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An Examination of Oxidative Passivated Surfaces on 19th Century Colt Revolver Barrels

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AN EXAMINATION OF OXIDATIVE PASSIVATED SURFACES ON
19TH CENTURY COLT REVOLVER BARRELS

by
MCKENZIE ALLISON FLOYD

SUBMITTED TO SCRIPPS COLLEGE IN PARTIAL FULFILLMENT OF THE
DEGREE OF BACHELOR OF ARTS

PROFESSOR MOERSCH
PROFESSOR WENZEL

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“If this gun could talk...”

- Popular saying among gun collectors

Abstract

Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) were used to examine a series of six revolver barrels manufactured by the Colt Patent Arms Manufacturing Company between 1853 and 1863. SEM micrographs revealed a vast range of surface morphologies among the corroded samples. XRD diffraction patterns showed varying levels of magnetite on the blackened samples, but hematite could not be identified. EDS was used to map elemental distribution and quantify elemental abundances on the gun surfaces; further investigation using this technique may reveal more definitive information on whether some elements present were deposited during patination.

Introduction

Six revolver barrels, manufactured by the Colt Patent Firearms Manufacturing Company between 1853 and 1863, demonstrate the different surfaces that could be produced by arms makers in the 19th century. They also demonstrate the various levels of corrosion and wear that have occurred since their production. Colt was one of many arms manufacturers that have played a role in the development of production technology in the United States, and who have supplied the weapons for the conflicts that have shaped this country's history. It is therefore not surprising that many American history museums own extensive firearms collections. As with other types of artworks and artifact collections, scientific analysis can be useful in making decisions regarding firearm conservation; the surfaces of firearms are of particular interest as the entry point for corrosive agents.

By the time Samuel Colt's Patent Firearms Manufacturing Company began producing firearms in 1836, it had long been standard practice for arms manufacturers to passivate the surface of the steel parts that made up their products. The phenomenon of passivity was discovered by Mikhail Lomonosov in 1738, and was subsequently confirmed by many others, including Michael Faraday.¹

Oxidative passivation results from the repetitive buildup of oxides on a steel surface created by many cycles of oxidation followed by brushing or wiping all but the densest oxidation products from the surface. The finished product is a laminated, protective patina distinguishable from atmospheric corrosion, which is less dense.¹ Such "compact, well-adherent oxides," though actually corrosion products in themselves, can prohibit the entry of further corrosive agents.² By the mid-19th century, steel passivation was a widely established practice in the weapons industry, and in addition to corrosion

resistance, it served the additional purposes of decoration and glare reduction.³ The partial protection these finishes provide is particularly relevant to their conservation, and it is helpful to understand the processes by which they were created.

The patinas produced by arms manufacturers in the 1800s were widely varied in color and production method. Many of these methods are now nearly obsolete due to inefficiency, expense, or the development of new, more effective protective coatings; however, many modern gunsmiths' and collectors' manuals contain instructions for patination that are quite close to those followed over 100 years ago. The most common way to categorize firearm patinas was, and still is, by color: "blued," "blackened," and "browned" surfaces are the most common. Yet each of these colors could be created in a number of different ways, using various methods of oxidation of the metal and/or reduction of its initial corrosion products.

The color of a browned surface results from the presence of hematite (Fe_2O_3), which is commonly known as rust. Browning was generally achieved via the application of or submergence in a chemical solution, for which there were numerous recipes varying the types and amounts of salts and acids in solution. One example of a traditional browning recipe is as follows:

"Equal weights of antimony chloride and 4 of sulphuric acid D.1.84 (by weight) are rubbed together with 2 parts of crude wood spirit or gallic acid until uniform, then applied to barrel: scratch when rusted, repeat until colour dark enough, smooth with polishing stick and olive oil and finish by lacquering."⁴

Colt Patent Firearms Manufacturing Company likely had its own recipe with which its pistols were browned, but according to Angier,⁴ many of the recipes contained similar

compounds. Secondary ion mass spectroscopy (SIMS) has been used to identify species from these solutions on the surface of newly treated steel,⁵ but it has yet to be seen if surfaces with 100 years of wear could yield the same type of definitive information.

A browned section could either be left, or “modified by the subsequent action of boiling water or steam” to yield a black finish.⁴ Some of the descriptions of browning solutions in Angier’s book note that repeated application can lead to a black finish as well.⁴ Thus, some blued or blackened treatments have been referred to simply as extensions of the browning process. The compound that causes this darker color, however, is an altogether different iron oxide known as magnetite, the chemical formula of which can be written as Fe_3O_4 , or $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$. This iron oxide is produced by the reduction of Fe_2O_3 , which can occur readily in high-temperature, aqueous conditions. There is some disparity in the literature regarding the formation and composition of passive magnetite films, which is likely due to varying oxides depending on the technique used to passivate the steel.⁶ Some studies have shown that magnetite first grows on the surface of the hematite, creating a layered formation of oxides, then eventually replaces it on the surface of the iron.⁷ Most sources describe a layered model, incorporating hematite, magnetite, and often other iron oxides such as goethite ($\alpha\text{-FeOOH}$).

Magnetite can also be produced by heating iron to 290-320 °C,² e.g., in a charcoal furnace or flame. Hughes claims that “the luscious blue seen on early Colt and Smith & Wesson revolvers was charcoal bluing.”⁸ This method involved heating larger gun parts in glowing charcoal, removing and wiping them down with a rag, and then placing them back into the heat. This was done repeatedly until the desired patina was achieved.³ Charcoal bluing produces a dark blue or grey sheen, and thus it is sometimes called

charcoal blacking. This method was quite efficient, taking only about twenty or twenty-five minutes,⁹ and therefore was quite economical for large-scale industrial patination when a dark finish was desired. Smaller parts were often flame-blued, which as the name suggests involved using a flame torch to oxidize the steel, followed by quenching it in oil when the desired color was reached to prohibit further oxidation.¹⁰ This process, also known as temper-bluing, produced a bright blue finish much thinner and less resistant to corrosion than charcoal-blued finishes.⁴

The exact method used by the manufacturer, whether it was extreme heat, a chemical solution, or a combination of both, could greatly affect the characteristics of the resulting surface. As described above, magnetite surfaces can range from blue to black depending on the method used to produce them, as well as how many oxidation cycles are applied. Angier noted that, due to changes to both the chemical browning/blacking solution, and less often to the after-treatment, “the coating can be given a more or less brownish, blueish, or black-blueish tone.”⁴ This flexibility enabled the creation of a variety of colors achieved by gun manufacturers in the 19th century. Other methods resulted in more exotic colors; for instance, the hardening process called color-case hardening results in an unpredictable array of hues across the treated surface (this method is not an example of passivation). Niter bluing, which involves immersing the steel part in a bath of molten salts, was yet another way to achieve a specialized finish, in this case one of peacock-blue color.

Passivated gun finishes were by no means invulnerable, due to the fact that even compacted magnetite can adsorb oxygen from the atmosphere; they reduce rather than prevent corrosion.¹¹ Furthermore, scratches and losses in the patina can allow access to

the steel substrate by corrosive agents. Generations of gunsmiths have observed differences in the corrosion resistance of the various surfaces, and most recommend applying further protective coatings in the form of hydrophobic lubricants. Angier,⁴ like many others, recommended applying wax, paraffin, vaseline or mineral oil to prevent corrosive agents such as oxygen and water from contact with the steel substrate. This has been supported by Kuznetov and Vershok's findings on the impedance of magnetite-coated steel electrodes, which show that the "most significant changes, in the protective ability... take place on filling the coating with mineral oils or aqueous solutions of inhibitors."¹¹ Such treatments are effective in blocking the pores of the magnetite/hematite surface, limiting the pathways of the corrosive agents to the steel beneath.

As the entry point for corrosive agents, blackened, blued, and browned surfaces play a significant role in the preservation of firearms. Conservation studies have been undertaken to understand and characterize atmospheric corrosion products on iron and steel artworks, both modern¹² and ancient.¹³ Yet the study of passivated surfaces like those commonly found on firearms has barely been addressed in the conservation science field. Steel passivation and its potential for corrosion resistance have been studied in-depth for industrial purposes, but in the current literature there is only one reference specifically addressing blued/blackened surfaces of guns from a conservation perspective.⁶ In that paper, the samples were not artifacts but rather steel prepared in the laboratory, using traditional methods like those discussed above. Newly blued surfaces were characterized using multiple analytical techniques, including X-ray diffraction

(XRD), but it is as yet unknown how blued and browned surfaces appear under similar examination after over a century of wear.

This study aims to provide a scientific investigation of gun steel preservation by studying browned, blued, and blackened surfaces on historic firearms. Scanning electron microscopy (SEM) paired with energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) have been used to characterize the surfaces of six samples produced by Colt Patent Arms Manufacturers between 1851 and 1863. Most of the areas addressed on the samples have blackened or browned protective coatings, but some blued and color-case hardened sample areas have also been analyzed. The goal of this study is to provide a comprehensive view of the varying degrees of corrosion and wear that can occur on passivated firearms over a period of 150 years.

Materials and methods

Samples

Six Colt revolver barrels from the Autry National Center in Los Angeles, CA, were analyzed. The surface appearance and historical information of the samples is summarized in Table 1.

Figure 1 shows the six samples with locations of investigated areas marked according to technique. Where multiple areas on one sample have been measured with SEM-EDS, the areas have been denoted with letters, e.g. area **1-b** on **Sample 1**.

Table 1. Sample descriptions. Information obtained from records at the Autry National Center in Los Angeles, CA. Information marked by * is officially unknown, and has been inferred based on historical research and comparison with the other samples.

