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## Bluing in The Victorian Era: A Chemical Investigation of Mid-Victorian Blued Firearms

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## Abstract

The following paper outlines an investigation into the chemistry of blued Victorian firearms. Specifically, the samples studied are three pieces of a Snider-Enfield Breech Loading Rifle, a lock plate, a breech block, and the screw of the firing pin. The tests and research conducted explore both the bluing itself as well as the chemical and physical interactions between the bluing and the metal underneath. The process of bluing was used to act as a passivation layer to inhibit corrosion, as it is a common concern with ferrous materials such as the iron and steel used in the production of firearms. The passivating layer is a thin patina of only a few hundred microns at most. Therefore, it is rather susceptible to scratches and thinning if the piece is used frequently. If undisturbed, a blued layer can inhibit the formation of hematite thus preventing harmful corrosion. This is the most valuable aspect of bluing both from practical and preservative positions, being useful to the original owners of the pieces and the archaeologists alike.

The tests conducted for this research include stereomicroscopy, confocal microscopy, X-ray fluorescence, X-ray diffraction, and laser ablation inductively coupled plasma mass spectrometry. Unfortunately, the laser ablation technique could only be performed on the screw due to size constraints with the equipment. Subsequently, the confocal microscopy was only conducted on the screw as it was used to observe the effect of the laser ablation; all other analytical methods were conducted on all three samples. The goal of conducting these tests is to determine which methods of bluing would likely have been used during the Mid-Victorian Era, give insight on how the bluing interacts with the metal, and determine if re-bluing pieces would be safe. The data obtained from the XRF indicated the presence of copper, nickel, and zinc in the blue patina of all three pieces, this suggests the method used to blue them was the *Unnamed Field Method #1* from Samuel Field's 1925 book on the colouration of metals. In addition to the XRF the XRD provided more general information on the composition of the pieces and denoted the presence of goethite in the breech block and lock plate, but not the screw. The XRD also revealed the presence of a substance that is likely copper acetate ( $\text{Cu}(\text{CH}_3\text{COO})_2$ ) thus indicating a possible variant on the *Unnamed Field Method #2*, which typically uses lead acetate ( $\text{Pb}(\text{CH}_3\text{COO})_2$ ). Finally, the screw, as the only sample to undergo the LA-ICP-MS, showed significant levels of manganese, primarily related to the metal itself. This suggests the use of a different kind of steel to produce the screw when compared to the larger pieces that did not exhibit manganese.

Overall, this research has resulted in the uncovering of a couple possible methods of bluing in the Victorian Era. While more research into the matter on both the scientific and historical fronts is required to have a complete understanding of the processes used. The methods suggested to have been used by the chemical data are in line with the physical appearance of the pieces and has no contradictions with the limited historical records. Finally, the possibility of re-bluing historic pieces for the purpose of restoration does not seem like it would cause any harm to the piece or eliminate the previous bluing. The screw had the most possibilities for methods with its wider range of elements present at the surface, which means if the abundance is from multiple attempts at bluing all methods can still be detected, not just the top layer.



## Introduction

The Mid-Victorian Era was a time of great innovation but some things from the past remained standard until later on. In modern times stainless-steel is used when the fear of rust is prominent for a tool, weapon, vehicle, or structure but, stainless steel was not invented until the 20<sup>th</sup> century. Before the advent of stainless-steel other techniques were used to mitigate corrosion of ferrous metals; one such technique is bluing (Brown, 1977). The following study details a brief history of bluing as well as a chemical analysis of three pieces of blued rifle parts from the 1860's with the oldest being from 1864 and the newest being as from as late as the early 1870's. The tests conducted will help indicate what type of bluing was most likely used on these pieces as well as some information on how the blued layer interacts with the metal underneath. The study of these blued pieces and the interactions of bluing with the metal should provide insight on how bluing could be used in the conservation of ferrous metals, in particular pieces that were once blued but have since had their bluing worn down over time.

The following paper is an investigation of blued firearms from the Victorian Era. Bluing is a type of chemical and/or heat treatment that can be conducted upon iron and steel. There are many kinds of bluing that have been used throughout history to varying degrees of popularity. The primary objective of this research is to determine the most likely candidate for the method or methods of bluing used in Victorian times. Between the vast number of methods and the lack of any historical records pertaining to the bluing of firearms in the British Empire the only way to determine the type used on the selected samples is through chemical investigation. Various analytical techniques were used to study the blue patinas on the samples as well as the metal itself to an extent. Firstly, was some general microscopy with the use of a stereomicroscope to better view the damage to the patina. The testing that was conducted was done in three parts, starting with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) before moving on to X-ray fluorescence and X-ray diffraction. Confocal microscopy was also used to examine the holes made by the laser ablation. By using these varied techniques, a more accurate representation of the elements present could be determined. In essence, this chemical research serves the purpose of filling in the gaps in the historical records of firearms manufacturing in Victorian Britain.

PLATE X.  
NAMES OF PARTS OF THE RIFLE.

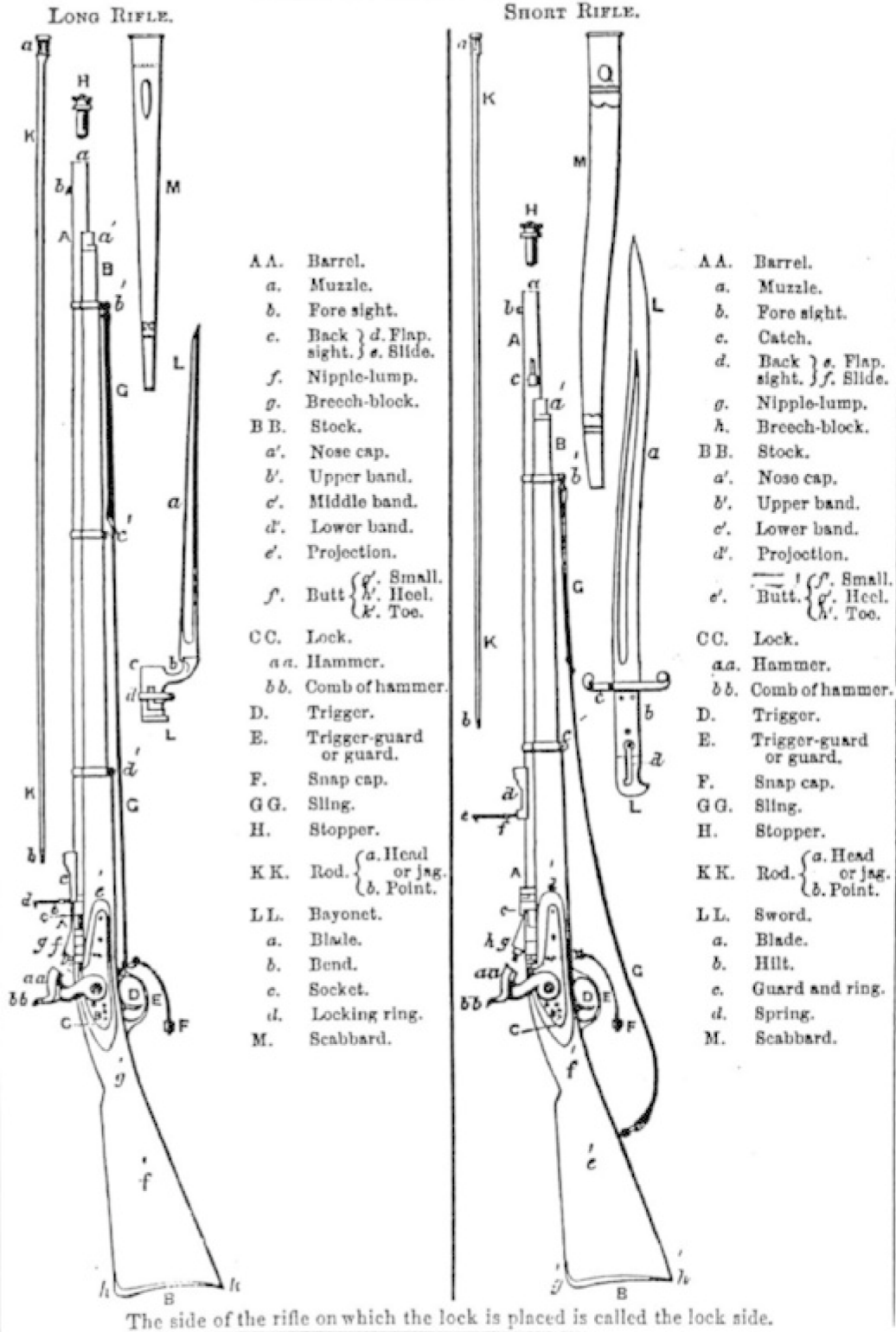


Figure 1 Diagram of the Snider Enfield (both a standard 3 bander and a Serjeant's 2 bander) (Field Exercise and Evolutions of Infantry as Revised by Her Majesty's Command, 1867).

The three pieces under investigation are all parts of the same Mk II Snider Enfield Breech Loading Rifle, which was standard issue in the British army from 1866-1871, after which the Martini-Henry took precedence (Heptinstall, 2016). The three pieces are a lock plate, a breech block, and a screw, they are denoted by letters CC, g, and f respectively on the left side of the diagram in *figure 1*, seen on the previous page. The Snider Enfield is a converted rifle, which is why the three pieces have a range of ages with the lock plate being older than the breech and screw. Additionally, the screw and breech are likely made of a mild steel while the lock plate is made from iron (Heptinstall, 2016). These pieces in particular are currently the property of Parks Canada and The Halifax Citadel National Historic Site of Canada and are still in use. Therefore, the bluing is not fully intact, particularly on the lock plate and breech block. This is actually fortuitous as it allows for easier sampling and comparison of both the bluing and the underlying metal as there have been very few studies conducted on Victorian metals.



# Chapter 1: A Brief History of Bluing

## 1.1 The Origins of Bluing

Ornate decoration of metals has been practiced for millennia, with various techniques being utilized to create the most beautiful pieces possible. Etching, embossing, gilding, and even artificial patination have been used across time and cultures (Giunlia-Mair, 2020). Among the many processes to have been created bluing is one of the more recent, relatively speaking. Bluing processes have been around for centuries with the oldest known blued pieces dating back to the Late Middle Ages and Early Renaissance. In the 16<sup>th</sup> century bluing was becoming popular as a technique to go hand in hand with gilding, which had been a popular method of decorating armour for centuries prior (Breiding, 2003). Armour decorating dates to ancient times, but it was not until Medieval times that exceptionally ornate pieces like the suit of plate armour shown in *Figure 2* came about (Breiding, 2003).



*Figure 2* Armor Garniture of George Clifford (1558–1605), Third Earl of Cumberland (MET) (Public Domain)

By combining the newly invented bluing with the pre-existing gilding, armourers and blacksmiths could create more aesthetically pleasing designs. An added benefit of bluing was that it did not weaken the armour as embossing would. While embossing makes the metal thinner, bluing does not cause any noticeable change to the thickness of the metal, therefore it does not change the durability of the armour. Essentially, bluing was developed for two reasons, one of which was merely a consequence of the other. A method of decorating armour was needed but it could not diminish the integrity of the metal, therefore a patina was the best choice. In theory bluing and gilding are similar as both were methods of decoration that involved changing the colour of the metal, the difference was that one was done through adding a layer of new material and the other was done through chemical treatment of the surface of the pre-existing metal.

While the oldest confirmed blued specimens date back only a few hundred years there is evidence to suggest that bluing has been around for much longer. A 2009 paper by Brian Gilmour and Alessandra Giumlia-Mair discusses the possibility of bluing having been used at the beginning of the Iron Age. While these early Iron Age pieces have not been observed to have been blued there are primary sources that indicate bluing was a possibility. Some artifacts have silver inlays that would not make sense against polished iron, which is also silver in colour, but would provide aesthetically pleasing contrast against blued iron (Gilmour and Giumlia-Mair, 2009). Additionally, several Roman sources describe iron in a way that suggests it was blued; they mention the dark blackish colour of it, sometimes with it even appearing purple (Gilmour and Giumlia-Mair, 2009). This evidence combined with the knowledge that blued patinas are thin and susceptible to erosion provides a strong base for the theory that bluing is much older than previously thought. Further research into bluing in antiquity is required to either confirm or deny the theory but it is a point of interest in the history of bluing ferrous materials.

## 1.2 The Purpose of Bluing

As mentioned, the original purpose of bluing was for the aesthetically pleasing hue it provided to steel and iron. This was the primary concern for suits of armour that were mainly being used for tournaments and show rather than for battle (Breiding, 2003). The dark hue gave contrast to other methods of decoration such as gilding and inlays of different metals. However, bluing has a much more practical function than medieval knights and lords realized. The anti-corrosion properties of bluing were unparalleled at the time of its invention. So, while it was intended to serve function only for appearances in actuality it was an accidental discovery of the best way to preserve ferrous metals before the advent of stainless steel. In a similar vein to its aesthetic appearance, the change in colour produced by bluing was also significant in reducing glare. By going from the shining silver tone of polished iron and steel to the dark bluish black, blued pieces become much less reflective. This reduction in reflectivity creates a significant advantage to riflemen as there will be little to no glare from their barrels while aiming. In essence, while bluing was intended only for decoration its future purpose of being a corrosion inhibitor was more significant a discovery while also providing a significant tactical advantage when used on weaponry.

## 1.3 Types of Bluing

There are many types of bluing with varying levels of coverage and thickness of the patinas. In general, bluing is achieved by bathing metals in acid solutions, sometimes heated, Júlia Tauber (Tauber, 2019) goes into these various methods in detail in her paper on bluing mild steel. Many of the recipes listed in Tauber's paper are from the early 20<sup>th</sup> century rather than the Victorian Era but for the most part they are still methods that would have feasibly been in use in the Victorian Era. Methods mentioned by Tauber include *nitre bluing*, which uses a solution of potassium nitrate ( $KNO_3$ ) and manganese dioxide ( $MnO_2$ ) and the *Parker Process*, which is similar but substitutes the potassium nitrate ( $KNO_3$ ) for phosphoric acid ( $H_3PO_4$ ) (Tauber, 2019). There are also methods that do not include the use of chemicals such as bluing with a butane ( $C_4H_{10}$ ) torch, that under Tauber's testing, yielded a more homogenous result than the chemical

methods but at the cost of a much thinner patina, thus making it more useful for aesthetic pieces rather than functional ones (Tauber, 2019). This homogeneity can likely be attributed to the greater level of control possible when using a torch than a chemical bath.

There is also a method in Samuel Field's book *The Chemical Coloring of Metals and Allied Processes*, which uses two different solutions in sequence in the same method to directly colour the steel to a "black smoky shade" (Field, 1925). This method does not have a name listed but shall be referred to as *Field's Unnamed Method #1*. This method had the ingredients of copper sulphate ( $CuSO_4$ ), hydrochloric acid (HCl), and water for the first solution and copper sulphate ( $CuSO_4$ ), hydrochloric acid (HCl), and arsenious oxide ( $As_2O_3$ ) for the second solution (Field, 1925). Field also described another method for bluing iron and steel that requires fewer ingredients, likewise, it also did not have a name listed and as such will be known as *Field's Unnamed Method #2*. In this recipe a solution of lead acetate ( $Pb(CH_3COO)_2$ ), sodium thiosulphate ( $Na_2S_2O_3$ ), and water is used to achieve a variety of colours including blue, purple, brown, and black (Field, 1925). Among these general methods of bluing there is also a method specifically for gun barrels mentioned in Field's book known as *Buchner's Method*. This recipe calls for the use of gallic acid ( $C_7H_6O_5$ ), ferric chloride ( $FeCl_3$ ), antimony chloride ( $SbCl_3$ ), and water, which is then heated (Field, 1925). There is no reason given as to why this method is specifically fit for gun barrels.

