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**An Examination of Alterations to
Mississippian Period Native Copper Artifacts from the
Collection of the National Museum of the American Indian**

1. Abstract

Two Mississippian period native copper artifacts (National Museum of the American Indian [NMAI] 17/0151 and 17/3096) were examined to inform their treatment and that of an associated group of artifacts. This project grew out of research on the metallurgical techniques used during the Mississippian period by Kim Cullen Cobb, an Andrew W. Mellon Conservation Fellow at the NMAI. Various instrumental analysis methods, including x-ray fluorescence (XRF), scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS), Fourier-transform infrared spectroscopy (FTIR), gas chromatography/mass spectrometry (GC-MS), and Raman spectroscopy were used to characterize the artifacts and old repair materials. In addition, metallographic microscopy and cresol red monitoring were performed to elucidate effects imparted by past treatments. Identification of the repair materials as cellulose nitrate prompted the expectation for copper nitrate as a corrosion product. However, only cuprite and malachite, which are typical archaeological copper corrosion products, were identified. This analysis has shown that the repair material is not currently causing further damage to the artifacts. Due to the unpredictable degradation of cellulose nitrate, however, it should be removed.



2. Introduction

The artifacts examined in this study (figs. 1 and 2) are made from native copper, which is a naturally occurring high purity metal, generally containing 99% or higher copper content.

Research and analysis has established that the copper was then formed into thin sheet artifacts by hammering and annealing. The



Figure 3: “A Cahokia Market” by Michael Hampshire depicting the gorgets being worn. Courtesy of Cahokia Mounds State Historical Site, Collinsville, Illinois.

artifacts examined in this study are relatively small and are known as gorgets. The term is derived from the French word *gorge*, meaning throat, and was originally used to denote a piece of armor protecting that section of the body. The word evolved over time to describe ornamental collars, wimples, and patches of color on the throat of a bird or other animal, particularly hummingbirds. In this case, gorget refers to a pendant worn around one’s neck. During the Mississippian period gorgets were made out of shell and copper, both precious materials that they traded for and collected nearby (fig. 3). A number of sourcing studies using trace-element analysis have come to the general consensus that the copper came from sources in both the Upper Great Lakes and Appalachian Mountains.

The artifacts date from the Mississippian Period, which is generally thought to have started between 400-900 CE and continued until European contact during the 1600s, reaching the peak of its development around 1200 CE

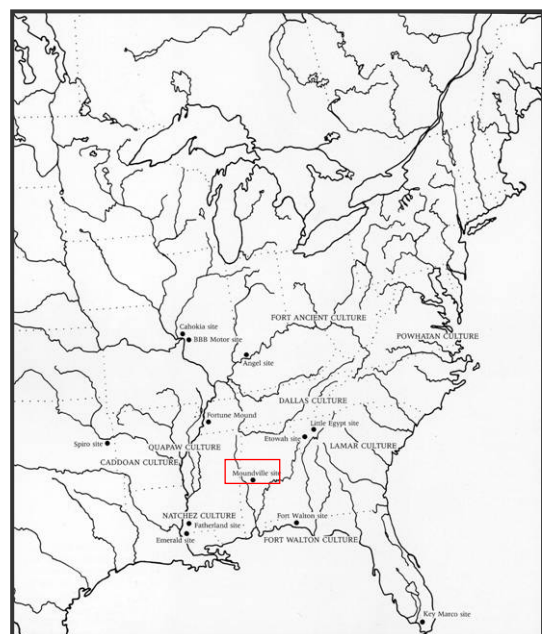
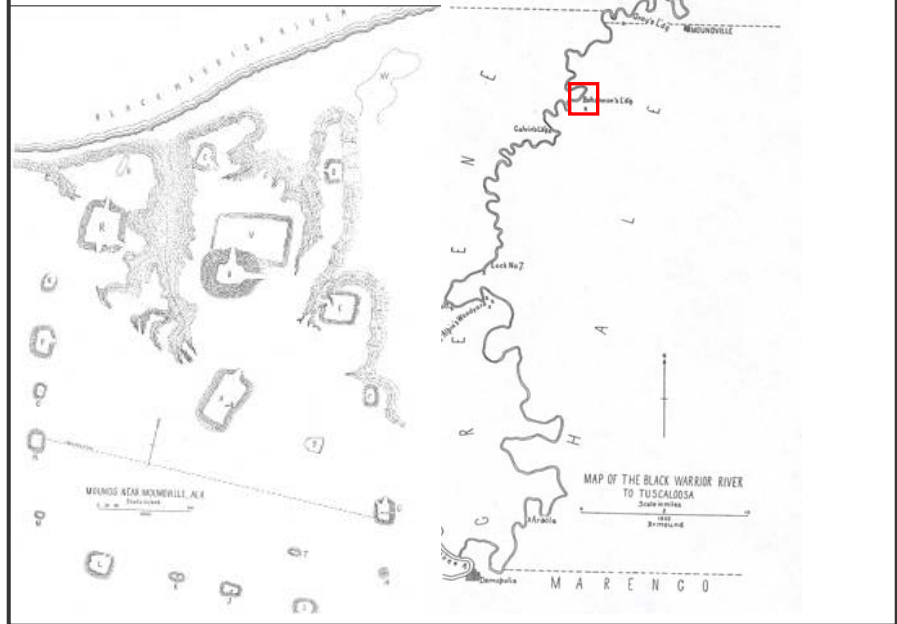