Sample	Barrel Shape	Barrel Length	Patina	Factory Location	Year of Manufacture	Model
1	Round	4.5 in.	Much has been worn down to plain steel, although some dark glossy grey is still intact, particularly on the lower breech. Blued screws. Color-case hardened plunger and frame.	Hartford	1863	Colt Model 1862 Police
2	Round	8.0 in.	Deep brown, slightly worn. Plunger retains the darkest and most even color.	Hartford	1861	Colt Model 1860 Army
3	Octagonal	7.5 in.	Most of the original dark grey patina has been scratched or worn away. Small reflective areas on the underside of the barrel are still intact.	London	Ca.1855	Colt Model 1851 Navy
4	Octagonal	5.5 in.	Dark grey, largely intact with minimal scratching or wear.	Hartford	1863	Colt Model 1862 Pocket Navy
5	Octagonal	7.5 in.	Dark brown, with minimal scratching, but much pitting.	Hartford*	1856	Colt Model 1851 Navy*
6	Octagonal	7.5 in.	Dark grey, with minimal scratching or wear except on the right side of the front end of the barrel.	London	1853	Colt Model 1851 Navy

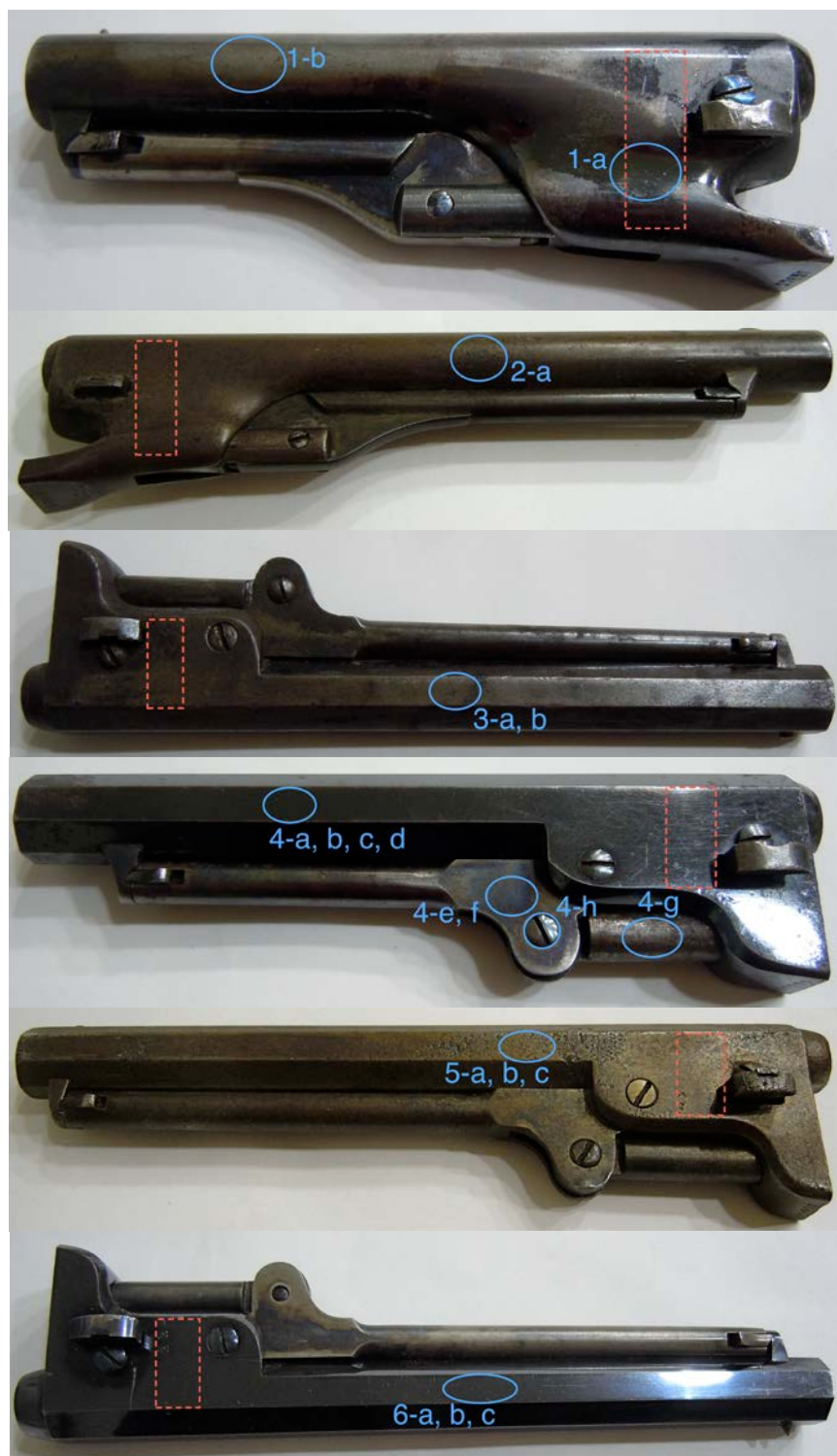


Figure 1. Six revolver barrel samples, numbered 1-6 in order from top to bottom. Areas marked with blue circles were analyzed with SEM-EDS, while those areas marked with red rectangles were analyzed with XRD.

X-Ray Diffraction

A Rigaku Ultima IV X-ray diffractometer (Rigaku, The Woodlands, TX) with Cu K_{α} radiation was used for XRD analysis. A platform was crafted to hold the samples level within the chamber (Fig. 2), which allowed for analysis of the breech area of each sample. The system was operated at 40kV/ 40mA, and samples were scanned at a speed of 0.0700°/min between 10° to 65°. Due to slight inaccuracies in mounting geometry, all diffraction patterns were angle-corrected by matching the strong iron peak in the sample diffraction patterns to the strong iron peak at 44.67° given in previous literature (PDF #98-000-0259).¹⁴

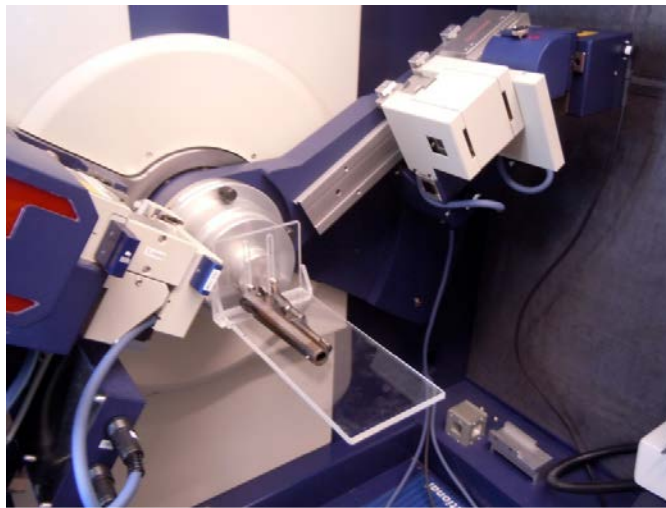


Figure 2. X-ray diffraction setup for revolver barrel analysis.

Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy

A LEO 982 field emission scanning electron microscope (Carl Zeiss Microscopy, LLC, Thornwood, NY) was used to study the topography and morphology of specific areas on each sample. Due to space restrictions within the SEM chamber, the barrels ranging in size between 7.5 and 8 inches could only be examined in limited areas along the central part of the barrel. The two smaller samples were examined in a variety of

different areas. Micrographs were taken at a working distance of 6-9 mm, with a power of 10-15 kV. EDS analysis was performed with a Bruker AXS Quantax EDS system. An aperture of 5, a working distance of 8-9 mm, and an accelerating voltage of 10-15 kV was used for EDS analysis.

Results and Discussion

XRD Results

Figure 3 shows XRD diffraction patterns of the six samples, overlaid with reference patterns for magnetite and hematite.¹⁵ **Samples 4** and **6** had well preserved blackened surfaces, and their diffraction patterns showed tall, sharp peaks consistent with magnetite. **Samples 1** and **3** were both blackened as well, but their magnetite surfaces were largely scratched or worn away. X-ray diffraction patterns of these samples showed that magnetite is present, although the peaks were not as intense as those of the well-preserved samples. The diffractogram of **Sample 1** showed only a large iron peak, indicating that the areas worn away were likely free of other crystalline species, e.g., hematite.

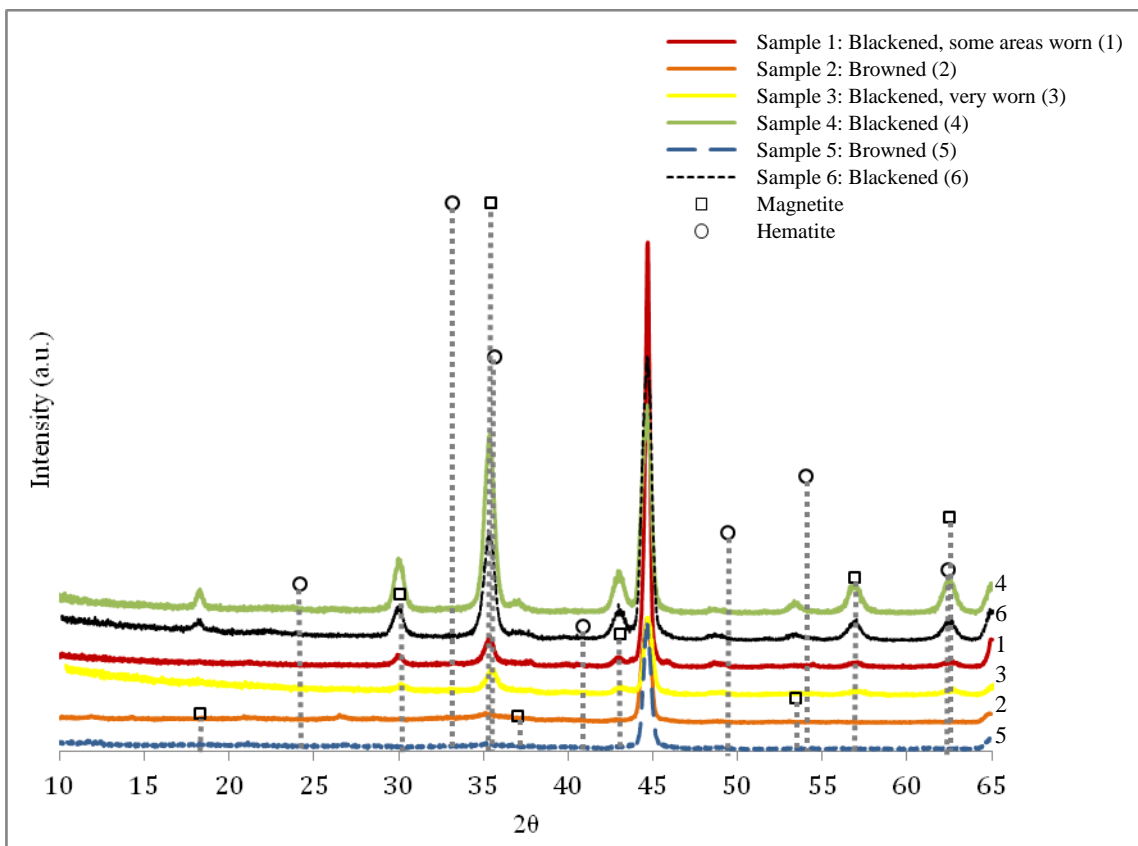


Figure 3. XRD diffractograms of Samples 1-6, with overlaid patterns of hematite and magnetite.

It has previously been observed that neither hematite nor magnetite can be identified on chemically treated samples.⁵ Although the chemically treated browned barrels (**Samples 2** and **5**) did have small peaks consistent with magnetite, they were wide and shallow, indicating a mostly amorphous surface with very small crystallites. The relatively good condition of **Sample 2** in comparison to **Sample 5** may have contributed to the slightly stronger peaks. Hematite could not be identified on any of the samples. The presence of strong magnetite peaks on **Samples 1, 3, 4, and 6** showed that these barrels were thermally treated, which confirmed historical assessment of patination methods used by the Colt Patent Arms Manufacturing Company.