Other methods of bluing include *hot caustic bluing*, which uses similar chemicals to the *Parker Process* mentioned by Tauber, *rust*, and *fume bluing*, which both use nitric ( $HNO_3$ ) and hydrochloric acid (HCl), and *browning*, which utilizes mercury salts (Fjestad, 2018). All these methods are ones that could feasibly have been used historically, but there are no published documents that describe the methods used by the Birmingham Small Arms Company. *Browning*, at least, has been noted to have been used in the Regency Era, with note being made in the *General Regulations and Orders for the Army, 1811*. Therefore, the testing conducted on the samples chosen for this research will have to be used to



determine the methods used. As there are so many methods of bluing there is no consensus on which methods are the best, whether the best be defined as most effective at stopping corrosion or best as in with the most pleasing colour. The sheer number of methods (of which the ones mentioned are a mere fraction) means determining the methods used on these rifle parts is a difficult process. Without any precise historical records pertaining to the production methods of firearms the only basis of comparison for the samples in question is the list of recipes that could feasibly have been used in the Mid-Victorian Era.

## Summary of Bluing Methods

Method	Chemicals	Characteristics
<i>Nitre Bluing</i> (Tauber, 2019)	potassium nitrate ( $KNO_3$ ) and manganese dioxide ( $MnO_2$ )	Creates an iridescent blue, similar in appearance to a peacock feather.
<i>Parker Process</i> (Tauber, 2019)	phosphoric acid ( $H_3PO_4$ ) and manganese dioxide ( $MnO_2$ )	Dark grey patina. Rust must be polished off before conducting this method.
<i>Buchner's Method</i> (Field, 1925)	gallic acid ( $C_7H_6O_5$ ), ferric chloride ( $FeCl_3$ ), antimony chloride ( $SbCl_3$ ), and water	Transitions from pale blue to purple, to plumbago-grey during the bluing process.
<i>Butane Torch</i> (Tauber, 2019)	butane ( $C_4H_{10}$ )	Homogenous, but thin, patina.
<i>Field's Unnamed Method #1</i> (Field, 1925)	copper sulphate ( $CuSO_4 \cdot xH_2O$ ), hydrochloric acid (HCl), and arsenious oxide ( $As_2O_3$ )	Creates a black smoky shade, which becomes darker by repeated exposure to the secondary solution.
<i>Field's Unnamed Method #2</i> (Field, 1925)	Solution of lead acetate ( $Pb(CH_3COO)_2$ ) and sodium thiosulphate ( $Na_2S_2O_3 \cdot xH_2O$ )	Has a darker appearance if left in the second solution for a longer period of time.
<i>Hot Caustic Bluing</i> (Fjestad, 2018)	potassium nitrate ( $KNO_3$ ), sodium hydroxide (NaOH), and water	Patina is nearly black.
<i>Rust Bluing</i> (Fjestad, 2018)	nitric ( $HNO_3$ ) and hydrochloric acid (HCl)	Can be patchy due to inconsistent rusting, patchiness is determined by the consistency in the rusting prior to the chemical bath.
<i>Fume Bluing</i> (Fjestad, 2018)	nitric ( $HNO_3$ ) and hydrochloric acid (HCl)	Similar to <i>Rust Bluing</i> but creates a thinner layer.
<i>Browning</i> (Field, 1925)	mercury salts or antimony chloride ( $SbCl_3$ ), and olive oil.	Creates a dull reddish-brown surface with little to no shine.

*Table 1 Summary of Bluing Methods.*

## Chapter 2: Samples and Instruments

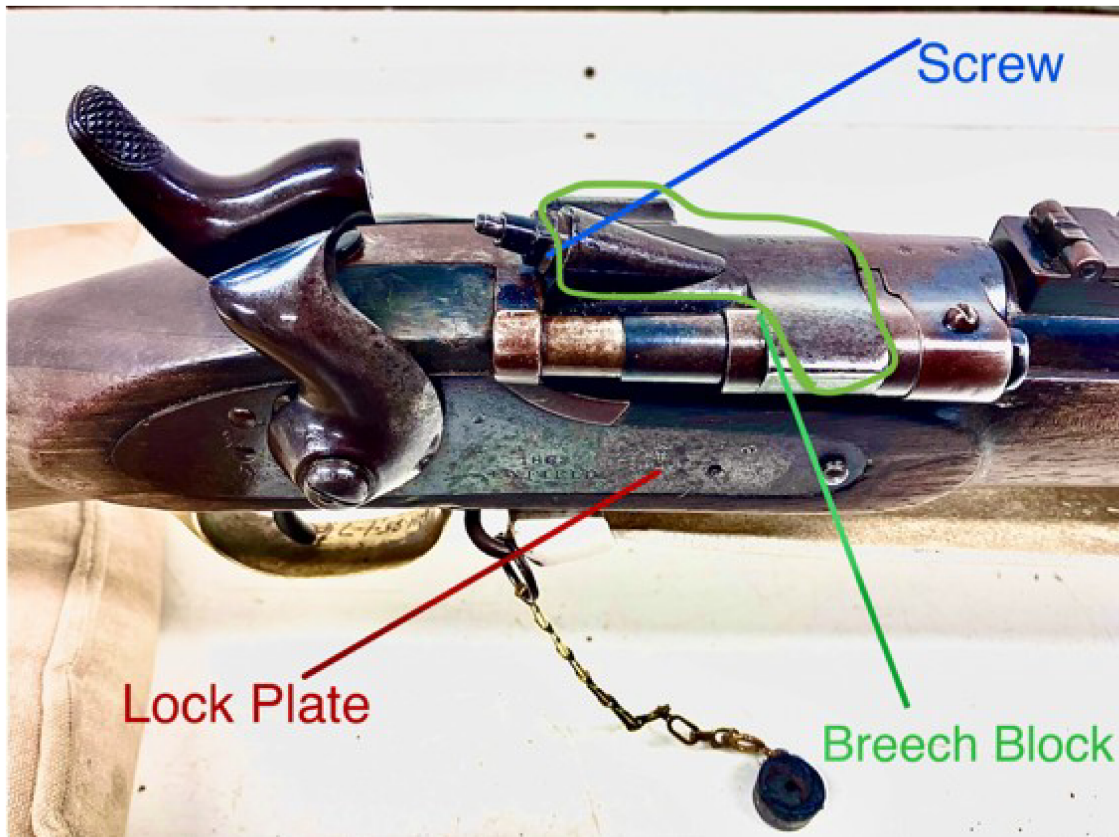


Figure 3 Mk II\*\* Snider Enfield noting the portions used in this research.

### 2.1 Samples

The samples studied for this research are the lock plate, breech block, and firing screw of a Mk II Snider-Enfield Breech Loading Rifle, all of which are labelled in *figure 3*. While they were made after the Industrial Revolution, they still have many variances between each other. Their weight and materials can differ depending on which company made them. At least one of the samples was built by the Birmingham Small Arms Company, as indicated by the stamp that was pressed into the breech block. However, because the B.S.A. Co. was not founded until 1865 the lock plate (stamped for 1864) could not have been made by them and was likely made instead at the Royal Small Arms Factory in Enfield (Lumley, 1989). Either way, both companies worked under the same contracts from the British Army so are likely at least similar if not the same in their techniques and materials. While the lock plate is certainly from 1864 as shown by its inscribed production date, the breech block and screw are more difficult to pinpoint. Though all three samples are from the same rifle,

over time the rifles have had pieces swapped in order to make repairs so it cannot be guaranteed that all three pieces were originally intended for the same rifle. Additionally, the Mk II Snider-Enfield was not introduced until December of 1866 and remained in production only for a few years before being replaced by the Mk III after 1869 (Heptinstall, 2016). The Mk III Snider-Enfields are confirmed to have been made of steel as they were the first standard issue steel rifles used by the British infantry service and it was deemed mandatory for any rifle barrels produced after 1869 to be made of steel in accordance with the *Lists of Changes, No. 1759 of the 13<sup>th</sup> of January 1869* (Heptinstall, 2016). This, however, does not mean the breeches of the Mk II Snider-Enfields were not steel, just that the barrel would have certainly been wrought iron. With the lock plate pre-dating the introduction of the Snider-Enfield, that means it originally belonged to the Pattern '53 Enfield from which the Sniders were converted. It is therefore safe to assume that the lock plate is blued iron rather than blued steel. This should not have much of an effect on the bluing process, which is supposed to form a passivation layer of magnetite on the metal as the lack of presence of a small percentage of carbon would not be enough to inhibit the formation of this layer. While the barrels of the rifles are made of iron, the material for the breech block is unconfirmed, either being iron or a very mild steel of 0.1% - 0.3% carbon according to the Royal Armouries of London. The use of such a mild steel could be due to cost effectivity as mild steel was less expensive to produce and the Snider Enfield was being produced at a high volume of approximately 670,000 units during its British service life (Skenneron, 2003). Mild steel is also less brittle than regular steel, which would have been beneficial for firearms production, but it had the side effect of being more prone to corrosion (Hall, 1951). This proclivity for corrosion would have been nearly as harmful as the brittleness though, as black powder residue is corrosive to metals, especially if the rifles are not cleaned in a timely manner.

As they were produced by either the Birmingham Small Arms Co. or the London Small Arms Co. the metal would have been sourced from Thomas Firth and Sons of Sheffield. There are no known surviving records from Thomas Firth and Sons covering the period in which the Snider-Enfields were produced so an exact type of steel used is not currently known. Some of the confusion on the matter of whether steel or iron was used to produce these weapons comes from the definition of steel used by the manufacturers. According to Whitworth, the line between iron and steel

was not defined by carbon content but instead by its tensile strength (Whitworth, 1874). Any iron-based alloy that exceeded 28 tons per square inch of tensile strength was to be called steel, regardless of its carbon content (Whitworth, 1874). Likewise, anything below this threshold was referred to as wrought iron. Therefore, they put more value into the production methods rather than the chemical composition and as such any chemical data pertaining to Victorian gun metals must have been obtained through modern research of which there is little to none.

### 2.1.1 The Lock Plate

The first of the samples is called a lock plate. The lock plate is a thin flat piece of metal used to hold the mechanisms for the hammer in place and keep them protected from outside forces. It is the largest of all the samples measuring 13.9 cm long and 3 cm wide at its largest point. It is also the thinnest of the samples at only 4 mm for the main sections and 1 cm at the portions with the internal locking mechanisms for the hammer and springs. According to the few available sources, the lock plate is also likely the only of the three samples that is made from wrought iron instead of mild steel (Heptinstall, 2019).



*Figure 4 Top view of the lock Plate.*

### 2.1.2 The Breech Block

The second of the samples is the breech block of the Mk II Snider-Enfield. This breech block is identifiable as being from a Mk II Snider-Enfield from the shape of the side tab and its lack of safety button, which was not introduced until the Mk III. It is also distinguished from being a Mk I Snider-Enfield as The Halifax Citadel does not have any Mk I's in their possession since the Mk I was only in production for 3 months and are therefore very rare. (Heptinstall, 2016) The breech block is also a larger sample, measuring 6 cm long, 2.6 cm across (with an additional 1.7 cm for the hinge), and a diameter of 3 cm (*figures 5 and 6*).



*Figure 5 Light box photo of the interior facing side of the breech block.*



*Figure 6 Light box photo of the exterior facing side of the breech block.*

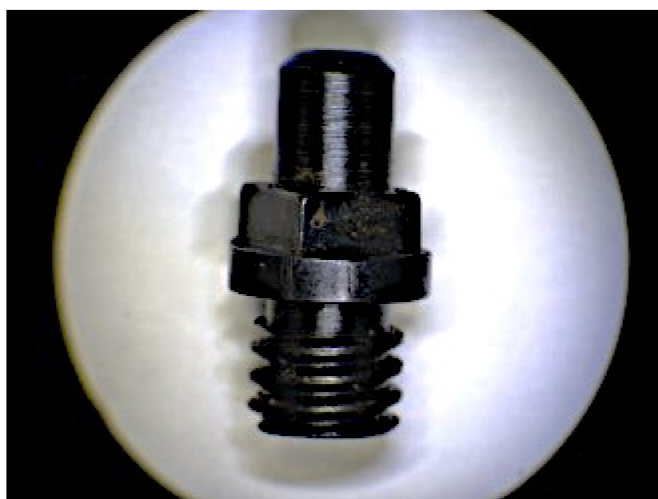
The breech block is the main part of the mechanism that allows for loading the rifle from the rear, it opens and closes on a hinge essentially acting as a small door. As the conversion to breech loading started in 1866 this piece is slightly newer than the lock plate (Heptinstall, 2016). Additionally, as mentioned, the breech block is likely made from mild steel as by 1869 all rifles were required to be made with steel and even before that steel was preferred for the breech conversions as the smaller parts needed to be stronger in order to withstand the repeated ballistic force of the black powder (Whitworth, 1874). Thin wrought iron would not have been sufficient for withstanding such repeated explosions.

### 2.1.3 The Screw

The screw is the smallest of the samples measuring just 1 cm in diameter and 1.8 cm long (*figure 7*). Despite being the smallest though, the screw is the best preserved of all the samples. Notable of the screw's appearance is its nearly black colour rather than the silver colour commonly associated with steel. This black colour is indicative of proper bluing with the intent of being a passivating layer rather than more ancient or modern techniques that focus more on obtaining a strong blue hue for aesthetic purposes. Additionally, like the breech block the screw is more than likely made of mild steel rather than wrought iron due to its age. Its function is to hold the firing pin in place and as such is primarily an internal piece, thus being shielded from the elements and significant erosion.



Figure 7 Light Box photo of the screw



*Figure 8 The screw under stereomicroscopy*

## 2.2 The Instruments

There were many techniques used in the analysis of the three samples including stereomicroscopy, confocal microscopy, LA-ICP-MS, X-ray fluorescence, and X-ray diffraction. The following section provides the details of the instruments used and a brief overview of what they were used for.

### 2.2.1 Stereomicroscope

The model of stereomicroscope used was a Nikon SMZ 645 stereoscope, with a circular LED system, and a magnification range from 8x to 50x, and it is located in the geoscience building of the University of Padua. The stereomicroscopy was used to observe the degradation of the pieces at a more refined scale. Photos were also taken of the samples through this microscope using a Nikon Coolpix P.6000 digital camera, fixed to an eyepiece of the stereoscope using an adapter for the purpose of pinpointing desirable locations to sample both for the blued and raw areas. The enhanced view of the patina and degradation to the samples provided a better understanding of how the bluing protected the metal while also giving a visual indication of how it interacts with the metal. The texture of the metal showing through the patina was easily observed with the stereomicroscope. The enhanced view also clearly showed the difference between the bluing and the raw areas as the miniscule abrasions to the patina were clearly visible; this will be discussed further in Chapter 3.





Figure 9 Camera mounted on the stereomicroscope.

## 2.2.2 Confocal Microscope

The confocal microscope used for this project was the Olympus LEXT OLS4100 confocal laser scanning microscope equipped with five objectives (2.5x, 5x, 10x, 20x and 50x) and a 405nm laser. The processing and compilation of the images was done using the accompanying Olympus LEXT OLS4100 software package version 3.1.15. This microscope is located in the geoscience building of the University of Padua.



Figure 10 The confocal microscope used.

### 2.2.3 X-Ray Diffraction

The X-Ray Diffraction (XRD) was done with a PANalytical X'Pert PRO diffractometer in Bragg-Brentano geometry equipped with a cobalt X-ray tube and a X'Celerator detector. The working conditions were CoK $\alpha$  radiation, 40 kV voltage, 30 mA current, 3-70° 2 $\theta$  range, step size 0.02° and 1 s counts per step. Further analysis for determining the metal and corrosion phases present was done using the X'Pert HighScore Plus software. The device is located in the geoscience building of the University of Padua.



