the metal by sweaty human hands or placement of the metal plaque against the flank of a sweating animal such as a horse. Removal of the organic copper salts and gas chromatographic mass spectrometric analysis of the residues might be able to determine which of the two mechanisms is the most likely, or it could be a combination of both processes. The formation of corrosion products deep within the incised lines associated with the coarse filing of the plaque is consistent with the scratching having taken place early in the history of the object and that the object is not a reproduction made in recent times using genuine 19<sup>th</sup> century materials. The presence of titanium (dioxide) pigments in the letters is a modern contrivance as the white pigment has a distribution that is characteristic of the paint having been wiped across the plaque to make the lettering more distinct. Original black shellac infill for the letters and numbers will undergo significant degradation on exposure to sunlight and weathering over decades and much of the original material appears to have been lost.

**There is no evidence to suggest that this plaque does not reflect its purported origin of having been made in 1848 for Ludwig LEICHHARDT for his ill-fated expedition.**

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<b>Spot 006a</b>		
<b>Element</b>	<b>Wt %</b>	<b>At %</b>
C K	33.88	55.59
O K	23.53	28.99
Si K	0.74	0.52
S K	0.31	0.19
Cl K	0.62	0.34
K K	0.2	0.1
Ca K	0.36	0.18
Fe K	36.9	13.02
Cu K	3.46	1.07

<b>Spot 006b</b>		
<b>Element</b>	<b>Wt %</b>	<b>At %</b>
C K	29.45	63.48
O K	5.41	8.76
Si K	0.21	0.19
S K	2.16	1.75
Cl K	0.42	0.31
K K	0.2	0.13
Ca K	0.15	0.1
Fe K	0.68	0.32
Cu K	61.31	24.97

<b>Spot 006c</b>		
<b>Element</b>	<b>Wt %</b>	<b>At %</b>
C K	45.72	61.1
O K	25.76	25.85
Mg K	1.32	0.87
Al K	1.55	0.92
Si K	3.43	1.96
S K	8.57	4.29
Cl K	0.49	0.22
K K	0.34	0.14
Ca K	9.44	3.78
Fe K	0.44	0.13
Cu K	2.96	0.75

<b>Spot 006d</b>		
<b>Element</b>	<b>Wt %</b>	<b>At %</b>
C K	76.98	88.52
O K	8.62	7.44
Mg K	0.58	0.33
Al K	0.45	0.23
Si K	0.51	0.25
S K	1.04	0.45
Cl K	0.46	0.18
K K	0.48	0.17
Ca K	0.39	0.13
Cu K	9.83	2.14
Fe K	0.66	0.16

<b>Spot 010 b</b>		
<b>Element</b>	<b>Wt %</b>	<b>At %</b>
C K	43.79	57.97
O K	27.51	27.34
Al K	11.2	6.6
Si K	10.48	5.93
S K	0.13	0.06
Cl K	0.16	0.07
K K	0.26	0.11
Ca K	0.14	0.06
Ti K	3.91	1.3
Mn K	0.05	0.01
Cu K	1.99	0.5
Zn K	0.11	0.03
Pb L	0.26	0.02

<b>Ratio of Cu:Zn</b>		
<b>Location</b>	<b>Wt %</b>	<b>At %</b>
spot 1a	1.80	1.84
spot 1b	1.68	1.73
general "WI"	1.62	1.67
spot 2	1.87	1.93
spot 3	na	na
spot 004a	76.72	78.70
spot 004b	9.02	9.23
spot 004c	na	na
spot 004d	3.46	3.56
spot 006a	na	na
spot 006b	na	na
spot 006c	na	na
spot 006d	na	na
spot 010b	18.09	16.67