Qualitative analysis of SEM micrographs

Figure 4 shows the morphology of well preserved barrel surfaces at 5000x magnification. The most well preserved blackened (magnetite) surfaces were on **Samples 1, 4, and 6**, while the least damaged browned (hematite) surface was that of **Sample 2**. SEM micrographs of the magnetite surfaces showed uniform topography with polishing scratches; comparison with secondary electron images taken by Tellèz and coworkers⁵ showed that the magnetite surfaces were in fact very close to how they would have appeared when the barrels were first manufactured. In contrast, no polishing scratches could be seen in the relatively amorphous hematite coating. However, the surface of the hematite film demonstrated larger variations in morphology than the magnetite films.

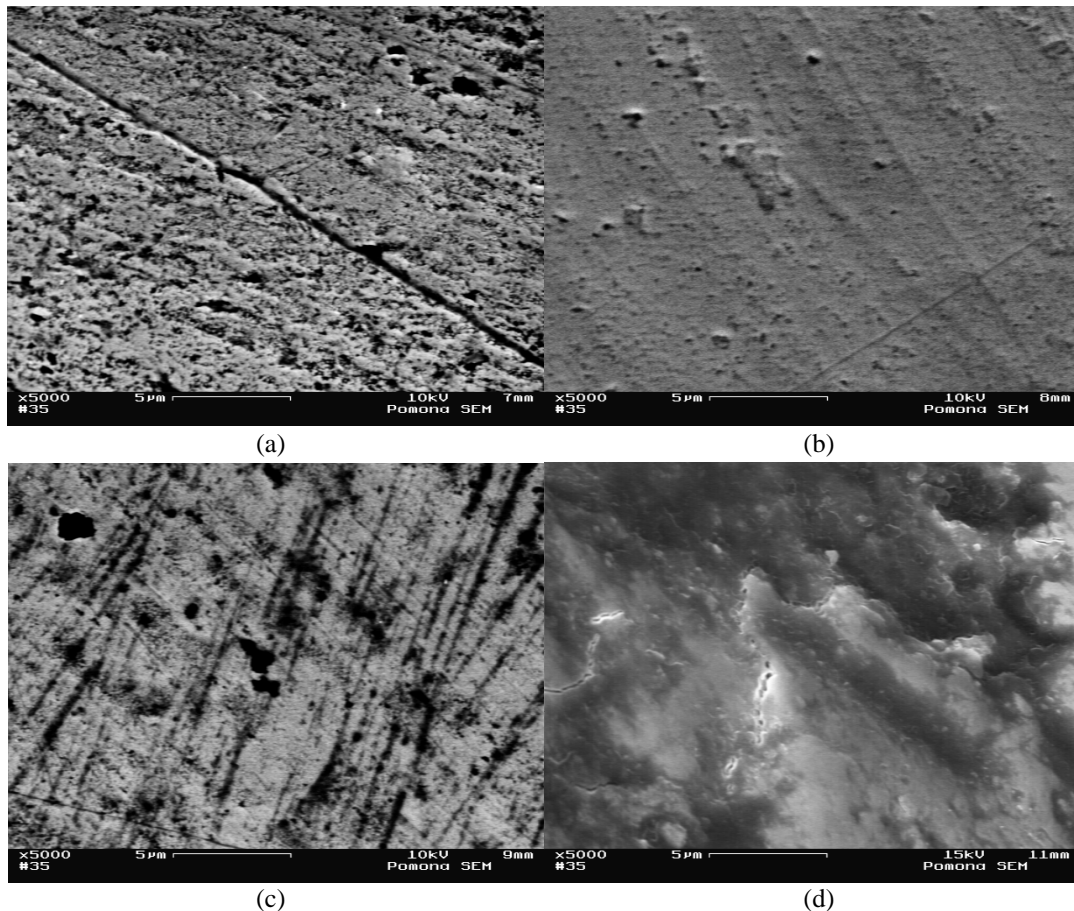


Figure 4. Well-preserved blackened (magnetite) surfaces on (a) Sample 1 (area 1-a), (b) Sample 4 (area 4-a), and (c) Sample 6 (area 6-a), and an intact browned (hematite) surface on d) Sample 2 (area 2-a) at 5000x magnification.

Higher magnification images of the magnetite surfaces revealed relatively homogenous, porous topography, characterized by round particles embedded in pockets that spread consistently across the surface (Fig. 5). These particles were on the scale of 50 nm, which is consistent with Cornell's description of magnetite particles produced by precipitation.⁶ Higher magnification of the browned surface on **Sample 2** showed in greater detail the amorphous topography of hematite.

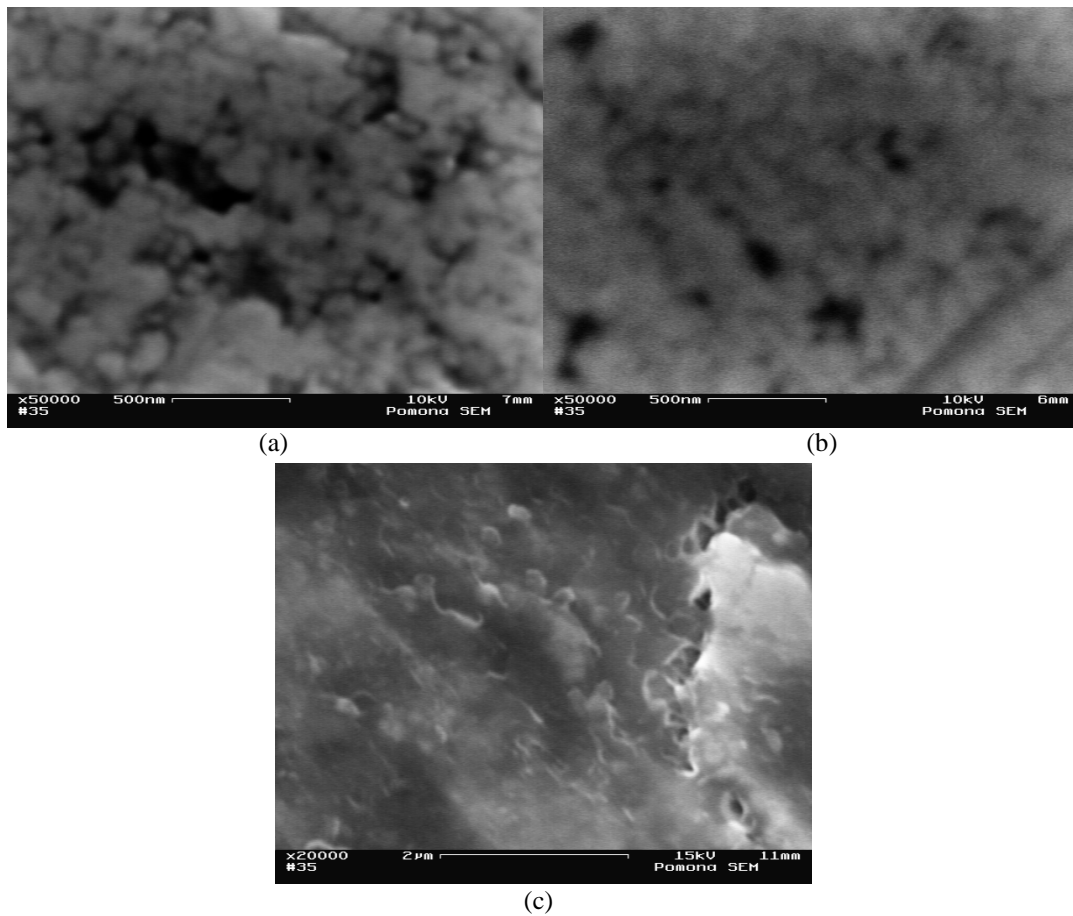


Figure 5. 50000x magnification of magnetite grains on (a) area 1-a and (b) area 6-a. (c) 20000x magnification of hematite formation on (c) Sample 2, area 2-a.

Damage to the well-preserved magnetite surfaces was minimal and occurred mostly in the form of small losses, such as that shown at 20000x magnification in Figure 6. Particles in the missing area were much larger than the magnetite film particles.

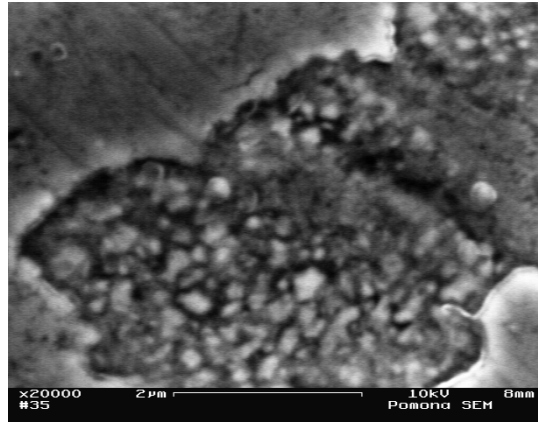


Figure 6. 20000x magnification SEM micrograph of magnetite loss on the surface of Sample 6.

Sample 3 had many small, reflective areas, indicating that it was originally blackened, but underwent much wear over the years. Figure 7 shows increasingly magnified images of **Sample 3**, demonstrating where corrosion occurred. At 1000x magnification, the larger scratches caused by wear after its production were distinguishable from those on the magnetite surfaces in Figure 3, which were caused by polishing during production. Corrosive products appeared to have formed where the magnetite surface was scratched away. This is an example of “crevice attack,”⁶ which occurs where discontinuity in the surface increases the availability of corrosion reactants. Scratches to the magnetite film exposed the iron alloy beneath, leaving it susceptible to corrosive attack.