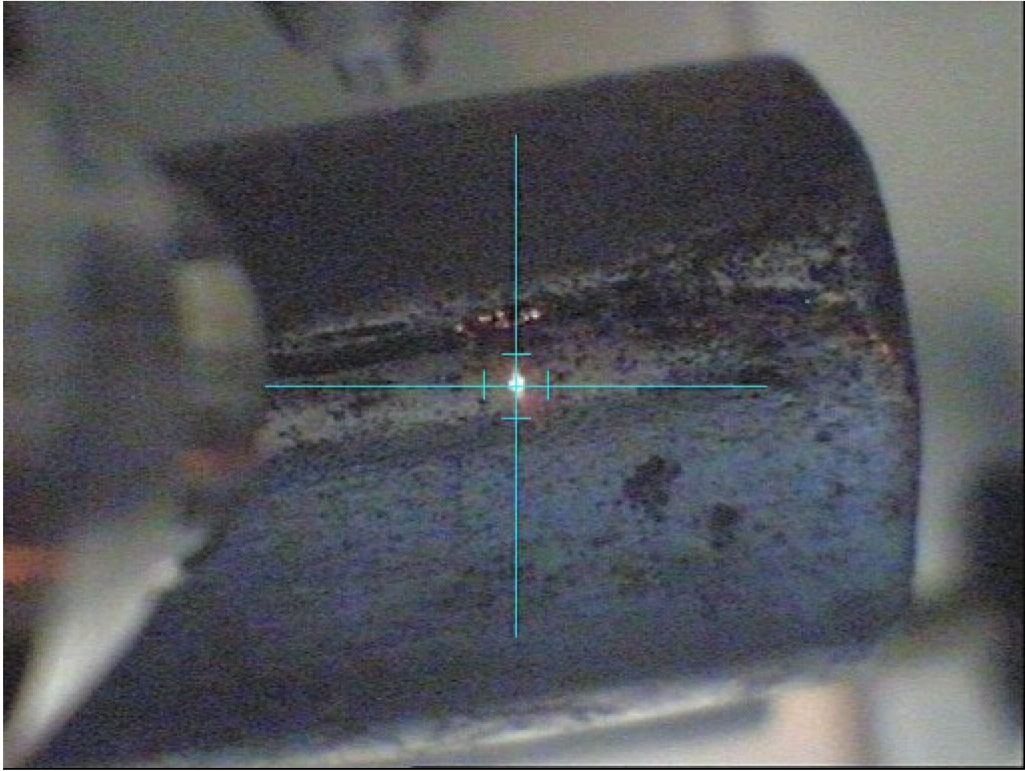
*Figure 11 The breech block mounted in the diffractometer.*

### 2.2.4 X-Ray Fluorescence

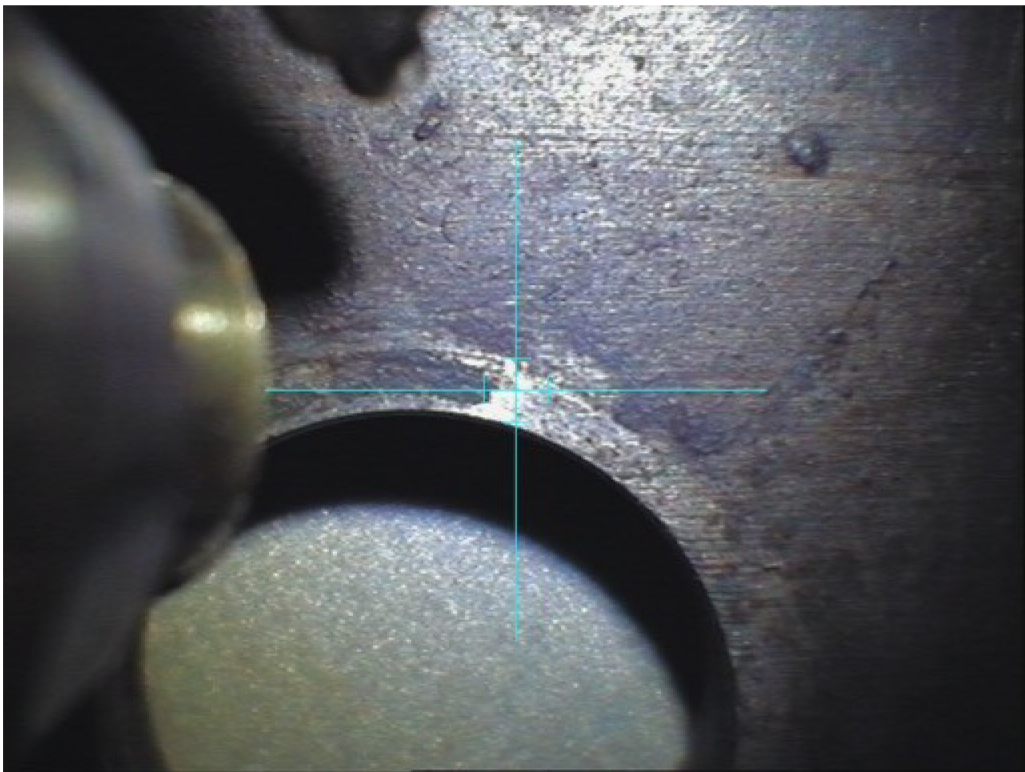
The device used for this research was a portable XRF Artax 200 Bruker, equipped with X-ray source with molybdenum anode, spot size of 0.200 mm diameter, SSD energy-dispersive detector. The conditions of acquisition for the samples were a voltage 45 kV, Cathode current 0.750 mA, 4096 acquisition points. It is located in the chemistry department of the University of Padua. Samples were taken from both blued and bare areas of all three samples. The *figure 12* show the machine and *figures 13-15* show some of the points that were studied for each sample.



*Figure 12* The XRF set up with the lock plate in position.



*Figure 13 Point 10, a bare portion of the breech block.*



*Figure 14 Point 3, a bare portion of lock plate.*

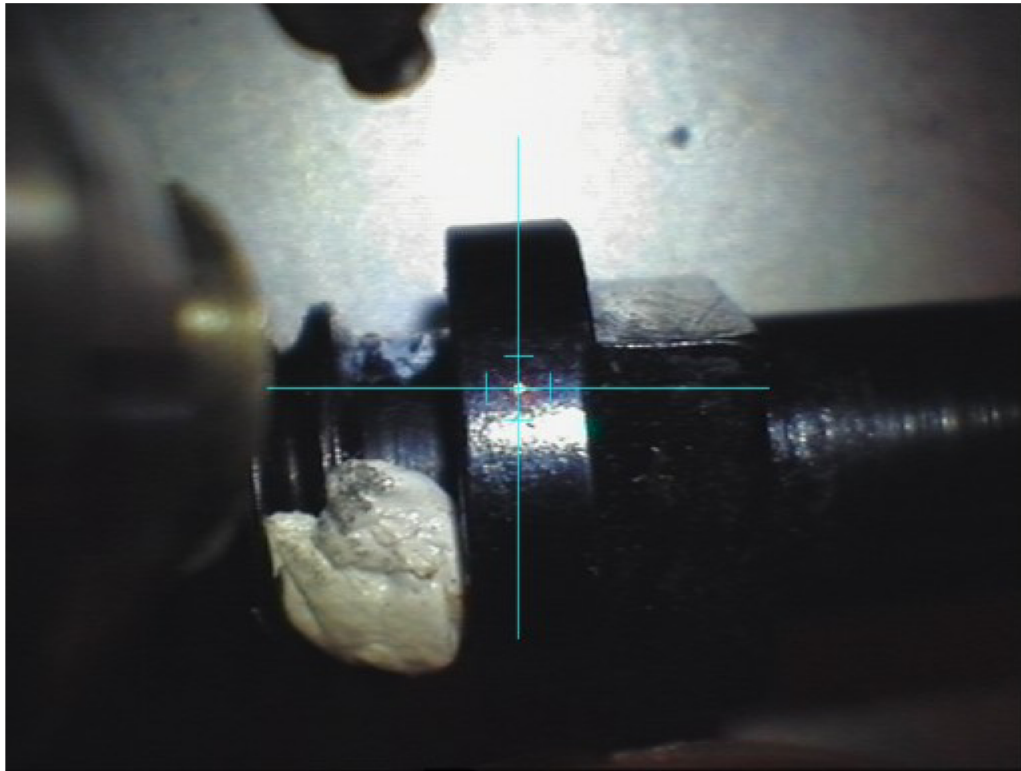
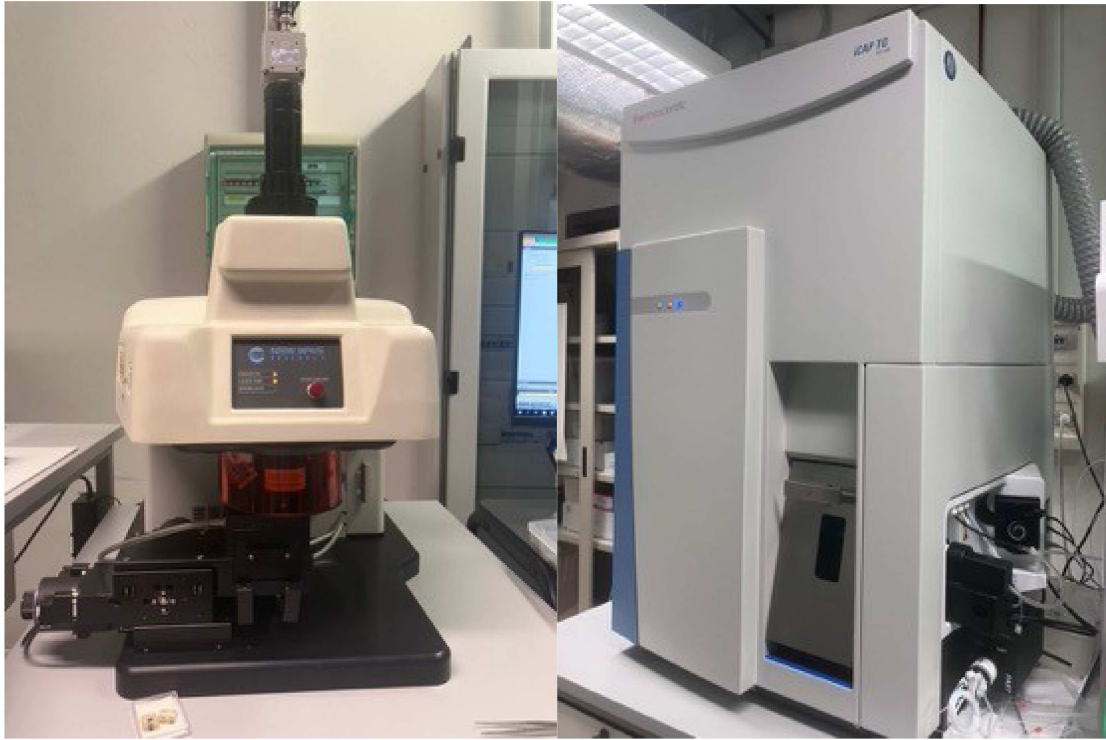


Figure 15 Point 8, a blued portion of the screw.

### 2.2.5 LA-ICP-MS

The system used for the LA-ICP-MS tests was the UP-213 Laser Ablation System by New Wave Research. The temperature of the laser was upwards of 10,000 °C, which was sufficient for vaporizing the metal. The machine in question was the one belonging to the University of Modena and Reggio Emilia, Italy and may be seen alongside its corresponding mass spectrometer in *figure 16*. 20 ablations were conducted across 15 points of the same sample. Only the screw was able to be tested in this manner as the other two pieces were too large to fit into the machine. The stereomicroscopic photos taken prior to this testing were used to pinpoint the sample locations across the screw.



*Figure 16 Laser Ablation System and Mass Spectrometer*

## Chapter 3: Data and Results

### 3.1 Stereomicroscopy

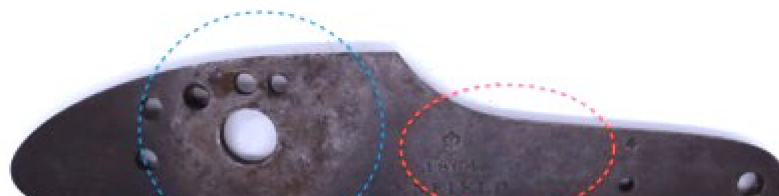
The stereomicroscopy aided in revealing the extent of the damage to the samples. There are various areas that were affected by rust and corrosion. In this section those areas will be looked at in greater detail. To start is a table with brief general descriptions of the condition of each sample.

Sample	Production Date	Bluing Condition	Proposed Material
Lock Plate	1864	Wear is consistent with use; the bare areas are in high-touch areas either from hand placement when using the rifle or from cocking the hammer. The bluing is a matte, dark grey.	Iron
Breech Block	1866 $\geq$ D $\leq$ 1875 (Heptinstall, 2016)	Wear is sporadic in both placement and level of damage. The bluing is a matte, dark grey.	Mild Steel
Screw	1866 $\geq$ D $\leq$ 1875 (Heptinstall, 2016)	Bluing is in near perfect condition with minimal wear in any locations, it is a shiny, black with a slight blue tint.	Mild Steel

Table 2 General information of the physical aspects of the samples.

#### 3.1.1 The Lock Plate

The lock plate is the only sample with a date stamp on it, being from 1864. The wear in the bluing on the lock plate is consistent with its use with the bulk of the damage centring around where the hammer is attached to the rifle (circled in blue in *figure 17*). The repeated friction of the hammer being cocked and released is the cause of the reduction in the bluing. There are also some smaller areas of reduced patina from unknown causes, though they are likely also from general wear to the rifle after decades of use (also pictured in *figure 17* in red).



*Figure 17 Lock Plate with circled damages*

These additional areas are mostly consistent with where one would place the edge of their hand while working the hammer. The inconsistencies with the thinning of the patina are also indicative of them being from peoples' hands as they are patchy. Essentially, they show the presence of repeated friction but in a manner that is not precise, thus being the result of human interaction rather than the consistency resulting from a mechanical process. Interestingly, with the lock plate it appears that the bulk of the bluing was and/or is on the outer face. While initially this seems logical as the outer portion is the side that would require the protective properties of the bluing there is the matter of how the bluing process is conducted. As nearly all historic bluing methods require bathing the metal in solution it is unusual for one side to have stronger bluing than the other (Field, 1925). It is possible the interior half of the lock plate had a coating placed onto it to inhibit the formation of the blue patina though this seems an unnecessary and time-consuming step. Therefore, one must assume that the interior bluing has since near completely worn off for unconfirmable reasons.



*Figure 18 The royal cypher with rust damage.*



Also, of note with the lock plate is the higher presence of rusting around the engravings on the lock plate such as the royal cypher and Enfield stamps (*figures 18 and 19* respectively). The Enfield stamp and the royal cypher both have significantly more rusting than any other part of the lock plate when observed with a stereomicroscope. This suggests that the bluing was done before any of the stampings and engravings were made to the plate as the process cut deep enough to go through the blue patina in some areas, which appears to be quite thin. The stamps seem to have compressed the metal in comparison to an engraving process, which would have the removal of material. Whether this thinness is from the actual process or just the wearing down of it over time is also not something that can be confirmed without documents pertaining to the production of the Snider-Enfield. Unfortunately, the records from the Birmingham Small Arms Company from that time have been lost so confirmation of the methods used can only be hypothesised through scientific investigation such as with this study.



*Figure 19 Engraving on the breech block showing no signs of rust (left) and the engraving on the lock plate with significant rust (right).*

### 3.1.2 The Breech Block

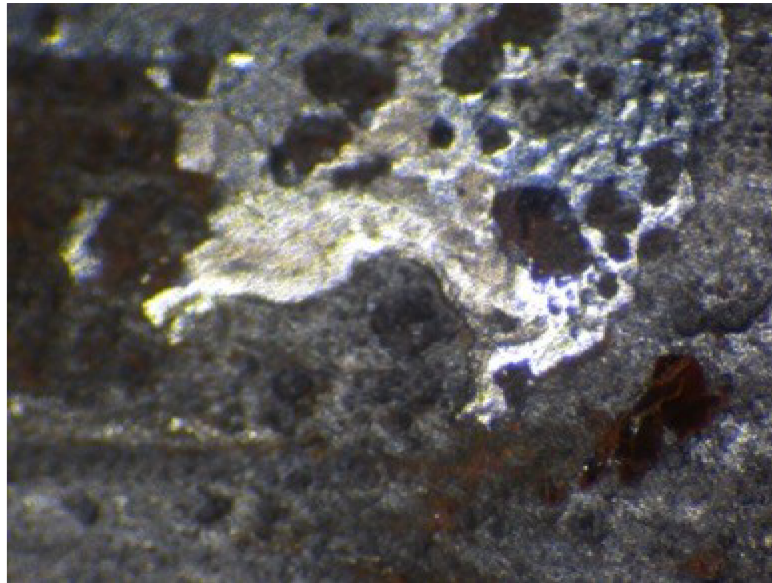
Contrary to the lock plate, the rusting on the breech block is not centred around the stamps. In fact, the stamps are some of the areas with the best intact bluing on the sample, thus suggesting that unlike the lock plate, the stamps on the breech block were made before the bluing process was conducted. This could be due to the fact that the breech block is newer than the lock plate, subsequently indicating a change in production methods. The lack of rusting around the stamps does not however, mean there is a total lack of rusting on the breech block. In actuality, the breech block has significant rusting compared to the lock plate with the majority of it centring around the grooves on the tab used to open it, the scratches, and the areas that have been chemically weathered.

The breech block is the sample with the most wear to the blue patina, primarily on the interior side of the block. The exterior has some erosion of the patina but overall, it remains intact. The one major area of damage to the exterior side of the breech block can be seen in *figure 20*.



*Figure 20 Severe erosion to the exterior side of the breech block(left), with the formation of various coloured patinas and similar patinas on the interior side (right).*

The areas of damage on the exterior of the breech block are pitted (*Figure 21*) and sporadic, which suggests they were caused by the presence of a corrosive material rather



*Figure 21 Pitting on the surface of the breech block.*

than the general weathering and erosion caused by prolonged use as seen with the lock plate. There are also several patinas that have formed on the surface of the breech block ranging widely in colour. There are patinas that are black, yellow, orange, and even a dark red (*figure 20*). The interior of the breech block having next to no remaining bluing is likely due to the near constant exposure to black powder and its fouling. Black powder fouling is highly corrosive to metal and if not cleaned off in a timely manner will cause severe damage, even with the bluing in place. There is also significant wear to the patina on the edges of the breech block, as to be expected from their continued use.

### 3.1.3 The Screw

The screw is an exceptional piece where the bluing is almost completely intact with only a small amount of wear on the edges. The most significant wear to the screw is on the square portion, this damage is likely due to the use of a snap cap, a small cover for the firing pin that acts as a safety mechanism (circled in red in *figure 22*). The presence of the snap cap could explain the pattern of wear on the screw as the edges would rub against each other when placing and removing the cap. There is also practically no rust on it with the exception of some on the threads of the screw (*figure 23*). However, this

rust appears to be sitting on the surface, and therefore is likely residue from the portion of the breech block the screw attaches to.



Figure 23 Threads of the screw showing only surface debris and no damage to the bluing.

The screw is expected to provide the best chemical data for the blue coating present of all the samples. It is the most homogenous and with the least degradation, with the majority of it being very smooth with no pitting or serious scratches like the other pieces. It also appears to be a thicker layer as it displays a much more prominent blue-black hue to it compared to the others. The thicker layer means it will be easier to sample the

bluing without disturbing the unaltered metal underneath. This should provide an uncontaminated sample that showcases the bluing and just the bluing while also not being so thick that examination of the lower layers is still possible without causing any significant damage to the screw.

### 3.2 LA-ICP-MS

The data collected by the LA-ICP-MS yielded the confirmation of the presence of various elements that are present in many of the bluing recipes. The mean and median values were both used in this analysis, but a focus has been put of the median values. There were some values that were significant outliers among the results and as such the median values, which follow the same trends as the mean values, were deemed more accurate.

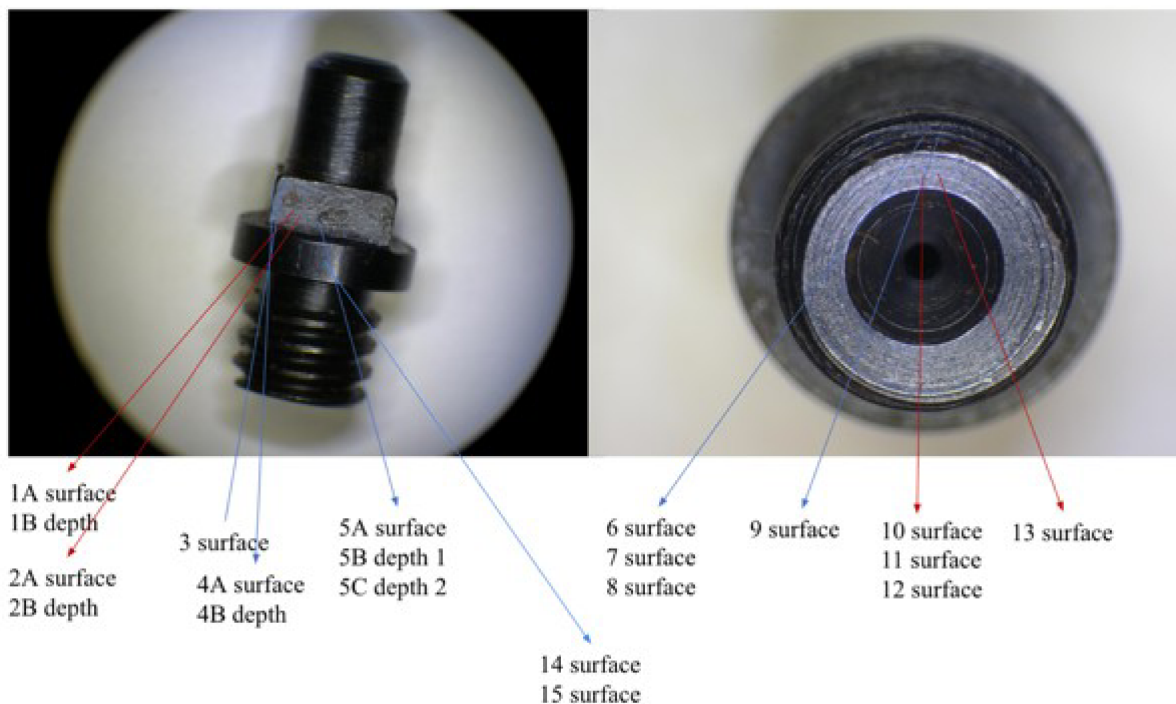


Figure 24 Diagram of the sample locations for the LA-ICP-MS.

Just below is a condensed table (*Table 3*) of the mean and median counts for the most prominent elements detected during this analysis for the blued and bare portions. The next two pages are tables depicting the same data but in reference to specific sample points rather than a generalization. Point 10 is in red as the counts are possibly unreliable due to machine error. *Table 4* depicts the mean values of these elements in ppm, and *Table 5* shows the median values, also in ppm.

	C	P	S	Cr	Mn	Cu	Zn	Sb	Pb
<b>Blue Median</b>	1124	10	355	137	5205	179	56	19	1206
<b>Blue Mean</b>	1302	11	367	138	6079	215	71	28	1489
<b>Metal Median</b>	602	12	211	123	9434	63	8	7	2258
<b>Metal Mean</b>	739	12	248	125	9501	92	14	9	2385

Sample	Material	Depth	Ablation #	C_mean	P_mean	S_mean	Cr_mean	Mn_mean	Cu_mean	Zn_mean	Sb_mean	Pb_mean
Point 1A	Bare Metal	Surface	1st ablation	1394	12	527	124	19690	295	48	31	7634
Point 1B	Bare Metal	Depth	2nd ablation	445	12	165	137	11456	42	6	4	26134
Point 2A	Bare Metal	Surface	1st ablation	922	11	148	137	8049	50	9	6	1234
Point 2B	Bare Metal	Depth	2nd ablation	1065	13	119	136	12088	40	5	5	2325
Point 3	Blue Patina	Surface	1st ablation	764	10	834	126	12412	50	28	3	1249
Point 4A	Blue Patina	Surface	1st ablation	3286	18	1884	132	5860	427	105	81	1837
Point 4B	Blue Patina	Depth	2nd ablation	2246	13	739	125	6509	95	22	10	730
Point 5A	Blue Patina	Surface	1st ablation	1866	10	189	137	5302	213	73	24	825
Point 5B	Blue Patina	Depth	2nd ablation	1127	9	0	122	6113	79	19	8	824
Point 5C	Blue Patina	Depth	3rd ablation	355	8	134	114	7727	44	6	7	1099
Point 6	Blue Patina	Surface	1st ablation	120	11	14	159	4819	554	174	76	3899
Point 7	Blue Patina	Surface	1st ablation	1647	12	35	148	4572	193	73	26	1588
Point 8	Blue Patina	Surface	1st ablation	1723	7	66	168	3819	238	104	23	1498
Point 9	Blue Patina	Surface	1st ablation	2311	8	107	143	7048	168	58	8	974
Point 10	Bare Metal	Surface	1st ablation	2559	12	140	136	5813	1507	66	14	1313
Point 11	Bare Metal	Surface	1st ablation	331	14	204	124	7267	35	4	3	1083
Point 12	Bare Metal	Surface	1st ablation	507	15	218	126	6908	40	7	3	1352
Point 13	Bare Metal	Surface	1st ablation	542	11	143	113	5591	38	4	3	620
Point 14	Blue Patina	Surface	1st ablation	0	7	25	114	4804	61	13	5	671
Point 15	Blue Patina	Surface	1st ablation	0	12	149	119	6076	29	8	3	858

Table 4 Mean values for elements in ppm by sample location.

Sample	Material	Depth	Ablation #	C_med	P_med	S_med	Cr_med	Mn_med	Cu_med	Zn_med	Sb_med	Pb_med
Point 1A	Bare Metal	Surface	1st ablation	1149	12	581	120	20143	178	27	19	7546
Point 1B	Bare Metal	Depth	2nd ablation	0	12	93	136	11032	37	4	4	2204
Point 2A	Bare Metal	Surface	1st ablation	534	12	36	136	7512	41	6	5	1060
Point 2B	Bare Metal	Depth	2nd ablation	287	11	0	140	11116	37	4	5	2289
Point 3	Blue Patina	Surface	1st ablation	632	10	641	125	7116	36	12	3	938
Point 4A	Blue Patina	Surface	1st ablation	2804	16	2303	129	5809	306	88	60	1388
Point 4B	Blue Patina	Depth	2nd ablation	1810	13	0	124	6710	53	15	8	676
Point 5A	Blue Patina	Surface	1st ablation	1841	10	73	135	5007	175	52	20	707
Point 5B	Blue Patina	Depth	2nd ablation	888	9	0	122	6125	57	10	6	819
Point 5C	Blue Patina	Depth	3rd ablation	0	9	146	111	7776	43	6	5	1134
Point 6	Blue Patina	Surface	1st ablation	0	11	0	156	4775	493	138	34	2482
Point 7	Blue Patina	Surface	1st ablation	1401	12	0	141	4540	157	68	22	1473
Point 8	Blue Patina	Surface	1st ablation	1273	7	71	178	3666	213	86	21	1467
Point 9	Blue Patina	Surface	1st ablation	2165	8	71	145	5326	152	50	7	944
Point 10	Bare Metal	Surface	1st ablation	480	9	104	130	5632	64	10	3	1225
Point 11	Bare Metal	Surface	1st ablation	303	14	231	124	7118	29	2	3	1041
Point 12	Bare Metal	Surface	1st ablation	512	13	112	124	6929	39	5	3	1010
Point 13	Bare Metal	Surface	1st ablation	514	11	94	112	5469	29	2	3	632
Point 14	Blue Patina	Surface	1st ablation	0	6	0	113	4616	50	5	4	575
Point 15	Blue Patina	Surface	1st ablation	0	11	40	115	5985	26	3	3	882

Table 5 Median values for elements in ppm by sample location.



### 3.2.1 Primary Elements

The results received from the testing of the screw show the presence of various elements in a range of values. Elements with values below 1 ppm were not considered to be of relevant amounts, but there were multiple findings that were well above this threshold. Five primary elements were noted throughout the sample, being carbon (C), chromium (Cr), manganese (Mn), sulphur (S), and lead (Pb).

The carbon had average values ranging from 331 ppm to 3286 ppm along with two sample points where no carbon was detected. The median values ranged from 287 ppm to 2804 ppm, excluding the areas that came back with no results for carbon. These two points for the mean and four points for the median are anomalous and are likely an error. Generally speaking, the carbon levels tend to be higher at the surface, in particular at the blued areas. The highest carbon level was found at point 4A, which is both a surface level point and a blued area. The lowest median carbon value of 287 ppm, while also a surface level sample, is from a portion where the bluing had worn off.

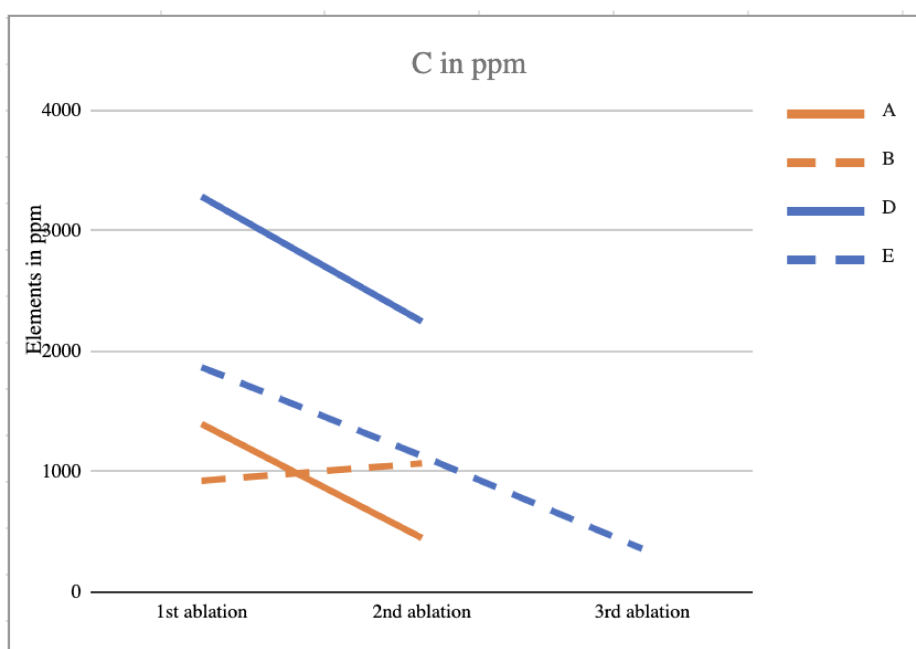


Figure 25 Carbon levels based on depth and location with median ppm.

The chromium on the other hand was very consistent in its readings in the sense of a narrow range in values. The lowest value from it came from Point 13 with a value of 113 ppm (mean) or 112 ppm (median) whereas the highest value came from Point 8 with a value of 168 ppm (mean) or 178 ppm (median). These two points are bare and blued

respectively and both from the surface. This narrow range of values indicates that the chromium is evenly distributed among both the patina and the steel, thus being irrelevant for determining the make-up of the patina.

In greater abundance than all other elements detected is manganese. The lowest reading for manganese 3819 ppm (mean) or 3666 ppm (median) seen in Point 8, a value higher than even the upper margin of the carbon content. The highest value of manganese is shown in Point 1A with a value of 19690 ppm (mean) or 20143 ppm (median), meaning this point is nearly 2% manganese. The pattern with the distribution of manganese is a bit less consistent than the carbon but generally has the trend of values being higher in the bare metal and at the surface. The exception being Points 1A and 1B, this is the only point recorded at the surface and at depth where there is a decrease in manganese levels, however the level at depth is still significantly higher than most of the other surface readings.