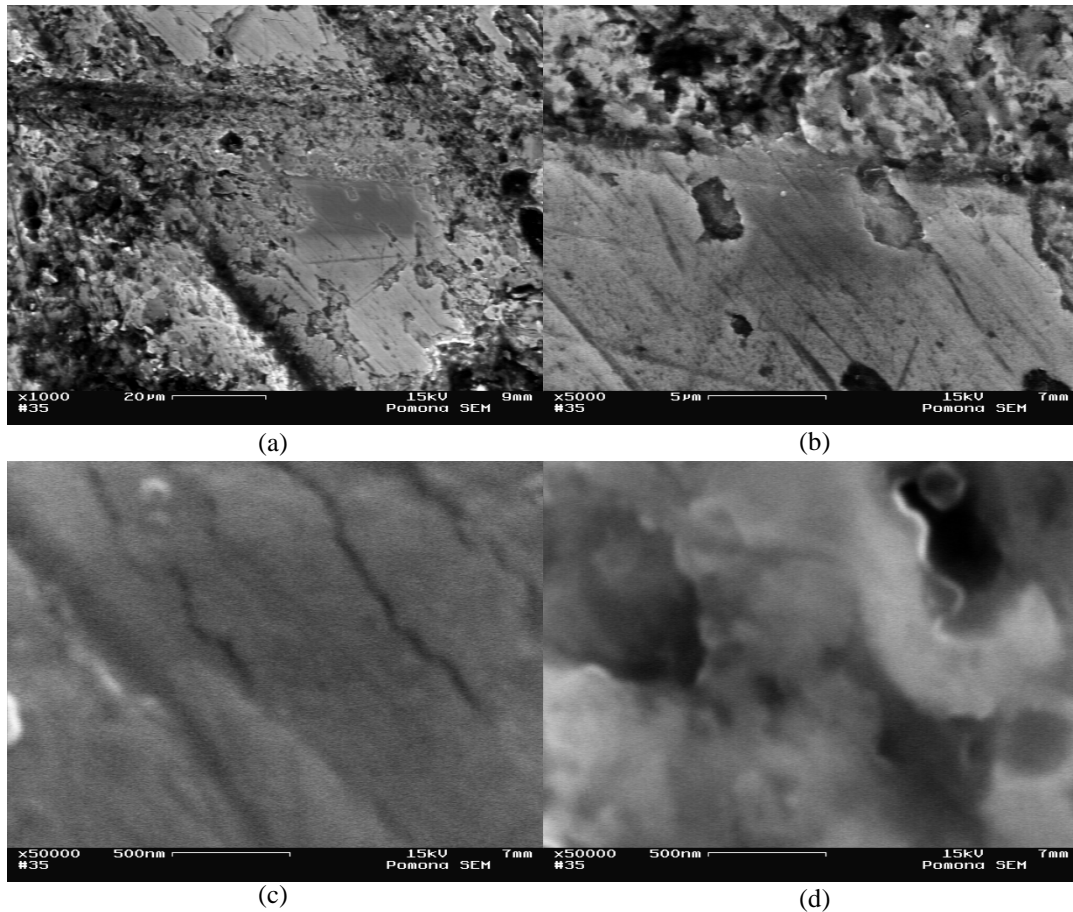


Figure 7. SEM micrographs of area 3-a at (a) 1000x magnification, (b) 5000x magnification, (c) magnetite at 50000x magnification, and (d) corrosion product at 50000x magnification.

Sample 5 was the more damaged of the two browned samples, with extensive pitting across much of its surface. Three different SEM micrographs of one area (Fig. 8) demonstrate the various types of corrosion that can occur on such an artifact. Figure 8a shows cracks in the oxide patina as well as debris. Unlike losses to the magnetite films, pits in the surface on browned samples did not have defined edges (Fig. 8b). Areas of plain steel (Fig. 8c) were also present.

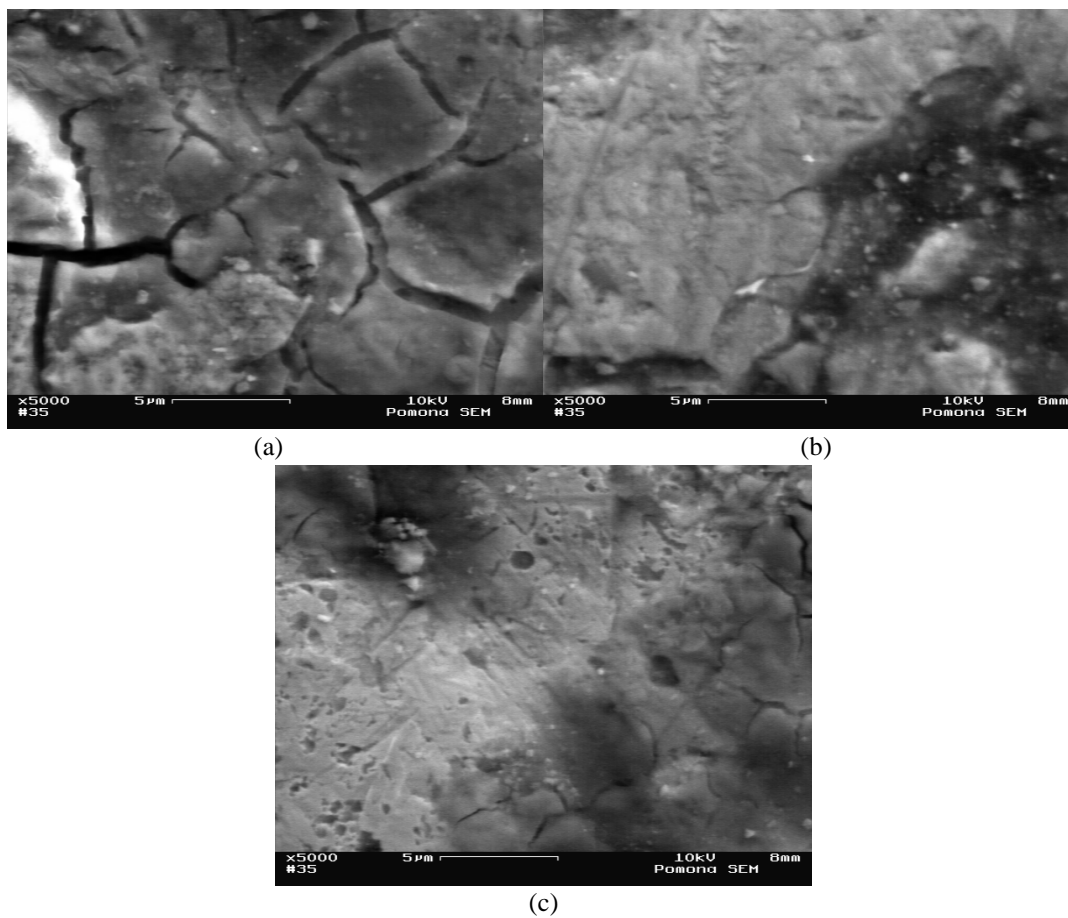


Figure 8. 5000x magnification SEM micrographs of areas (a) 5-a, (b) 5-b, and (c) 5-c. Each of these micrographs were taken from the same general area of Sample 5.

EDS spectra and percent elemental abundance

Figure 9 depicts trends associated with the relative abundance of oxygen and iron according to the type of surface. Well-preserved magnetite surfaces had relatively high peaks for oxygen and mid-range iron peaks. Worn and unpassivated surfaces had large peaks for iron, and small or no peaks for oxygen. The spectra of the browned surfaces possessed peaks for K, Na, Mg, Al, Si, S, Cl, and Ca, while those of the blackened surfaces did not. The presence of these elements may be attributed either to their preparation in chemical solutions, or the aggregation of debris over the past 150 years.

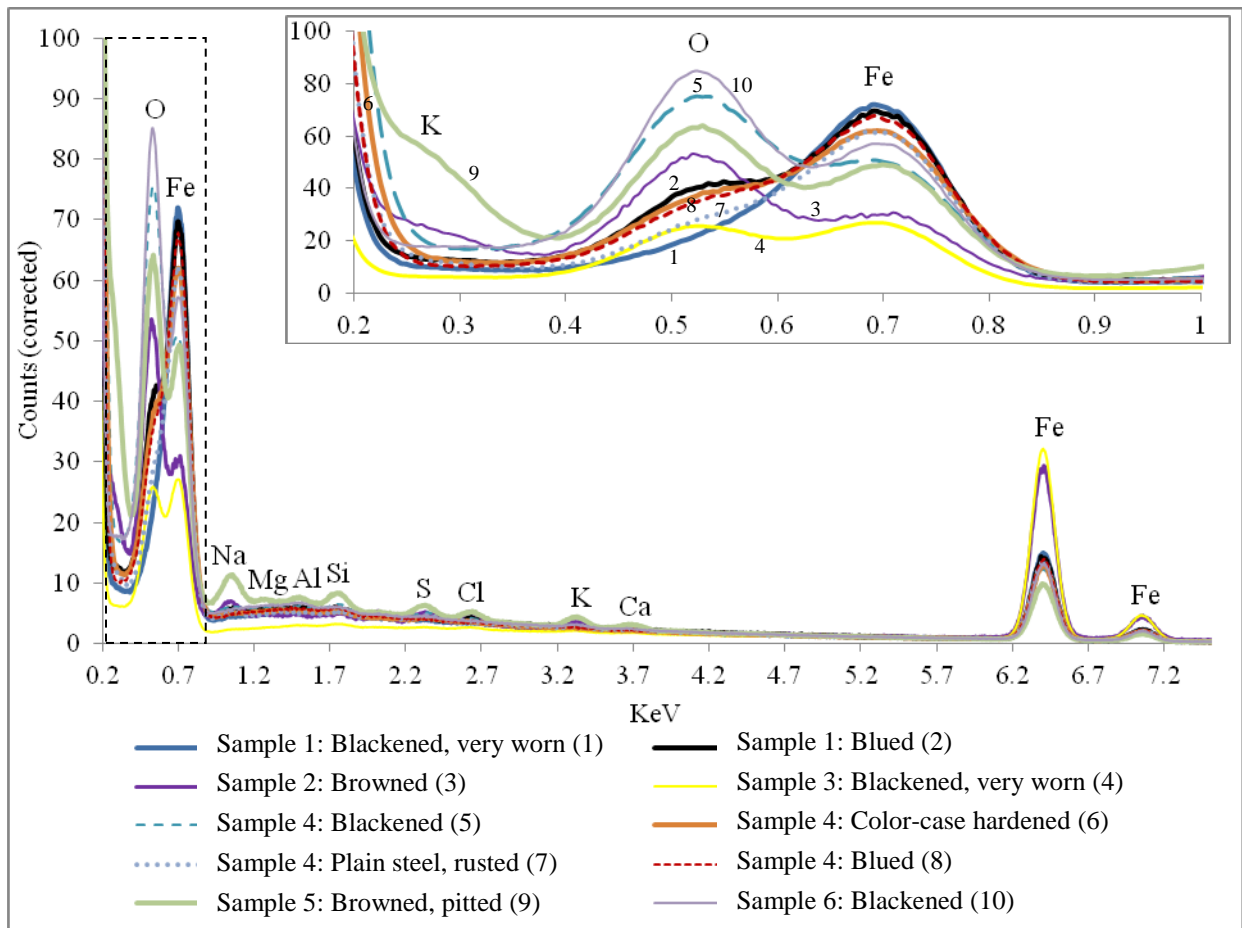


Figure 9. EDS spectra of areas on Samples 1-6. Peaks identified using Bruker ESPRIT software for EDS. Spectra for Samples 3, 4, 5, and 6 are averages of multiple EDS spectra in order to show general trends. Inset graph corresponds to dashed box on the main spectrum.

Table 2. Elemental Abundance results for selected areas.