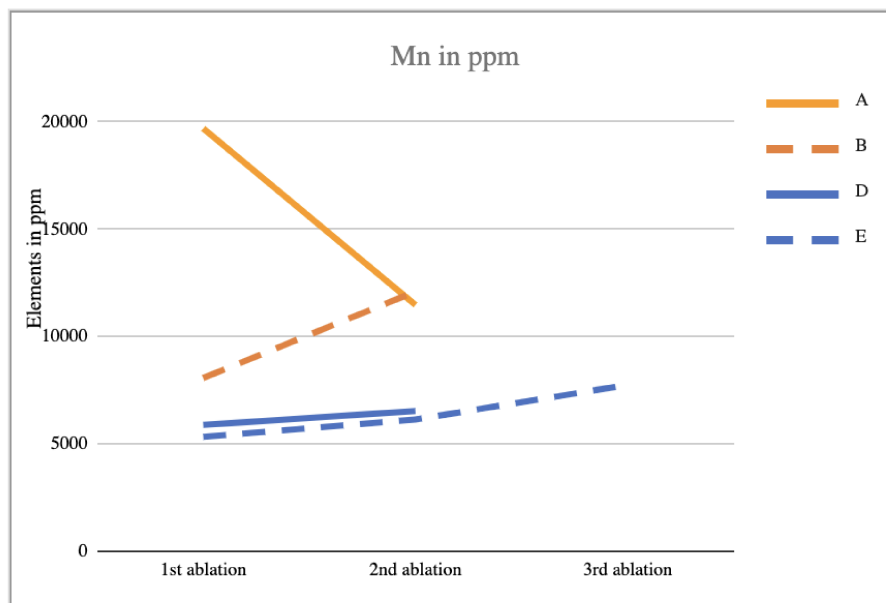


Figure 26 Manganese levels based on depth and location with median ppm.

Moving on to the sulphur, there is once again a wide range of values with the highest being Point 4A at 1884 ppm and the lowest being Point 5B with 0 ppm. Assuming the lack of any sulphur on Point 5B (as the points immediately above and below both have sulphur) is an error then the next lowest reading is Point 6 at 14 ppm. When looking at the median values, however, there are six points that came back with results for 0 ppm of sulphur. The three highest values for the sulphur are all from blued portions, one of which was at depth. What they also share in common is that they are all samples taken

from the edge of the square portion of the screw. This portion of the screw is the primary portion that would be exposed to black powder fouling. As sulphur is one of the main constituents of black powder it is possible the sulphur is a product of contamination, though, as sulphur is also in many of the bluing methods there is a chance it is still related to the bluing.

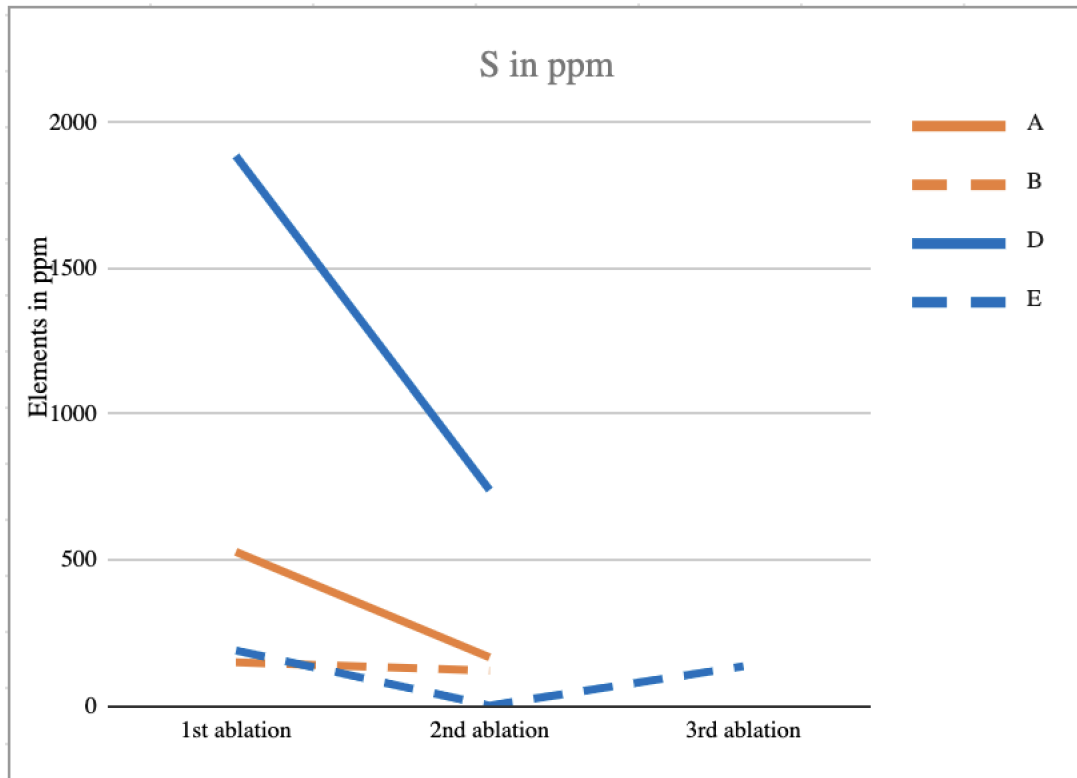


Figure 27 Sulphur levels based on depth and location with median ppm.

Finally, the lead values detected in this process have a clear outlier among all sample points. This is Point 1B where a mean value of 26134 ppm was recorded along with a median value of 2204 ppm. This is the single highest value among all elements and sample points. This value is indicative of the lead being related to the steel as it was recorded at depth for a point of bare metal. In an inverse to the carbon the lead has a tendency to have greater values at depth than at the surface, with the one exception being Point 4. This is further evidence that the lead is related to the steel. That being said, the median values of lead for the surface readings are still higher than most of the surface readings for the bare metal, which could be an indication of two sources for the lead, one being the metal itself and one being the patina.

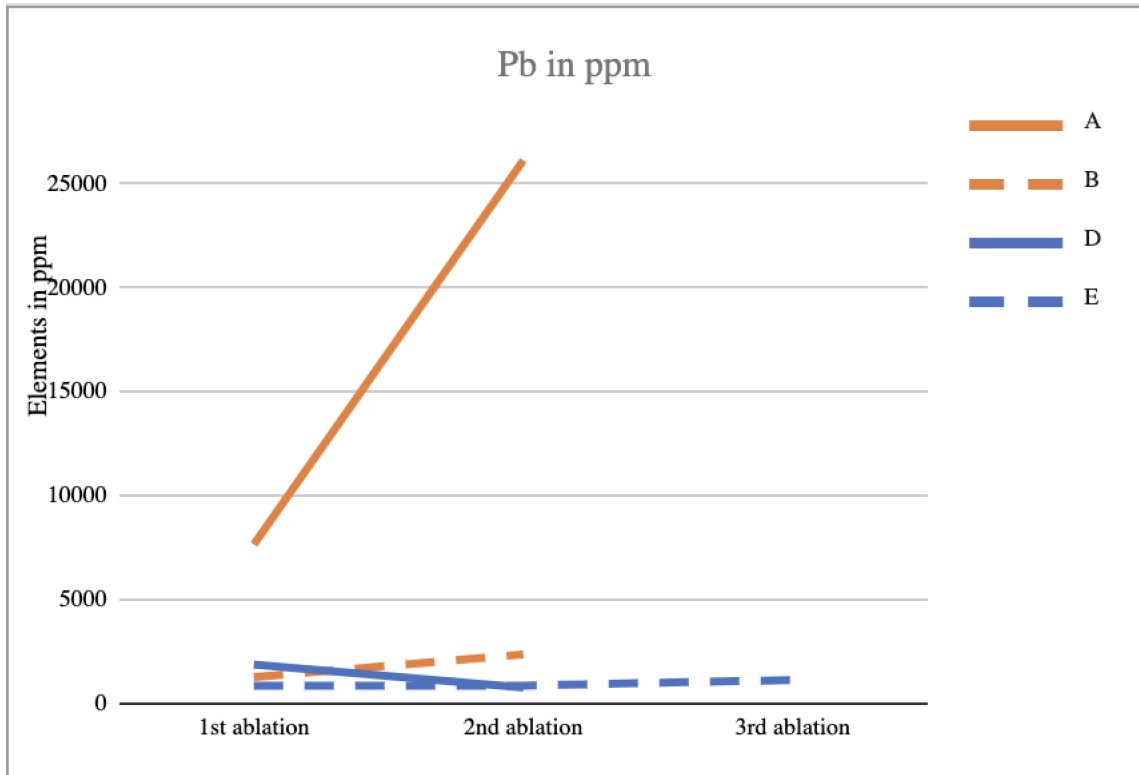


Figure 28 Lead levels based on depth and location with median ppm.

### 3.2.2 Secondary Elements

There were five elements that were deemed secondary as they had noticeable levels of prominence but did not severely outweigh the other elements, they are phosphorous (P), copper (Cu), cobalt (Co), Zinc (Zn), and antimony (Sb).

The phosphorus levels were relatively low with the highest of the mean values being 18 ppm and the highest of the median values being 16 ppm. There were no evident correlations between the phosphorous and the bluing as the levels were fairly consistent among all sample points. There was a slight decrease in the counts with depth but generally the blued and bare areas exhibited similar levels throughout.

The copper had the highest values of the secondary elements with Point 10 having a value of 1507 ppm for the maximum and Point 11 at just 35 ppm. The difference between these values is a point of interest as they were taken right next to each other. This is a likely indicator that Point 10 is another error as the next highest value is 554 ppm. With the exception of the outlier that is Point 10 the copper tends to be more prominent in the blued portions than the bare metal.

The cobalt, much like the chromium, has very consistent values with a range from 12 to 26 ppm with points 11 and 6 respectively. There seems to be no indication that the

cobalt is more related to either the patina or the steel, but rather they share essentially the same amounts overall.

The zinc is distinctly more present in blued areas over the bare metal. The highest value of zinc is at Point 6 with 174 ppm and the lowest is at Point 13 with just 4 ppm. The points with samples taken at depth clearly show a decrease in zinc levels across all locations. There are no outliers with both blued and bare portions showing a decrease in zinc at depth. While the zinc has generally low values it is the most consistent of all the recorded elements when looking at associations with blued versus bare areas, and surface versus depth.

The antimony has a strong decrease at depth compared to its surface values along with the blued areas exhibiting higher levels of antimony. With mean values reaching 81 ppm for the blued portions and a high of only 31 ppm for the bare metal there is a clear difference between the two portions of the sample.

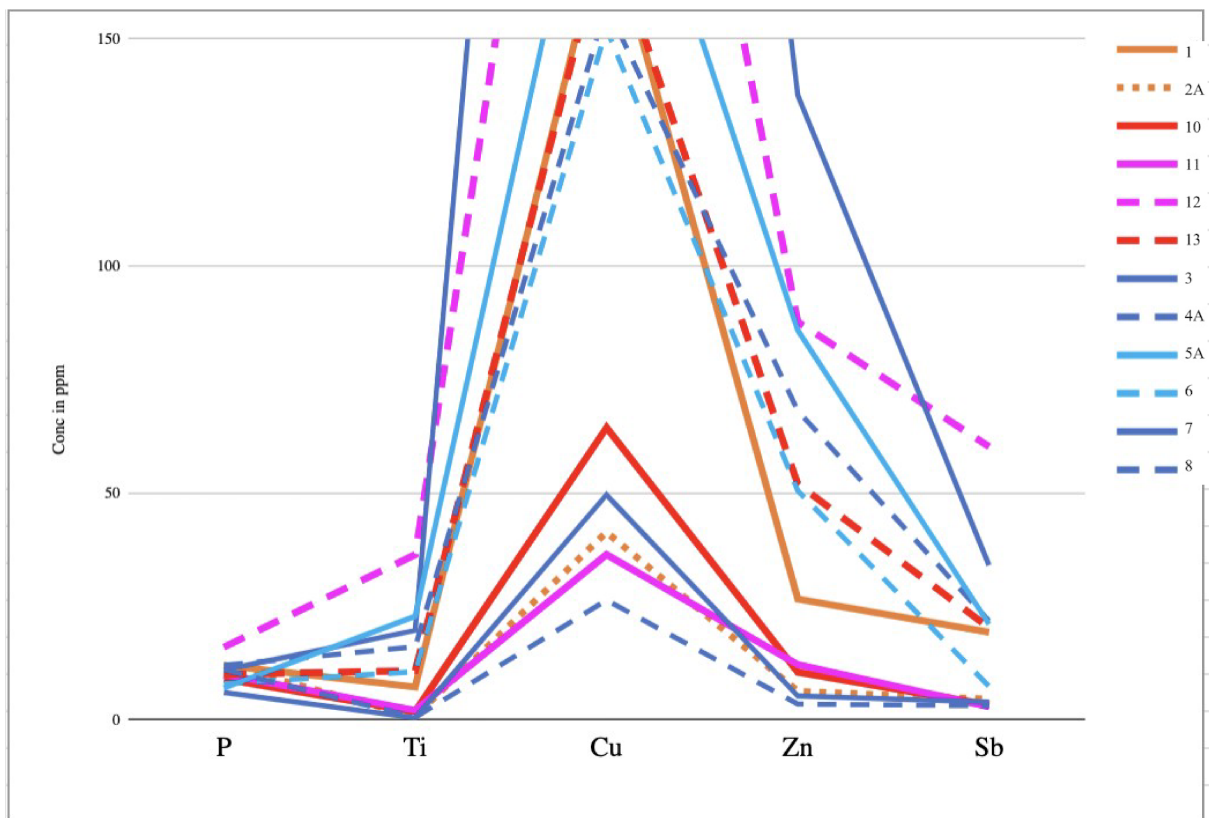


Figure 29 Abundance of elements related to the patina in median ppm. Blue tones denote blued areas, orange and pink tones denote bare metal.

### 3.2.3 Additional Elements

There were also 13 other elements detected by the test of varying degrees of prominence. They were, however, of an insignificant quantity and as such have been deemed unrelated to the bluing processes. There were rarer elements detected such as vanadium (V), aluminium (Al), gallium (Ga), molybdenum (Mo), yttrium (Y), and titanium (Ti). These elements were all found in low quantities of no more than 0.008% at the highest value for the aluminium and as low as 0.00000007% for the zirconium (Zr). For this reason these additional elements were not studied in detail as their values are statistically insignificant compared to the aforementioned elements that appeared in greater abundance.

### 3.3 Confocal Microscopy

The intended function of using confocal microscopy was to measure the depth of the holes made in the screw during the laser ablation. Unfortunately, the holes made by the laser seem to have either corroded over or were so severely melted by the laser that they became convex, with additional material having bubbled out of the hole as it cooled (*figures 31 and 32*). Therefore, the depth of the holes could not be determined with only guesses at the thickness of the patina being possible. This, however, did not make the confocal microscopy completely useless. As can be seen in *Figure 30* what appears to be a hole is actually a convex extrusion. This area is without a doubt one of the sample locations, and the only sample location with any evidence of the laser ablation. While it is possible the laser melted the sample so much it bubbled over and out of the hole another option is that the laser went through the bluing and exposed the metal beneath. By exposing the metal, it became reactive and susceptible to moisture and as such, rust formed in the approximate two weeks between the laser ablation and the confocal microscopy. While this does not help with the understanding of the interaction between the blue patina and the steel it does provide more insight on how effective the bluing is, even if the intervention of the laser ablation may affect the corrosion of the metal. As mentioned, the screw is the sample with the least amount of damage to the blued layer, so it has very little rusting. By creating these microscopic holes in the patina and the rust forming so quickly while the screw was not exposed to any harsh conditions it shows just how effective the bluing is at inhibiting the formation of rust. The rapid heating and

*Figure 30 Cross section of the topography of the below sample location (red is the highest points and violet is the lowest).*



cooling of the metal during the laser ablation makes the metal more defective and reactive.

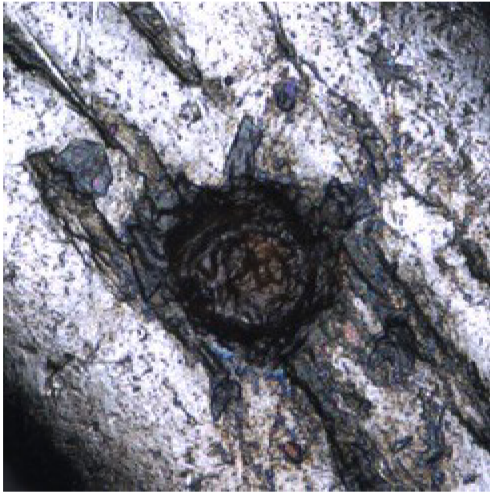


Figure 31 Sample point (screw) at 100x magnification

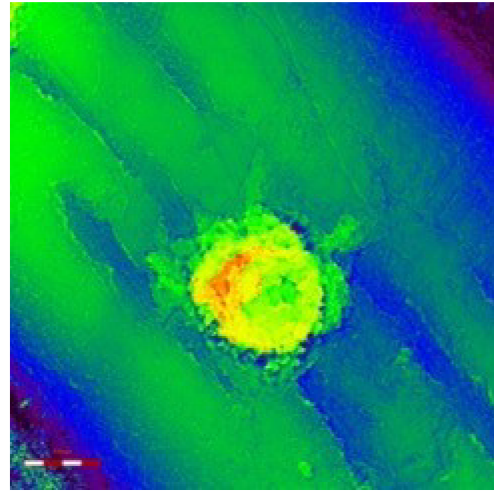
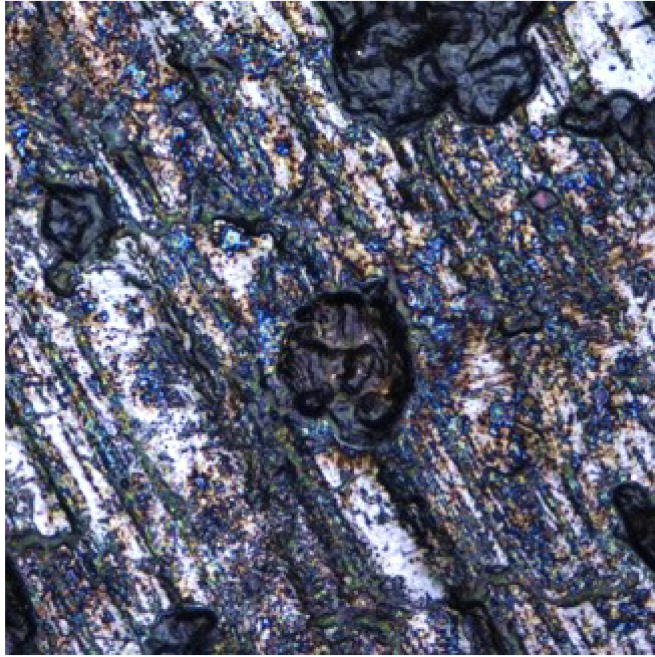


Figure 32 Topography of the same point

In addition to showcasing the effectivity of the bluing the confocal microscopy also allowed for a much more detailed view of the surface compared to the stereomicroscopy. As observable in *figure 33* there are sporadic areas where the steel appears bluer than the rest. These darker areas seem to be where the bluing is best preserved. While under stereoscopic microscopy the bluing appeared homogenous at this higher magnification it is clear that the surface is more heterogenous than initially thought. That being said, there is a greater area that is covered by the dark black and blue spots than not. This could indicate that the bluing solution stuck better to the gaps and grooves in the steel rather than a flat surface. The bluer portions appear to be rougher than the steel-coloured portions.



*Figure 33 100x magnification of the surface of the screw*



### 3.4 XRD

#### 3.4.1 Lock Plate

There are three primary phases that were identified through the X-Ray Diffraction for the lock plate. These phases include iron (Fe), goethite ( $\text{Fe}^{3+}\text{O}(\text{OH})$ ), and an organic compound that is possibly copper acetate ( $\text{Cu}(\text{CH}_3\text{COO})_2$ ). There was also the detection of another phase, this time of a clay, likely phengite ( $\text{K}(\text{Al},\text{Mg})_2(\text{OH})_2(\text{Si},\text{Al})_4\text{O}_{10}$ ). The clay is not perceived as having anything to do with the metal as its presence is likely due to contamination. Similarly, the organic compound is presumably the remains of the oil that is used to clean and maintain the pieces.

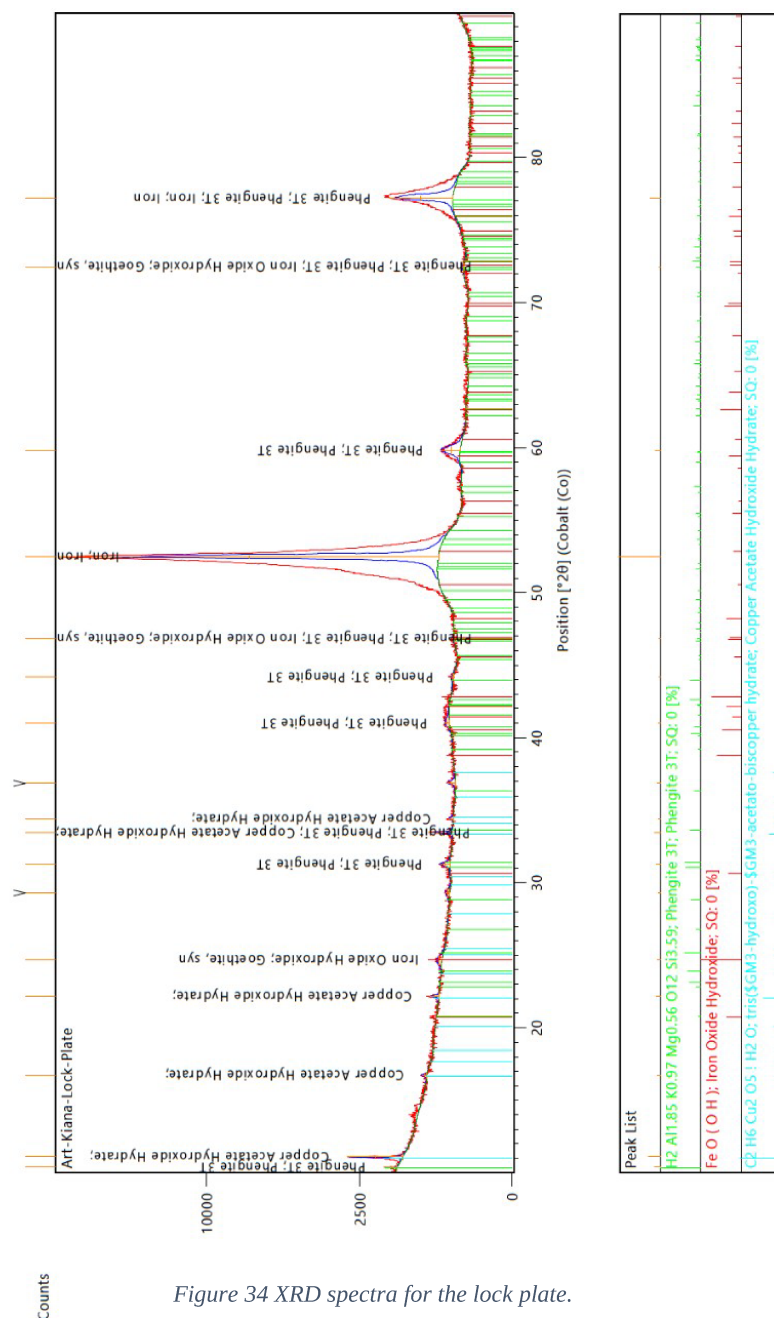


Figure 34 XRD spectra for the lock plate.

### 3.4.2 The Breech Block

The breech block had the same findings as the lock plate with the exception of the phengite ( $K(Al,Mg)_2(OH)_2(Si,Al)_4O_{10}$ ). Once again, the organic compound is likely the remnants of the oil used for cleaning the rifles, so, as with the lock plate, it will be ignored in the matter of observing the bluing.

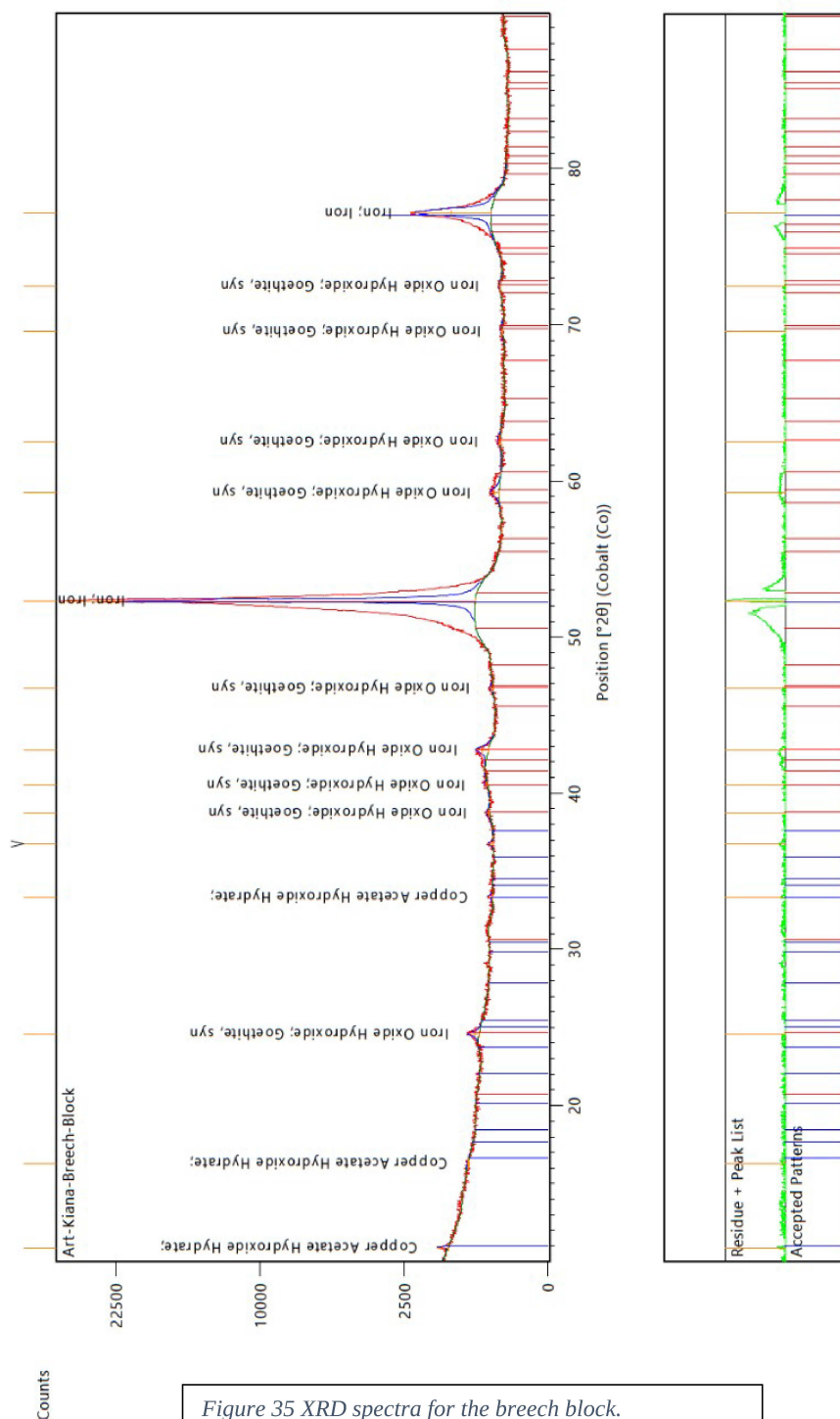


Figure 35 XRD spectra for the breech block.

### 3.4.3 The Screw

The screw was more homogenous in its composition possibly due to it being cleaner than the other samples, which is in line with it being the piece with the most intact bluing and as such has the most homogenous surface for analysis. The two phases that were identified were iron (Fe) and an iron alloy.

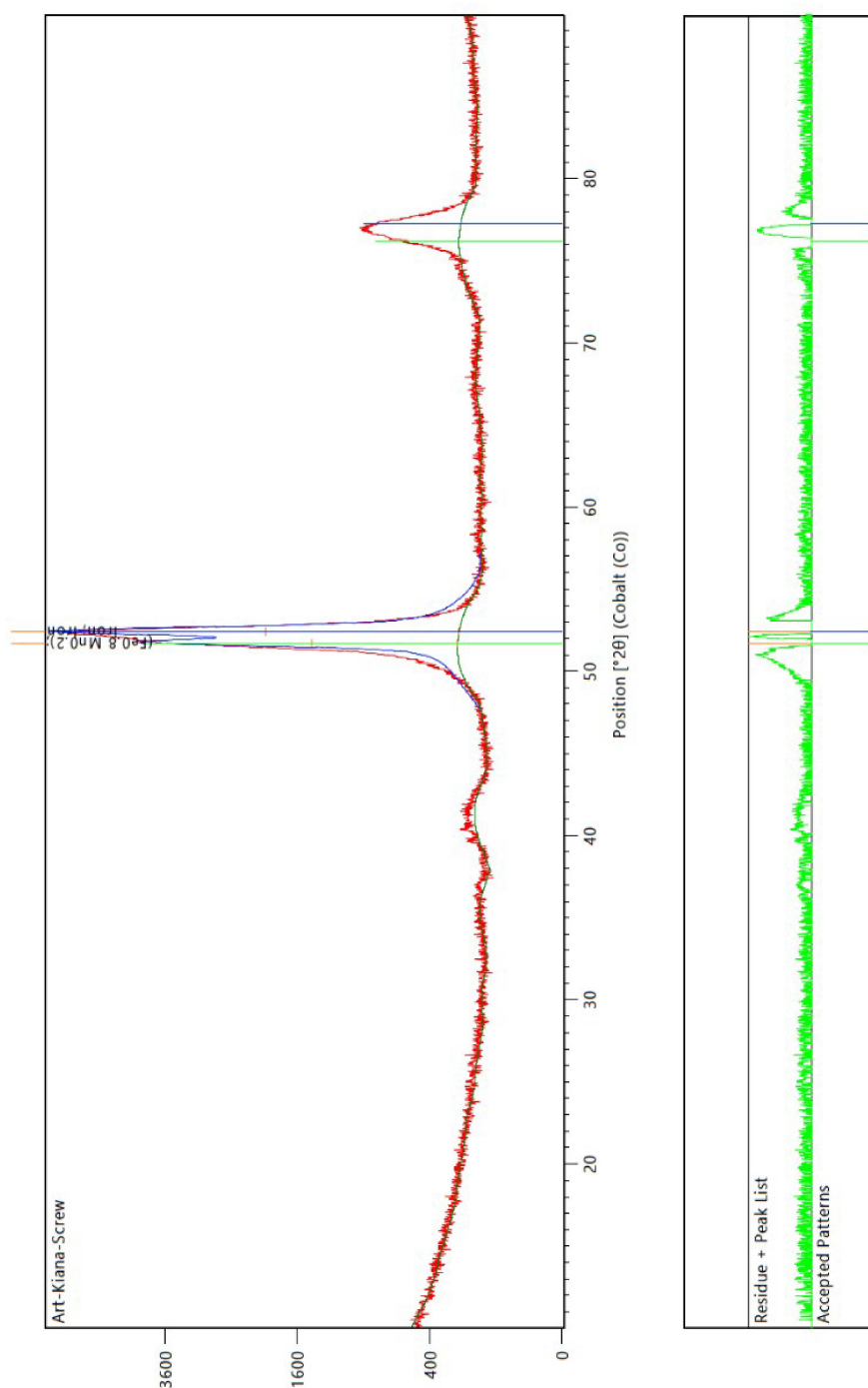


Figure 36 XRD spectra for the screw.