Sample	Surface type	Elemental abundance (error) (%)														
		N*	O*	Na	Mg	Al	Si	P	S	Cl	K	Ca	Cr	Mn	Fe	
1	Blackel, very worn (1-b)	0.00	1.70 (0.6)	0.59 (0.0)	0.46 (0.0)	0.31 (0.0)	0.39 (0.0)	0.00	0.02 (0.0)	0.03 (0.0)	0.08 (0.0)	0.11 (0.0)	0.36 (0.0)	1.29 (0.1)	94.66 (4.3)	
2	Browned (2-a)	0.00	29.43 (0.5)	8.03 (0.3)	2.83 (0.1)	1.73 (0.1)	1.35 (0.1)	1.19 (0.1)	1.35 (0.1)	1.44 (0.1)	0.97 (0.1)	0.62 (0.0)	0.27 (0.0)	1.16 (0.1)	49.65 (1.9)	
3	Blackel, very worn (3-a)	5.25 (1.4)	19.68 (1.7)	1.63 (0.1)	1.01 (0.1)	0.67 (0.0)	0.51 (0.0)	0.05 (0.0)	0.17 (0.0)	0.20 (0.0)	0.25 (0.0)	0.24 (0.0)	0.32 (0.0)	1.47 (0.1)	68.57 (2.4)	
3	Blackel, very worn (3-b)	0.00	12.35 (1.0)	2.19 (0.1)	1.13 (0.1)	0.95 (0.0)	0.62 (0.0)	0.07 (0.0)	0.24 (0.0)	0.49 (0.0)	0.38 (0.0)	0.19 (0.0)	0.36 (0.0)**	1.60 (0.1)	79.45 (2.5)	
4	Blackel (4-a)	7.29 (3.0)	30.31 (3.5)	0.80 (0.1)	0.75 (0.0)	0.44 (0.0)	0.59 (0.0)	0.00	0.01 (0.0)	0.02 (0.0)	0.08 (0.0)	0.20 (0.0)	0.23 (0.0)	0.87 (0.1)	58.41 (3.5)	
4	Blackel (4-b)	0.00	39.89 (6.3)	3.27 (0.1)	0.73 (0.0)	0.35 (0.0)	0.33 (0.0)	0.00	1.69 (0.1)	0.77 (0.0)	0.63 (0.0)	0.17 (0.0)	0.20 (0.0)	1.09 (0.1)	50.89 (2.9)	
4	Blackel (4-c)	11.39 (3.1)	30.73 (4.5)	0.51 (0.0)	0.51 (0.0)	0.24 (0.0)	0.15 (0.0)	0.00	0.01 (0.0)	0.00	0.04 (0.0)	0.19 (0.0)	0.24 (0.0)	0.86 (0.1)	55.11 (3.5)	
4	Blackel (4-d)	0.00	11.63 (2.3)	0.01 (0.0)	0.28 (0.0)	0.50 (0.0)	1.56 (0.1)	0.00	0.05 (0.0)	0.09 (0.0)	0.30 (0.0)	0.36 (0.0)	0.35 (0.0)	1.06 (0.1)	83.81 (3.9)	
4	Color-case hardened (4-e)	5.71 (2.2)	20.48 (2.8)	1.36 (0.1)	0.65 (0.0)	0.37 (0.0)	0.26 (0.0)	0.00	0.37 (0.0)	0.20 (0.0)	0.16 (0.0)	0.11 (0.0)	0.28 (0.0)	1.08 (0.1)	68.98 (3.6)	
4	Color-case hardened (4-f)	0.00	6.16 (1.3)	0.56 (0.0)	0.66 (0.0)	0.46 (0.0)	0.33 (0.0)	0.00	0.01 (0.0)	0.02 (0.0)	0.06 (0.0)	0.10 (0.0)	0.41 (0.0)	1.33 (0.1)	89.89 (4.2)	
4	Plain steel, very rusted (4-g)	0.00	7.89 (1.2)	1.15 (0.1)	0.23 (0.0)	0.12 (0.0)	0.12 (0.0)	0.18 (0.0)	0.44 (0.0)	0.10 (0.0)	0.19 (0.0)	0.17 (0.0)	0.37 (0.0)	1.17 (0.1)	87.86 (4.0)	
4	Blued (4-h)	0.00	8.89 (1.6)	0.73 (0.0)	0.75 (0.0)	0.64 (0.0)	0.70 (0.0)	0.01 (0.0)	0.03 (0.0)	0.03 (0.0)	0.08 (0.0)	0.12 (0.0)	0.34 (0.0)	1.04 (0.1)	86.65 (4.0)	
5	Browned, worn and pitted (5-a)	0.00	23.24 (5.8)	10.6 (0.3)	2.34 (0.1)	1.90 (0.1)	2.20 (0.1)	0.45 (0.0)	2.05 (0.1)	1.89 (0.1)	2.76 (0.1)	1.07 (0.1)	0.32 (0.0)	0.36 (0.1)	50.85 (2.2)	
5	Browned, worn and pitted (5-b)	0.00	37.20 (5.2)	4.91 (0.2)	1.53 (0.1)	1.37 (0.1)	2.67 (0.1)	0.11 (0.0)	0.11 (0.0)	0.87 (0.0)	1.11 (0.1)	1.34 (0.1)	0.25 (0.0)	0.50 (0.1)	47.02 (2.4)	
5	Browned, worn and pitted (5-c)	0.00	7.69 (1.2)	3.05 (0.1)	1.41 (0.1)	1.21 (0.1)	1.50 (0.1)	0.15 (0.0)	0.56 (0.0)	0.44 (0.0)	0.68 (0.0)	0.69 (0.0)	0.47 (0.0)	1.07 (0.1)	81.08 (3.4)	
6	Blackel (6-a)	4.20 (1.8)	29.05 (2.6)	0.98 (0.1)	0.83 (0.0)	0.78 (0.0)	0.41 (0.0)	0.02 (0.0)	0.11 (0.0)	0.05 (0.0)	0.33 (0.0)	0.20 (0.0)	0.29 (0.0)	0.85 (0.1)	61.91 (3.5)	
6	Blackel (6-b)	6.09 (1.9)	28.08 (2.8)	0.95 (0.1)	0.89 (0.1)	0.87 (0.1)	0.39 (0.0)	0.02 (0.0)	0.10 (0.0)	0.07 (0.0)	0.31 (0.0)	0.22 (0.0)	0.27 (0.0)	1.10 (0.1)	60.64 (3.5)	
6	Blackel (6-c)	4.94 (1.5)	26.23 (2.3)	1.01 (0.1)	0.91 (0.1)	0.62 (0.0)	0.43 (0.0)	0.01 (0.0)	0.08 (0.0)	0.05 (0.0)	0.25 (0.0)	0.17 (0.0)	0.25 (0.0)	0.70 (0.1)	64.34 (3.5)	

* Determined via net-count ratios.

**More than 20% may be contributed by Fe fluorescence

Table 2 summarizes the elemental abundance of various EDS mapped surfaces on each of the samples. The most oxygen-deficient areas (areas **1-b**, **4-f**, **4-g**, **4-h**, and **5-c**) were those with the most wear, or those that were never patinated, e.g., color-case hardened pieces. The low abundance of oxygen (1.70%) and high abundance of iron (94.66%) on area **1-b** is consistent with the XRD data regarding this area. The presence of nitrogen is generally associated with areas that have intact magnetite films. The elements Na, Mg, Al, Si, P, S, Cl, K, and Ca were most prevalent on the browned surfaces as seen in the EDS spectra. These ions could be present from the chemical solutions used to produce the browned surfaces; Angier includes many compounds which include these species in his list of common acids and salts used for browning solutions.⁶ The presence of these elements could also be due to the debris seen in the SEM images of the browned surfaces. Area **5-c** had a higher level of oxygen than **5-a** and **5-b**, an observation consistent with both the SEM micrographs of these areas and their EDS maps (see below), which show area **5-c** as a more pristine surface location. The relative consistency of Cr abundance could indicate that the steel alloys used to make the firearms contained small amounts of the metal.

EDS elemental mapping

Elemental mapping with EDS showed the distribution of specific elements across the gun barrel surfaces shown in the micrographs above. Maps of low-concentration elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Cr, Mn) did not yield definitive patterns and are therefore not shown or discussed below. All SEM images and EDS maps shown below are taken at 5000x magnification.

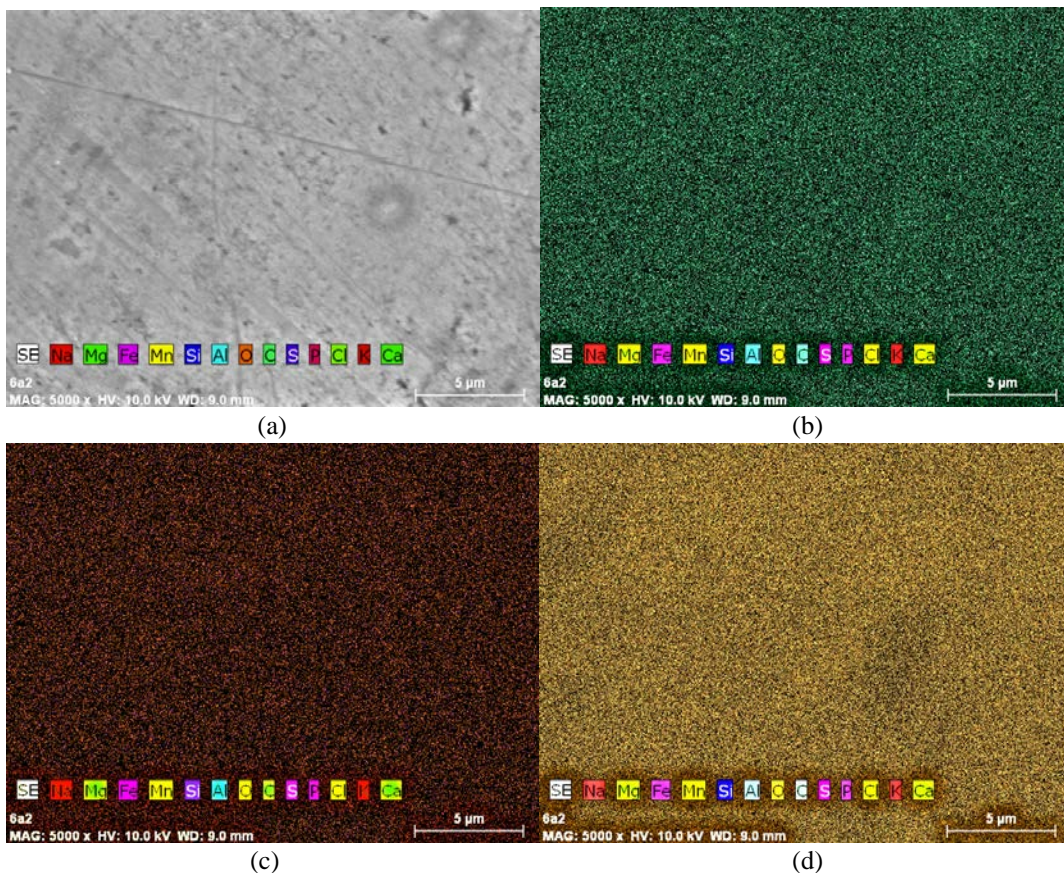


Figure 10. Secondary electron image (a) and elemental maps of (b) carbon, (c) oxygen, and (d) iron on well-preserved blackened (magnetite) surface on area 6-c.