### 3.5 XRF Data

The data acquired from the XRF is semi-quantitative, thus giving an estimation of the amounts of each element; this is due to a lack of standardization. The data received from the X-Ray Fluorescence testing is consistent with the data from both the X-Ray Diffraction and the laser ablation. There are a few exceptions to this with some different elements being detected by the XRF that were not noticed by either the XRD or the laser ablation. Various sample points were taken across all three samples. There were three points sampled on the screw, five on the lock plate, and four on the breech block. Samples were taken both from blued and non-blued areas.

Object	Material	Point of analysis	K12	K12	K12	K12	K12	K12	L1	K12	K12	K12	L1
			K	Mn	Fe	Ni	Cu	Zn	As	Se	Rb	Mo	Pb
Lock Plate	Metal	1bis	425		2603936	210	995	436			1246	1,00000	1123
	Metal	2	496		2654730	251	770	318			1566	1,01115	1195
	Blue patina	3	520		2634936	227	1715	810			1409	1,00098	2521
	Blue patina	4			7110944	514	1966	509			4105	1,64278	1973
	Blue patina	5	592		9631732	1207	2816	759			6085	1,87971	3776
Screw	Metal	6		40686	5316754	254	781	643			2348	1,41974	6014
	Blue patina	8		107189	13966037	2809	22617	17953			9773	2,21670	28223
Breech Block	Metal	9			7398284		1141	1397	633	913	3797	1,67864	7629
	Metal	10			5298695		1463	260	455		2595	1,43444	2634
	Blue patina	11	3657				3780	1588	691	2488	5344	1,82691	6336
	Blue patina	12	2582				5117	2112	489	969	3839	1,69339	4938

Table 6 XRF data standardized to molybdenum. (Yellow highlights denote elements related to the patina).

#### 3.5.1 The Lock Plate

The lock plate had the most sample locations out of the three pieces at 6. The samples were taken from areas with more intact bluing as well as areas where the bluing had been mostly worn down over time. Of the points sampled 3, 4, and 5 were blued while 1, 1bis, and 2 were from the bare metal. Point 1 was an anomalous reading and is therefore being ignored for any further analysis. There were three main elements detected during the XRF testing that are of significant note regarding the patina. These elements are copper, zinc, and nickel. Additionally, there were significant lead levels detected but this is likely more related to the composition of the metal rather than the patina. The amounts of copper on the blued portions are upwards of triple the amounts detected on the bare metal. Similarly, the zinc is roughly double the amount on the patina versus the bare metal, and the nickel is ranging from double to nearly six times the amount compared to the bare metal. There were,

of course, other elements detected in the lock plate, being iron and potassium. The iron is evidently from the metal and the potassium does not show any significant difference between the patina and the bare metal, so it is likely contamination, possibly from black powder. A point of note for an element that was not detected is manganese. Manganese was detected in high volume in the screw but there seems to be a distinct lack of any manganese in the lock plate.

### 3.5.2 The Breech Block

The breech block has a total of four samples, being points 9-12. There were two taken on the blued patina and two taken on the bare metal. Starting with point 9, which was from the interior of the breech block, an area lacking bluing, there were a few elements with a reliable reading other than iron, which was once again lead, copper, and zinc. Arsenic (As) and selenium (Se) were also detected in the breech block in unreliable amounts. Point 10 showed similar results to point 9, as it was also from a portion of bare metal. Some minor differences include more copper, less zinc, and a complete lack of selenium. For points 11 and 12, both taken from blued portions, there is a rise in the copper and zinc, just like with the lock plate. This sharp rise in these elements on the patina for all of the samples is a strong indicator that they are related to the composition of the patina. Both points also exhibit a rise in arsenic and selenium. The breech block is the only sample to have either of these elements.

### 3.5.3 The Screw

For the screw, points 7 and 8 were on blued portions while point 6 was taken from an area that has had some wear to the bluing. Point 7 only had one element other than iron and the elements related to the machine, such as molybdenum (Mo), which was silver (Ag). For this reason, like point 1, point 7 has been deemed an improper reading and will henceforth be ignored. As for point 6, it showed low values for nickel, copper, and zinc, but high values for manganese, iron, and lead. This reinforces the data from the LA-ICP-MS, which showed similar results for the bare metal. Point 8, being from a blued portion, once again had a large spike in levels of nickel, copper, and zinc. The levels of copper are upwards of 30 times those of the bare metal, likewise, the zinc increased over ten-fold. Overall, the

data from the XRF of the screw are in line with the data acquired from the LA-ICP-MS, and the findings reinforce each other.

## Chapter 4: Discussion

### 4.1 The Lock Plate

Based on the initial microscopy of the lock plate there are some methods of bluing that seem more likely than the others. There are four methods that, based solely on appearance are more likely to have been what was used and by utilizing the chemical data the list should be narrowed down. Firstly, there is the *Parker Process*, this method is a strong possibility as it creates a dark grey patina, much like the one seen on the lock plate. The second option is *Field's Unnamed Method #2*, as it also characteristically has a dark patina. The third possibility is *rust bluing* as it is known for creating a patchy finish. The patchiness of the lock plate could simply be due to its age but there is still the possibility that it has been patchy since it was formed, thus the chance that *rust bluing* was the method of choice. Additionally, rusting a piece is also an integral step to browning, which as mentioned, has been confirmed to have been a utilized method in the Regency Era. The similarities between the methods could have been seen as a logical transition point from browning to bluing. The fourth option is *Field's Unnamed Method #1*, which creates a smoky shade, which is also in line with the current appearance of the lock plate.

The XRF added the detection of lead, copper, and nickel to the considerations. What the XRF did not detect in the lock plate, however, is manganese. Since manganese is a primary component in the *Parker Process* the seeming lack of manganese eliminates this method as a possibility. While the nickel is not connected to any specific methods of bluing the lead is. *Field's Unnamed Method #2* utilises lead acetate ( $Pb(CH_3COO)_2$ ) in the bluing process, which could be the reason for the detection of the lead in the XRF testing. There is the possibility that, like the screw, the lock plate's base material simply has a high lead content but as no measurements at depth were taken for the lock plate that is merely speculation. Therefore, while it cannot be confirmed one way or the other the source of the lead, its presence, along with the specific colouration of the piece, does suggest that the *Field's Unnamed Method #2* could have been used to blue the lock plate.

There is also the matter of *Field's Unnamed Method #1*, which utilizes copper sulphate ( $CuSO_4 \cdot$ ) and arsenious oxide ( $As_4 O_6 \cdot$ ). While the arsenic was not detected in the

lock plate the high levels of copper do suggest the use of this method. The copper is also an element that has been noted to be related to the blue patina. This makes *Method #1* a more likely candidate than *Method #2*, as the lead connected to that method cannot be confirmed to be directly related to the patina.

When the chemical data from the XRD and XRF are brought into consideration certain methods become more likely than others. The XRD primarily indicated the presence of iron and goethite along with a substance that is likely copper acetate ( $\text{Cu}(\text{CH}_3\text{COO})_2$ ). The iron is of course expected as that is the base material of the sample. The goethite, however, is likely an effect of the bluing process rather than a cause. Goethite displays a colour of grey with a bluish tint in reflected light, which could be the source of the colouring of the blued portions. Unfortunately, the goethite does not provide any insight on possible bluing methods, but it appears to be the primary source to the colour of the patina. The copper acetate ( $\text{Cu}(\text{CH}_3\text{COO})_2$ ), however, does indicate the possibility of a mixing of the two *Unnamed Field Methods*. Essentially, it would be the second method but with a substitution of the lead acetate ( $\text{Pb}(\text{CH}_3\text{COO})_2$ ) for the copper acetate ( $\text{Cu}(\text{CH}_3\text{COO})_2$ ).

The process used to blue the lock plate seems to be between two methods, a combination of *Field's Unnamed Method #1* and *Field's Unnamed Method #2*, and *rust bluing*. The combination of *Field's* methods matches both the physical appearance of the lock plate and the chemical data with its abundance of copper. *Rust bluing*, however, also matches the physical description of the lock plate and the acids used would have left behind little to no trace of their presence after reacting with the metal. Additionally, *rust bluing* as a method is more similar to browning, which was the previously used process for British firearms, thus making it a more logical step in the advancement of protective patinas. In short, though *rust bluing* matches the appearance of the lock plate and has some historic precedence, the chemical data is pointing toward the use of a combination of *Field's Unnamed Method #1* and *Field's Unnamed Method #2*.

## 4.2 The Breech Block

The results for the breech block were remarkably similar to those of the lock plate, especially considering their different manufacturing dates and locations. This is indicative of relatively strict standards among British firearm production, at least for the materials. The

breech block has the same colour to its patina as the lock plate thus suggesting the same starting list for possible methods. Furthermore, the near identical results from the XRD also suggest the same method was used for both pieces. As with the lock plate there was lead discovered in the XRF analysis along with a spike of copper. This presence of copper is indicative of *Field's Unnamed Method #1* as that method utilizes two solutions containing copper sulphate ( $\text{CuSO}_4$ ). This method is described as creating a smoky shade to the metal, which seems to match the current appearance of the breech block. This means that there are three strong possibilities for the method used on the breech block. Both of *Field's* methods along with *rust bluing* fit with the chemical analysis and the limited historical records. As with the lock plate, *Field's Unnamed Method #1* combined with *Field's Unnamed Method #2* seems to be the most likely method used, in accordance with the chemical data.

### 4.3 The Screw

The screw is the outlier among the samples. While the lock plate and breech block displayed splotchy, dark, grey patinas the screw has a well preserved bluish-black patina. With this appearance there is a different set of possible methods to have been used on the screw. Based on appearances alone the most likely candidates for the bluing type of the screw are *hot caustic bluing* due to the nearly black patina, *nitre bluing* due to the distinct blue tint, and both of *Field's Unnamed Methods*. Of these methods there are once again some that become more likely when the chemical data is brought into account. When the chemical data is considered, further possibilities arise in the form of *Buchner's Method*, and browning due to the presence of antimony. However, the antimony was detected in small amounts, which either suggests it is present due to contamination or it is the remains of a previous chemical treatment.

Starting with the two *Field* methods, there is a possibility that *Field's Unnamed Method #1* was used much like with the breech block and lock plate. Based on the copper value detected in sample point 8 for the screw under the XRF testing there is a high possibility of this method having been used. The visual appearance of the screw is in line with general descriptions of this method, and it would explain the detection of copper. This would also be in line with the elevated levels of copper detected with the LA-ICP-MS where the blued portions generally denoted a higher level of copper than the bare portions. Likewise *Unnamed Field Method #2* also fits the appearance of the screw and as lead acetate ( $\text{Pb}(\text{CH}_3\text{COO})_2$ ) is the primary ingredient in the solution for this method it would correspond to the



higher lead levels detected in the screw. While the lead levels do appear to be associated with the steel itself rather than the bluing it was noted that the blued portions sometimes yielded higher lead levels at the surface than the bare metal did. Essentially, while the steel undoubtedly has a high lead content there still seems to be the presence of a surface layer of lead, which could be related to the bluing process or could be from pollution.

*Nitre bluing* is also a strong candidate when the chemical data is considered. With manganese dioxide ( $MnO_2$ ) being one of the two ingredients in *nitre bluing* the possibility of this being the method used is high. While the manganese readings for the LA-ICP-MS showed higher levels of manganese at depth the surface levels were still significantly higher than the other detected elements. This could be indicative of a surface layer along with the manganese integrated into the steel, much like with the lead. The manganese could also be due to the use of the *Parker Process*. These two methods are equally likely from a chemical point of view however each has their own flaws from an optical sense. The *Parker Process* descriptions from Field never indicate any blue tint, only a dark grey. Contrarily, *nitre bluing* is described as having an iridescent blue colour. While the screw has a blue tint it is not one that could be considered iridescent to the extent that *nitre bluing* is known for. Therefore, though the manganese is heavily prominent in the screw the appearance of the patina does not quite fit with either of the methods that make use of manganese dioxide ( $MnO_2$ ). While it is possible, they are merely presenting atypically, a confirmation of the use of either of these methods is not possible without further research.

The final proposed method for the screw is *hot caustic bluing*. The physical description of a near black patina suits the screw quite accurately, the chemistry however, does not. The ingredients used in *hot caustic bluing* are potassium nitrate ( $KNO_3$ ) and sodium hydroxide (NaOH) but neither potassium nor sodium were detected in any significant amount for any of the tests conducted. In essence, even though the screw has the appearance of a piece that has undergone *hot caustic bluing* the chemistry does not support the proposed use of this method, thus making it nearly impossible that this was the chosen method.

Of the many proposed methods of bluing for the screw there are once again multiple options that best suit the chemical and physical analyses along with the historical trends. *Field's Unnamed Method #1*, *nitre bluing*, and *Field's Unnamed Method #2* the are the three mostly likely candidates for the screw. These being based on the lead and copper levels respectively along with their visual similarities. In addition, it would seem that either

*Buchner's Method* or *browning* had at one point been conducted on the screw prior to the addition of the current surface layer. While there are a few options remaining, it should be noted that the combination of *Field's Unnamed Method #1* and *Field's Unnamed Method #2* has fit chemically and physically for all three samples, thus indicating it to be a more likely candidate than the others.

#### 4.4 Prior Research

There has been little in the way of prior research into blued iron and steel but there is one paper by a group of researchers concerning bluing of medieval armour. The article, titled *A Note on an Attempt to Investigate The Blueing of Armour by Using Ellipsometry*, details comparisons between the thickness of medieval bluing, Napoleonic bluing and modern iterations. This investigation found that the bluing on their samples was a double oxide layer rather than the single layer they predicted. They speak of bluing only in the sense of heat treatment rather than chemical treatment, meaning there are only a few similarities between their samples and the ones used in this investigation.



## Chapter 5: Conclusions and Further Research

### 5.1 Conclusions

The results from this research have pointed to multiple possibilities for the bluing methods used on each of the three samples. For the lock plate the most likely contenders seem to be *rust bluing*, or *Field's Unnamed Method #1* along with the possibility of *Field's Unnamed Method #2* due to the prominence of lead. The breech block had much the same results as the lock plate. The screw's patina, with its more pronounced blue tones seems to have been achieved through *Field's Unnamed Method #1*, *Field's Unnamed Method #2*, or *nitre bluing*, though this one is the least likely. While this seems to be a relatively long list of possibilities it is significantly fewer possibilities than with just a visual inspection of the samples. The fact that the data for all three samples correspond with *Field's Unnamed Method #1* of a copper sulphate ( $CuSO_4$ ) and hydrochloric acid (HCl) solution and a copper sulphate ( $CuSO_4$ ) and arsenious oxide ( $As_2O_3$ ) could indicate that this was the preferred method. The presence of a copper acetate ( $Cu(CH_3COO)_2$ ) like substance on the lock plate and breech block is also indicative of the use of a combination between the two *Unnamed Field Methods*. The British army is famous for being regimented in all that they do, it stands to reason that the production of their firearms would be no different. The fact that the chemical and physical data for all three samples are a match for either/both of these methods point toward them being the standard methods used for British firearms manufacturers. The chemical markers for the other possible methods, such as the lead, antimony, and manganese, are likely one of three options. The first option is that these elements are ingrained in the iron and steel. As the data was not sufficient to fully differentiate between blued and bare metal this is a possibility. The second option is that the pieces have been blued more than once and the other elemental markers are the remnants of previous bluing attempts that have since mostly worn off. If this is the case, it is essentially impossible to determine which methods would have been used first and which ones were attempted restorations. The final option is that a combination of the two *Field* methods was used, possibly a copper

acetate ( $\text{Cu}(\text{CH}_3\text{COO})_2$ ) based solution as opposed to the lead acetate ( $\text{Pb}(\text{CH}_3\text{COO})_2$ ) based one of the second method.

The results for multiple types of bluing and the inability to determine which methods were used first is an unfortunate finding regarding a better understanding of the chemical processes related to bluing in the Victorian Era. It would seem the possible mixing of the two *Field* methods is most likely for the lock plate and the breech block, but the screw remains unconfirmed due to the presence of more elements that were not found with the other samples. Both more chemical and historical research is required to find a definitive answer for the screw. However, the difficulty in determining which method was used does indicate that re-bluing historic pieces would be possible without damaging the piece. Since there are multiple techniques detected for each sample, this shows that re-bluing an historic sample would not erase the evidence of its original bluing. In essence, the re-bluing of historic pieces is safe both in terms of maintaining the chemical markers of the piece and for better preserving it for future display, or in the case of the rifle parts in this research, use.

To conclude, the research conducted for this paper has given some insight into possible bluing methods used in Victorian times. While a definitive answer for a method used on the Snider-Enfields was not confirmed the list was considerably narrowed. Additionally, as the combination of *Field's Unnamed Method #1 and #2* seemed to match all three samples there is a strong possibility that they were all blued using this technique, whether historically or through more modern intervention. Further research into bluing on both the chemical and historical sides would be beneficial to having a full understanding of firearms production in the Victorian Britain. While more definitive findings are still needed for this portion of the study the question of restoration of blued pieces has been answered. Through this research there has been no indication that the use of multiple bluing methods would be harmful to the metal, nor is a secondary bluing going to erase the primary bluing. This has been shown specifically with the screw which presents a chemical marker for two methods it does not have the physical characteristics of. In short, at least some of the Snider-Enfield's bluing seems to have been done with a combination of the two

*Unnamed Field Methods*, whether historically or modernly and the re-bluing of these rifles would not cause any harm or erase any of their previous treatments.

## 5.2 Further Research

### 5.2.1 Types of analysis

There are many types of testing that could not be performed on these samples, primarily due to them being functional rifle pieces that had to remain in their same condition. A cross section of one of the samples would have been beneficial for examining the interactions between the patina and the metal. This cross section could have been studied through reflected light microscopy as is done with other metals. If a sample were to become available that could be cut without issue, there is potential for this type of analysis to provide a great deal of information on both the thickness of the patina as well as whether there is a stark divide between it and the metal or if it is a more gradual transition.

A re-testing with the LA-ICP-MS would be ideal so that the confocal microscopy could be done immediately after. This would make the data more easily revisable and would give more concrete results on the differences between the layers of patina and metal. If this were combined with a cross section, it would give much stronger results for how the bluing and the metal behave in conjunction. Additionally, as the LA-ICP-MS was useful for the screw, being able to conduct this testing on the other samples would be beneficial.

Another test that would be of interest would be to test the effectivity of bluing in a controlled environment. This test would best be conducted with modern pieces that have been blued with historic methods so as not to risk harm to any artifacts. This theoretical test would have the blued steel subjected to various conditions that it should feasibly be able to withstand such as high humidity, rain, and abrasion. By conducting these tests with different bluing methods, the effectivity of them could better be determined and a best option for re-bluing might be decided upon. This study would be time consuming and require significant documentation of the effects

of erosion on the bluing. Essentially, this test would be an expansion of Tauber's study on the methods of bluing mild steel by focusing the same testing methods on pieces that have been weathered rather than freshly blued.

### 5.2.2 Areas of Interest

Production methods of small arms companies in the Mid-Victorian era would be beneficial to this research as it would provide a more concrete basis. If the proper documents from the companies who produced the Snider-Enfield could be unearthed, they could provide invaluable insight on how bluing was done in that period and how it was done on a large scale. Without these documents there can be no confirmation on what type of bluing was conducted, only a well-educated guess. Documents from these companies could also provide general information on the steel and iron they were using. While there is some information pertaining to Thomas Firth and Sons a full documentation of their use of iron and steel is not currently known to exist. Therefore, more historical research is required to get a full understanding of how bluing worked in the Mid-Victorian era.

In addition to added historical research more extensive chemical research would be greatly beneficial. The creation of a database regarding bluing would allow for easier identification of the various methods. By conducting historic bluing methods on modern pieces and then retrieving their chemical data there would be a strong basis for comparison to be made. One of the greatest struggles with this research was the lack of prior investigation into bluing techniques. This meant the only true comparisons that could be done were between the chemical data retrieved and the recipes for the various methods. While this did help narrow the possibilities the similarities between recipes were an issue. By having a database of the distinctions between the many types of bluing the identification of each technique would be much easier. While creating a database like this would be time consuming and expensive it would be greatly beneficial to future studies on blued metals.

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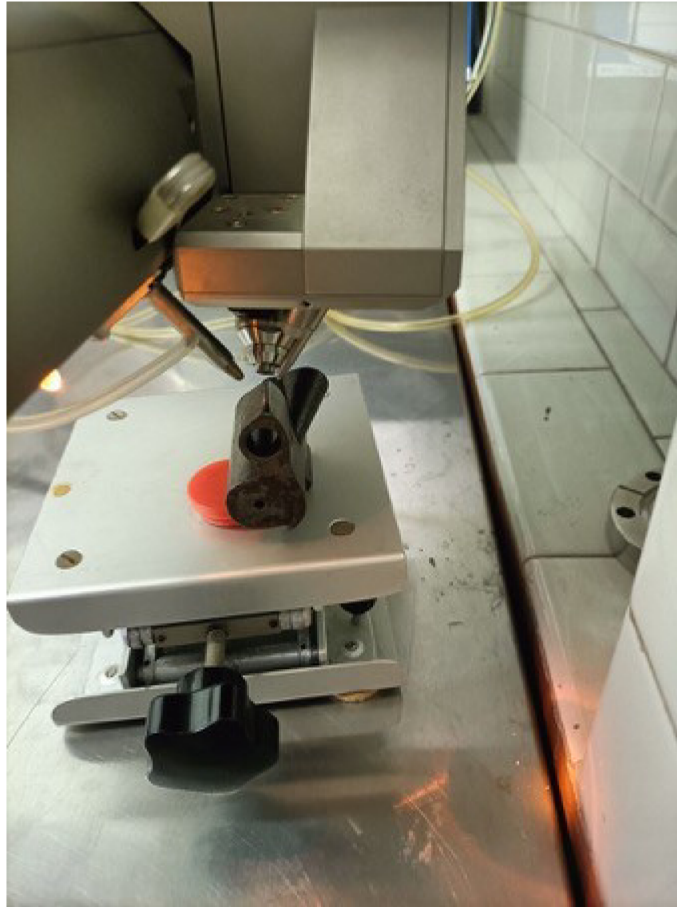
## Appendix

### A. Samples Under XRF Investigation



*appendix 1 Lock plate under XRF.*





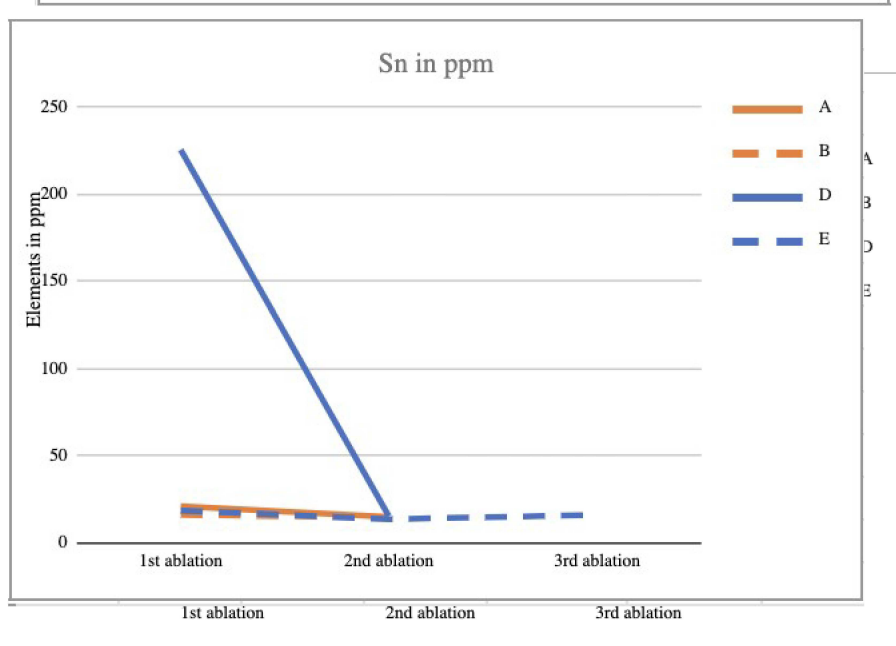
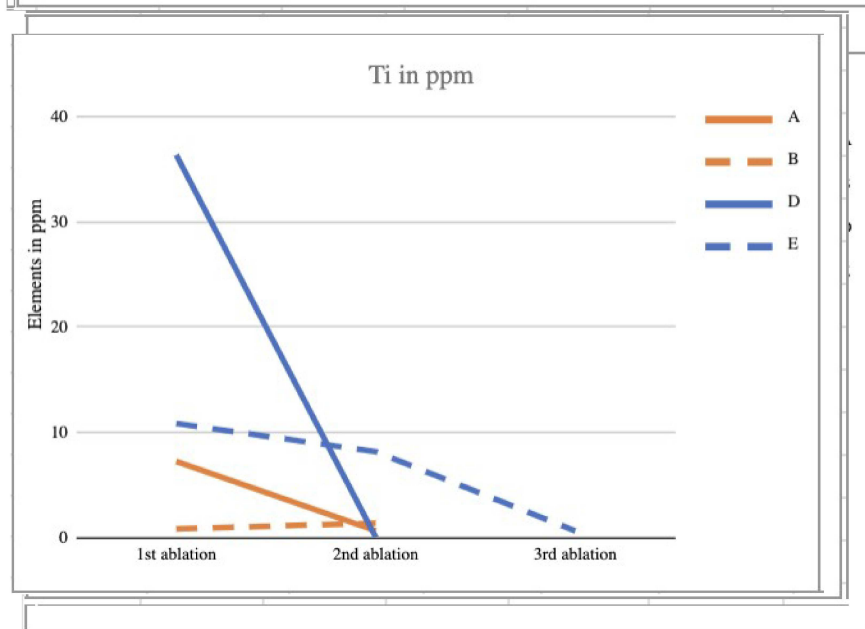
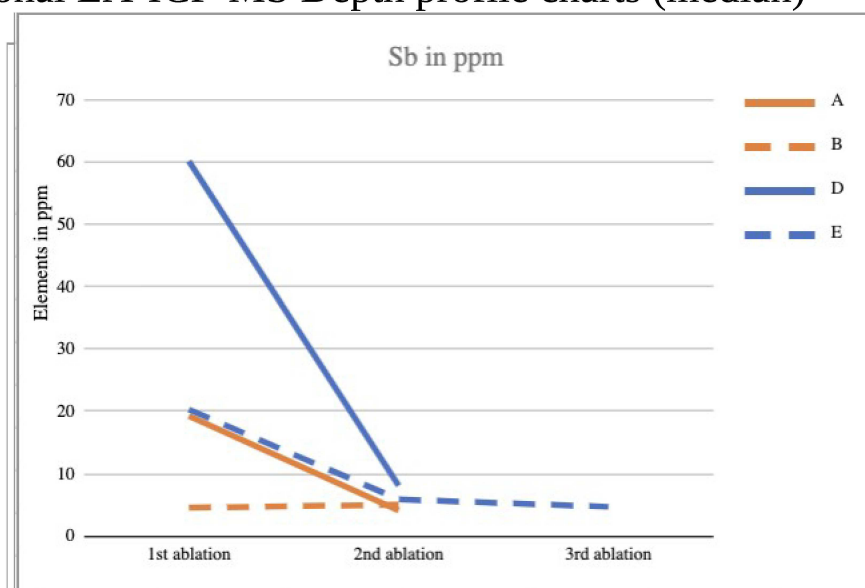
appendix 3 Breech block under XRF.

## B. XRF Data Tables

Object	Material	Point of analysis	K12	K12	K12	K12	K12	K12	L1	K12	K12	K12	L1
			K	Mn	Fe	Ni	Cu	Zn	As	Se	Rb	Mo	Pb
Lock Plate	Metal	1bis	425		2603936	210	995	436			1246	18297	1123
	Metal	2	491		2625458	248	762	314			1549	18501	1182
	Blue patina	3	519		2632346	227	1713	809			1408	18315	2519
	Blue patina	4			4328596	313	1197	310			2499	30058	1201
	Blue patina	5	315		5124060	642	1498	404			3237	34393	2009
Screw	Metal	6		28657	3744876	179	550	453			1654	25977	4236
	Blue patina	8		48355	6300367	1267	10203	8099			4409	40559	12732
Breech Block	Metal	9			4407319		680	832	377	544	2262	30714	4545
	Metal	10			3693905		1020	181	317		1809	26246	1836
	Blue patina	11	2002				2069	869	378	1362	2925	33427	3468
	Blue patina	12	1525				3022	1247	289	572	2267	30984	2916

appendix 4 Non-standardized XRF data.

### C. Additional LA-ICP-MS Depth profile charts (median)



## D. LA-ICP-MS Data Tables

	<b>C</b>	<b>Al</b>	<b>P</b>	<b>S</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Cu</b>	<b>Zn</b>	<b>Sn</b>	<b>Sb</b>	<b>Pb</b>
<b>Blue Median</b>	1124	62	10	355	13	9	137	5205	179	56	38	19	1206
<b>Blue Mean</b>	1302	91	11	367	47	9	138	6079	215	71	47	28	1489
<b>Metal Median</b>	602	32	12	211	2	9	123	9434	63	8	16	7	2258
<b>Metal Mean</b>	739	218	12	248	5	9	125	9501	92	14	17	9	2385

appendix 5 Means and Median of all major and minor elements in ppm.

<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Cu</b>	<b>Zn</b>	<b>Sn</b>	<b>Sb</b>	<b>Pb</b>
12	8	124	19690	295	48	23	31	7634
10	10	137	8049	50	9	16	6	1234
0	8	124	7267	35	4	15	3	1083
1	9	126	6908	40	7	16	3	1352
1	8	113	5591	38	4	13	3	620
<b>5</b>	<b>9</b>	<b>125</b>	<b>9501</b>	<b>92</b>	<b>14</b>	<b>17</b>	<b>9</b>	<b>2385</b>
6	1	9	5765	114	19	4	12	2948
5	9	126	12412	50	28	14	3	1249
266	9	132	5860	427	105	295	81	1837
14	9	137	5302	213	73	20	24	825
33	9	159	4819	554	174	15	76	3899
15	8	148	4572	193	73	17	26	1588
62	12	168	3819	238	104	17	23	1498
25	9	143	7048	168	58	13	8	974
1	8	114	4804	61	13	14	5	671
1	9	119	6076	29	8	14	3	858
<b>47</b>	<b>9</b>	<b>138</b>	<b>6079</b>	<b>215</b>	<b>71</b>	<b>47</b>	<b>28</b>	<b>1489</b>
84	1	18	2557	176	53	93	30	986

<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Cu</b>	<b>Zn</b>	<b>Sn</b>	<b>Sb</b>	<b>Pb</b>	
7	8	120	20143	178	27	21	19	7546
1	10	136	7512	41	6	16	5	1060
0	8	124	7118	29	2	15	3	1041
1	9	124	6929	39	5	16	3	1010
0	8	112	5469	29	2	13	3	632
<b>2</b>	<b>9</b>	<b>123</b>	<b>9434</b>	<b>63</b>	<b>8</b>	<b>16</b>	<b>7</b>	<b>2258</b>
3	1	9	6036	64	10	3	7	2962
2	9	125	7116	36	12	14	3	938
36	9	129	5809	306	88	225	60	1388
11	9	135	5007	175	52	18	20	707
20	9	156	4775	493	138	13	34	2482
16	7	141	4540	157	68	16	22	1473
23	13	178	3666	213	86	17	21	1467
11	10	145	5326	152	50	14	7	944
0	8	113	4616	50	5	14	4	575
1	9	115	5985	26	3	14	3	882
<b>13</b>	<b>9</b>	<b>137</b>	<b>5205</b>	<b>179</b>	<b>56</b>	<b>38</b>	<b>19</b>	<b>1206</b>
12	2	21	1001	149	45	70	19	580