Elemental mapping using EDS showed that the magnetite surfaces on **Samples 1, 4, and 6** had even distributions of Fe, O, and C. The secondary electron image and

elemental maps for area **6-b** demonstrated the type of formations common for the well-preserved blackened (magnetite) surfaces (Fig. 10). The blued surface, **1-b**, which also consists of magnetite, had patterns similar to those of the blackened surfaces.

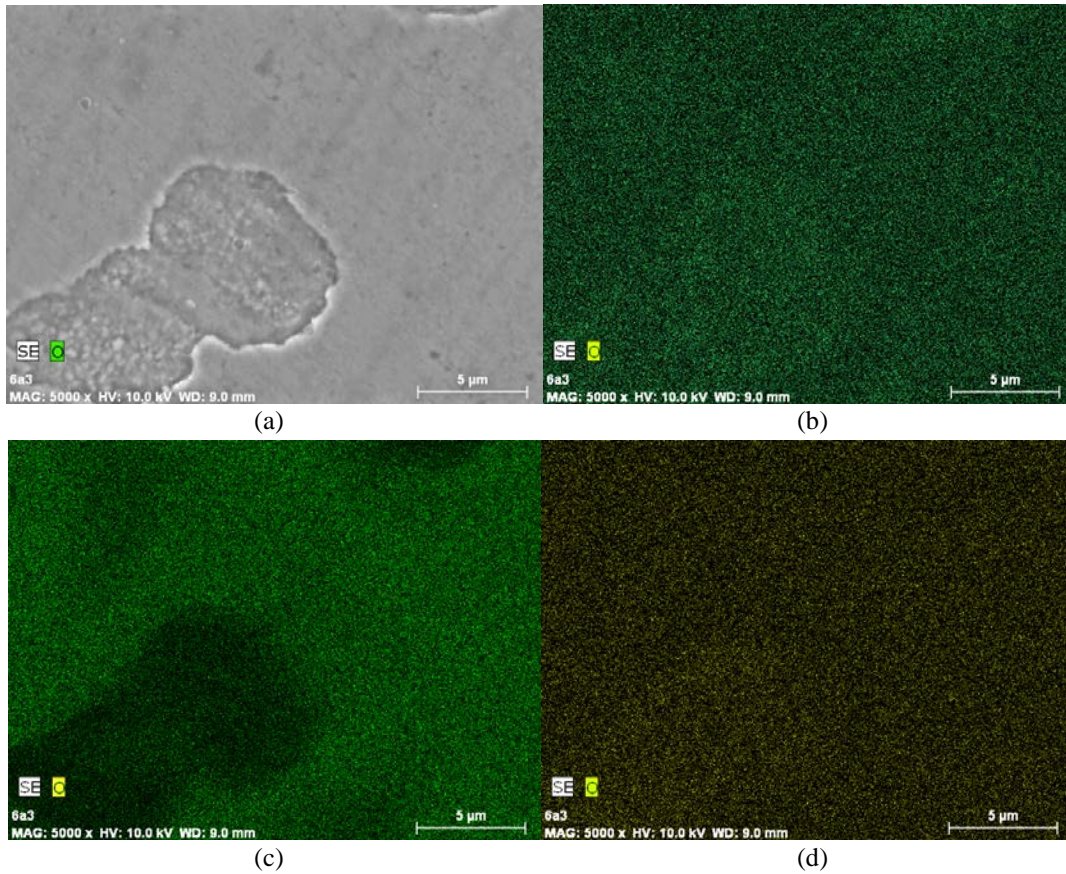


Figure 11. Secondary electron image (a) and elemental maps of (b) carbon, (c) oxygen, and (d) iron on well-preserved blackened (magnetite) surface with some loss on Sample 6-c.

The secondary electron image and elemental maps of area **6-c** (Fig. 11) demonstrated one type of loss that occurs on well-preserved blackened samples. The level of oxygen was significantly lower in the area of damage when compared to the intact magnetite film (Fig. 5b). This indicates that this area was loss rather than corrosion, for a rusted area would have had a relatively higher amount of oxygen (Fe_2O_3 or other

oxides) than the magnetite surface (Fe_3O_4) or steel (Fe-C alloy). These small losses were common on the magnetite surfaces analyzed in this study.

There were, however, corroded areas on the magnetite surfaces that showed evidence of oxides besides Fe_3O_4 . The scratched and worn surface of **Sample 3** had both types of damage: loss and corrosion. Elemental maps of area **3-a** showed a decrease in oxygen levels in the small areas of loss similar to those on **Sample 6**. The scratched area contained oxygen and high levels of iron, indicating the presence of iron oxides and plain steel (Fig. 12).

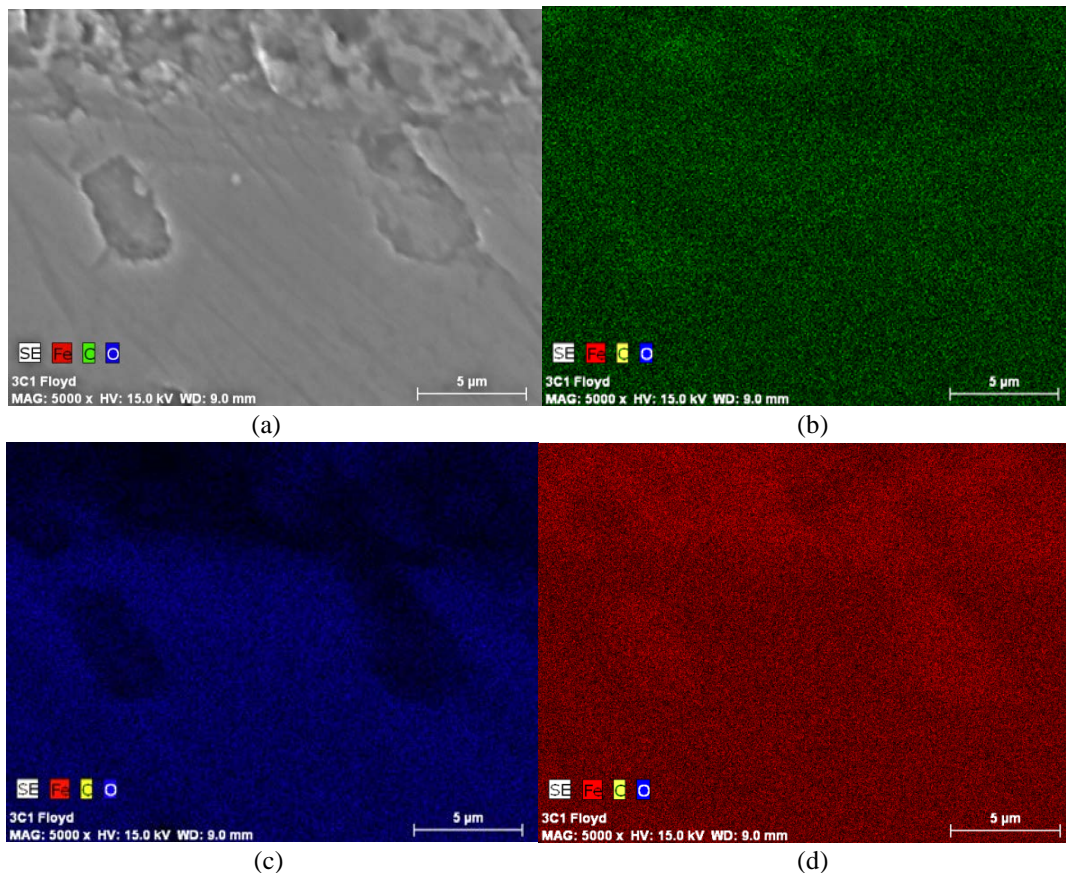


Figure 12. Secondary electron image (a) and elemental maps of (b) carbon, (c) oxygen, and (d) iron on the edge of a blackened (magnetite) surface on area 3-a.

Figure 13 shows an area of **Sample 3** with extensive corrosion. Areas with high levels of oxygen coincided with the presence of iron oxides. Higher levels of carbon were also present in the corroded areas compared with preserved magnetite areas. Although the losses were jagged and less contained than previous examples, they were nevertheless easily distinguishable from the surrounding magnetite film.

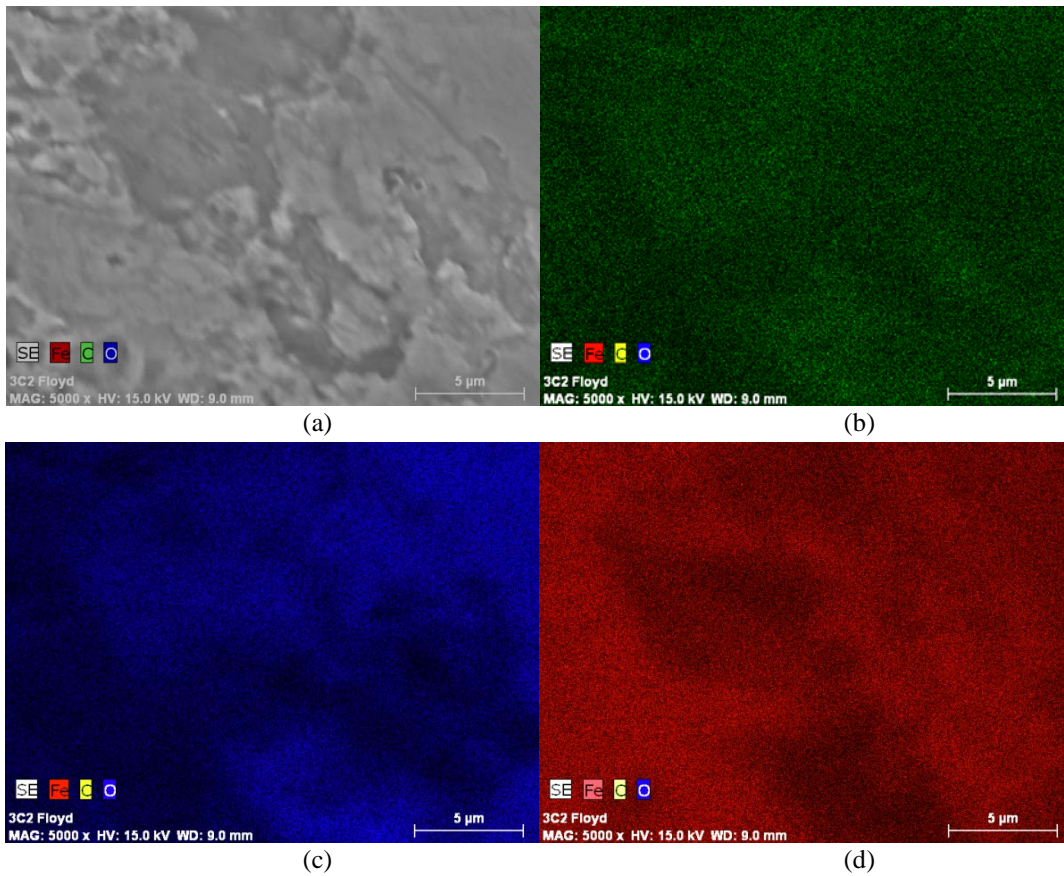


Figure 13. Secondary electron image (a) and elemental maps of (b) carbon, (c) oxygen, and (d) iron on the edge of a blackened (magnetite) surface on area 3-b.

Even those blackened samples with good-condition magnetite films had areas of serious corrosion. These areas were present on the edges of the octagonal barrels, where the surface was most likely to be scratched and worn. The EDS maps of area **4-d**

demonstrated this (Fig. 14). Figure 14c shows that more oxygen-rich compounds were present in the damaged areas. However, although higher oxygen levels were present in the damaged areas, the distribution of carbon (Fig. 14b) and iron (Fig. 14c) complicated the exact nature of the oxides. The presence of carbon was possibly due to the deposition of carbonaceous debris over time.

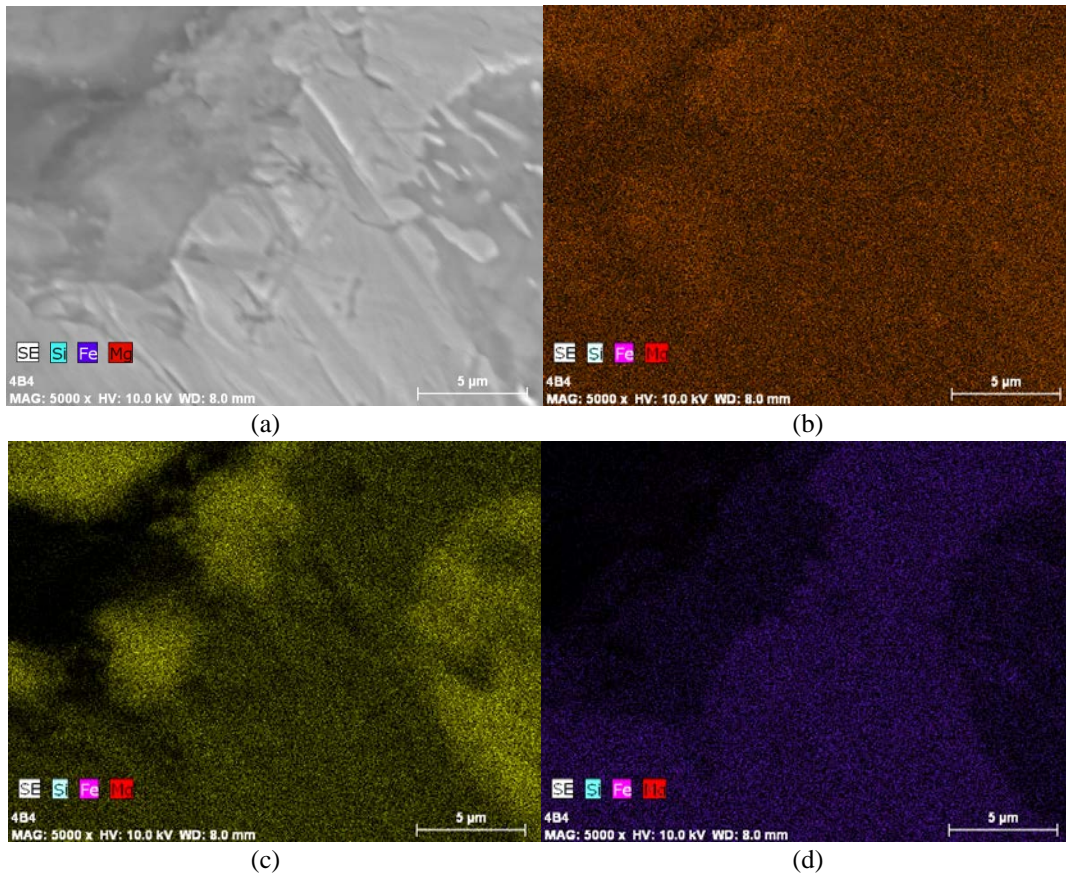


Figure 14. Secondary electron image (a) and elemental maps of (b) carbon, (c) oxygen, and (d) iron on the edge of a blackened (magnetite) surface on area 4-d.

The hematite surfaces, as discussed above, were less morphologically uniform than the magnetite surfaces. This was also reflected in the variegating patterns revealed in EDS elemental maps (Fig. 15). Minor crack-like morphologies were present (Fig. 15a).

Lower oxygen levels along these cracks showed that they were breaks in the oxide surface. The uneven distribution of Fe, C, and O on even the better-preserved hematite areas could have been due to the fact that hematite forms non-uniformly across the surface during chemical treatment.

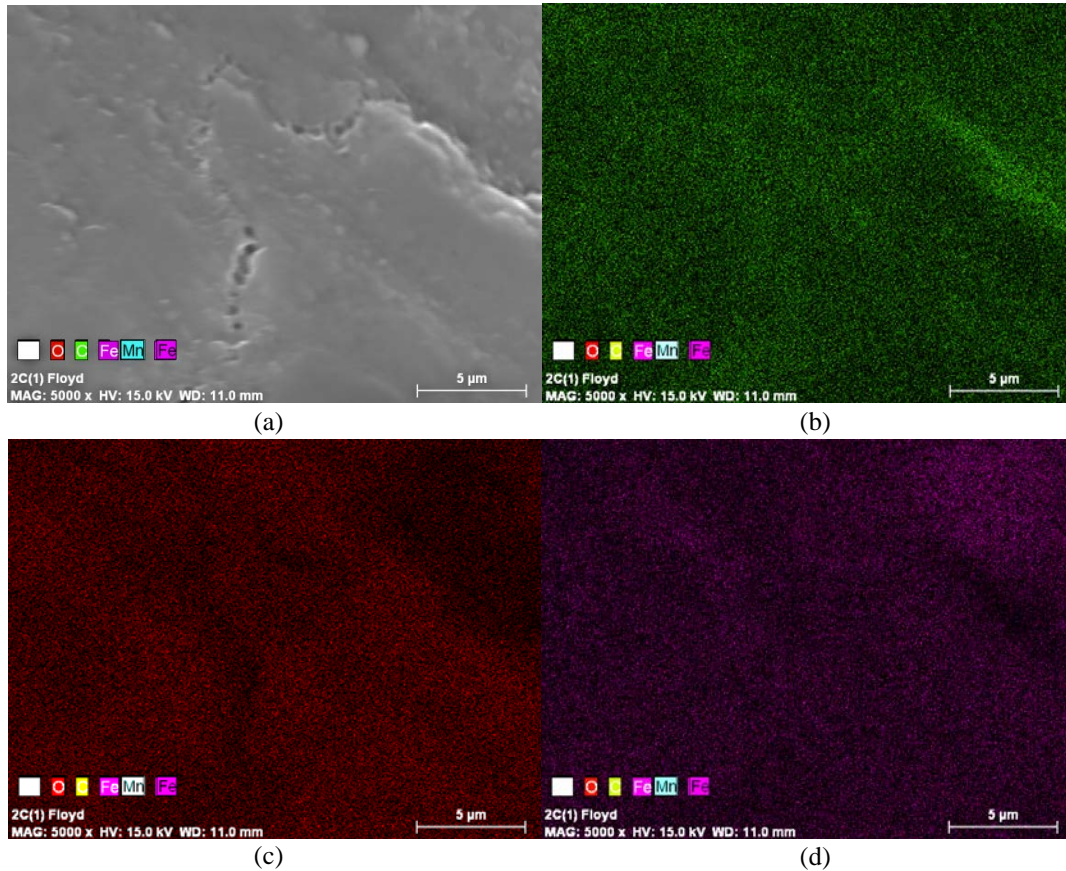


Figure 15. Secondary electron image (a) and elemental maps of (b) carbon, (c) oxygen, and (d) iron on a browned (hematite) surface on Sample 2.

Figures 16, 17, and 18 show corrosion patterns on an extremely pitted area on the hematite surface of **Sample 5**. Rather than clearly identifiable areas of loss and corrosion, as observed on the magnetite surfaces, the browned surfaces appeared to have overall

corrosion that was not completely distinguishable from the original, amorphous hematite protective coating.

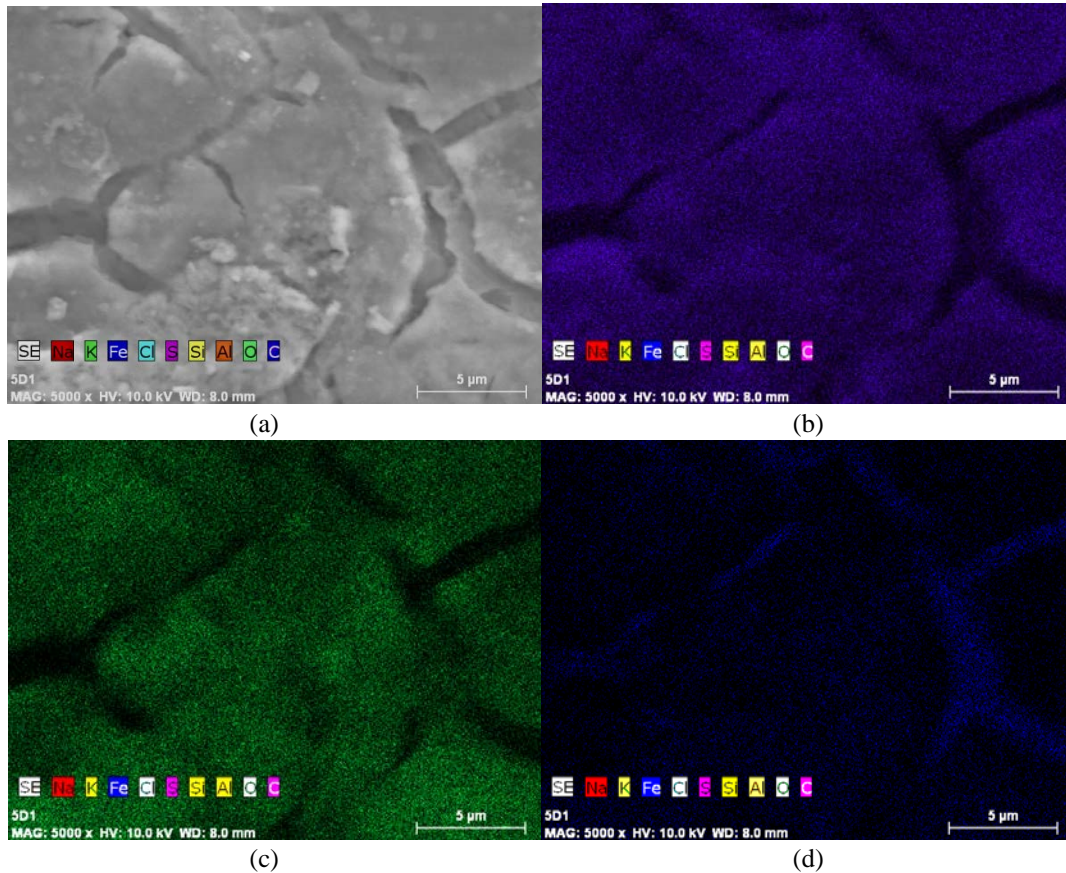


Figure 16. Secondary electron image (a) and elemental maps of (b) carbon, (c) oxygen, and (d) iron on browned (hematite) surface on area 5-c.

Figure 16 shows more carbon and oxygen in the crust, while high levels of iron were present in the cracks. Here, the oxygen- and carbon-rich crust pulled away to reveal the steel beneath. The chemical similarity of the hematite coating and the corrosion products make it difficult to assess the exact failure mode of the coating in this instance.

Characteristic of these areas of high corrosion on hematite samples was the large amount of debris. In some areas, this could be readily identified as carbonaceous material

by relatively high levels of carbon in areas of almost no iron or oxygen (Fig. 17). Together, figures 17a and 17b demonstrate the aggregation of carbonaceous materials in areas of surface loss. Such materials presumably accumulated over the lifetime of the object, likely from the application of lubricants. These lubricants would have prevented further corrosion, which was evidenced by the lack of oxides present in the carbonaceous area (Fig. 17c).

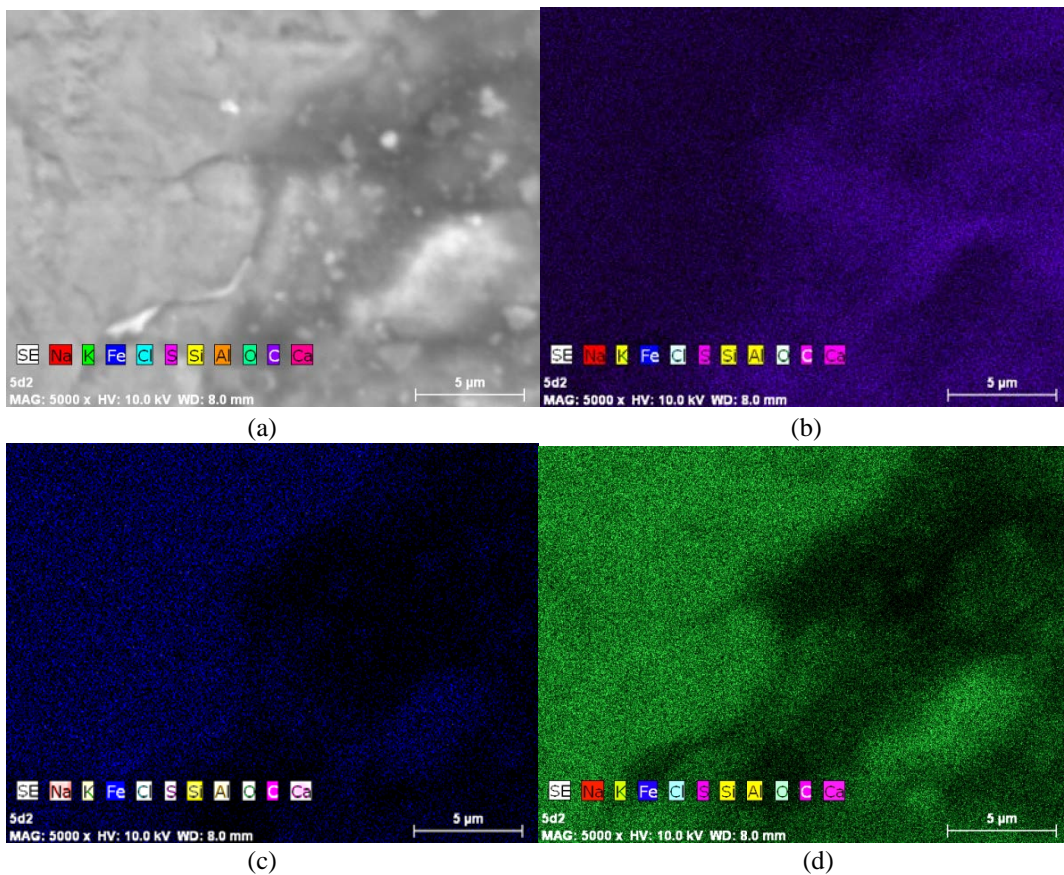


Figure 17. Secondary electron image (a) and elemental maps of (b) carbon, (c) oxygen, and (d) iron on browned (hematite) surface on area 5-b.

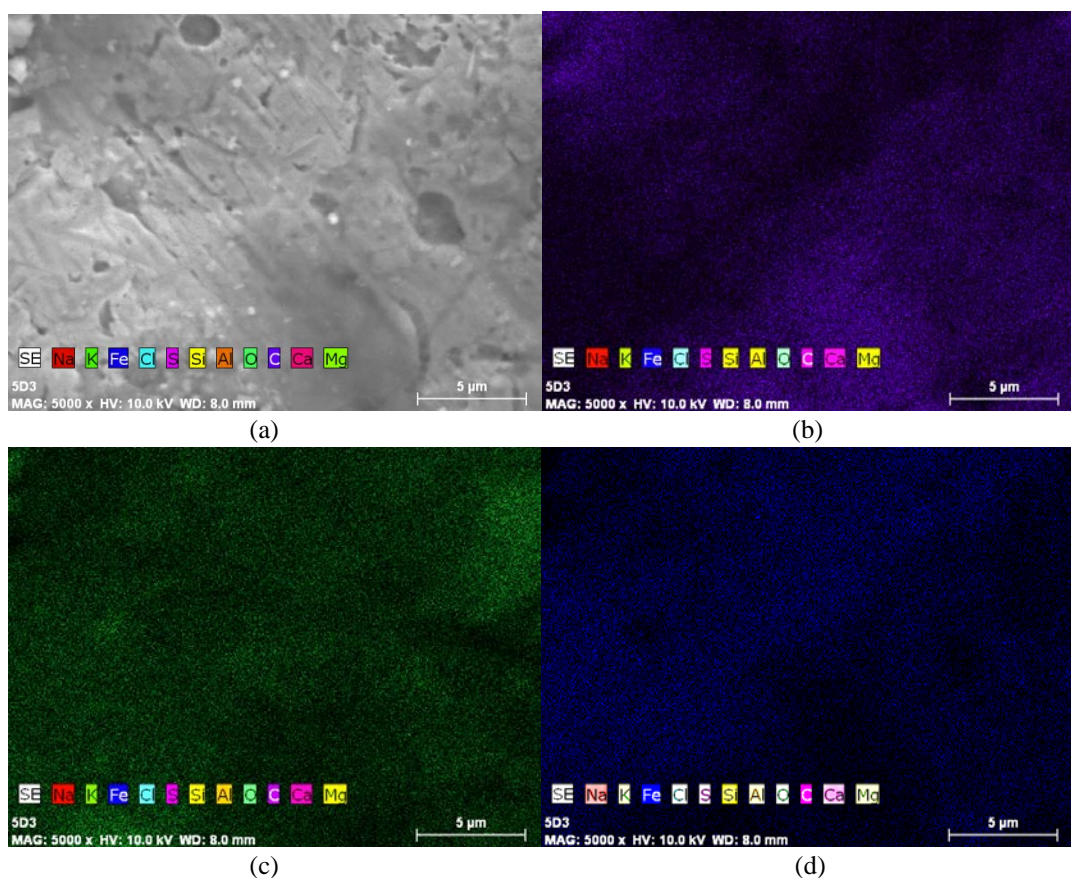


Figure 18. Secondary electron image (a) and elemental maps of (b) carbon, (c) oxygen, and (d) iron on browned (hematite) surface on area 5-c.

The distribution of iron in area **5-c** (Fig. 18d) coincided with the XRD and EDS elemental abundance findings of a large, sharp Fe peak (XRD) and high iron abundance (EDS) with little to no evidence of hematite present (XRD or EDS). This sample location was primarily made up of exposed steel, the morphology of which could be seen in the secondary electron image (Fig. 18a). This area demonstrated how losses in the oxide patina on the browned samples were much less well-defined than those on the blackened samples, sometimes resulting in the total loss of the original hematite protective coating.

Conclusion

Six historic revolver barrels manufactured between 1853 and 1863 by the Colt Firearm Company were analyzed using SEM, EDS and XRD. Examples of blackened and blued surface treatments were found to have magnetite coatings with well-defined XRD peaks. Under SEM, these finishes exhibited characteristic polishing scratches and surface morphology that was generally uniform, and could be compared to images of newly blackened/ blued steel.⁵ Elemental distribution maps taken using EDS showed some areas of coating loss and corrosion. The damage to these surfaces was generally isolated, and many losses had no corrosion products present.

Browned samples, presumed to be hematite, showed broad, shallow XRD peaks, indicating an amorphous coating of iron oxide. SEM and EDS analysis revealed inconsistent surface morphology. When compared to well-preserved blackened patinas, these surfaces were shown to have undergone more consistent corrosive damage. However, the mechanisms and degree of corrosive attack were harder to determine for the browned samples due to the similarity in appearance and chemical makeup of the original protective hematite film and the products of corrosive attack over the past 150 years. Comparison with newly manufactured browned steel using SEM-EDS is needed to determine the state of preservation of these samples.

The blackened finishes analyzed in this study are believed to have been produced by a charcoal blacking process. XRD results support this hypothesis; it has been previously found that thermally treated samples yield sharp reflection peaks, while chemically treated samples do not. The browned surfaces were chemically treated, although the specific chemical solution used is unknown. Further investigation into the

possibility of using EDS to analyze chemical treatment residues is needed; SIMS has been used to identify chemical treatment makeup on newly blued and blackened steel,⁵ and similar experiments should be undertaken using EDS.

The wide range of intact and corroded areas observed in this work provide insight into many of the types of surfaces that conservators face when working on antique firearms. Many of the differences between the original conditions and corrosion of the blackened, blued, and browned surfaces could not be observed with the naked eye, but nonetheless they convey an important story. Each object was exposed to different environments, and underwent different levels of wear. Each artifact is unique in its history and state of preservation, and must be treated accordingly. However, the general trends observed in this study, particularly those differing between browned and blackened surfaces, exemplify the type of wear that similar objects may display, depending on their treatment and conditions.

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