Figure 4: Mississippian period sites and culture areas. Moundville is outlined in red. Image from Brose, 92.

(Hudson 1976; Willey 1966; Brose et al. 1985). Clarence B. Moore excavated the artifacts examined in this study (17/0151 and 17/3096) from Moundville, Alabama in 1905 and 1906 (Knight 1996). Moundville is located in central Alabama (fig. 4) on the Black Warrior River. A circle of mounds encompassing 300

Figure 5: On the right, a map shows Moundville's location on the Black Warrior River. Below, a schematic of the Moundville site shows the mounds that define the site. From Knight, *The Moundville expeditions of C. B. Moore*, 129 and 341.



acres just along the river's edge defines the site (fig. 5). Moundville was occupied during the height of the Mississippian culture, between 1000 and 1500 CE. At its height the Moundville community included about 1000 inhabitants with a population of around 10,000 in the surrounding valley.

The two artifacts at the center of this study are representative of a larger group of artifacts from the Moundville site in Alabama. The group is categorized by their shape, size, design, and manufacture. In addition, many have been repaired with the same modern organic materials. The larger group of gorgets consists of circular and oblong forms all with pierced decoration and two perforated holes near the edge. These holes were most likely used to suspend the gorgets from around one's neck. The circular or 'D'-shaped piercings define a swastika form and are typically circumscribed by two concentric embossed circles. The circle on the oblong pendants is accentuated by an additional triangular piercing. Artifact 17/0151 (fig. 1), an oblong gorget, or pendant, is made up of various fragments. It is about ten centimeters in length and shaped similarly to an isosceles triangle. At the short side of the triangle, there are four holes, about 0.5 cm

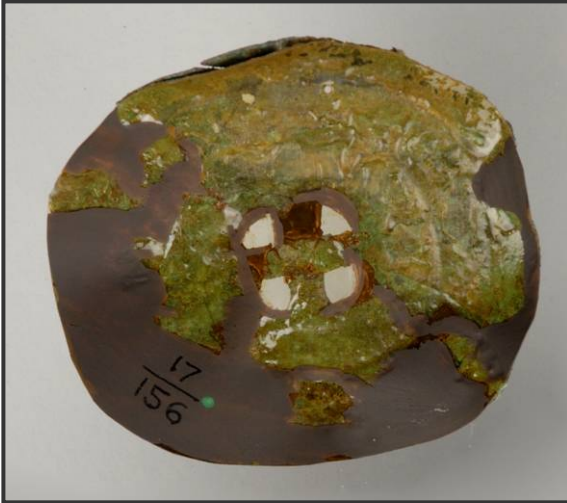


Figure 6: Back of NMAI 17/0156 with accession number visible in the lower left corner.

in diameter, pierced through the copper and a fresh-water pearl, now secured with adhesive, which was probably originally attached with a fiber thread. Comparison to other similar objects suggests that there were originally four 'D-shaped' holes. This piece has a yellowed film adhered to the back, presumably to hold the fragments together in the appropriate orientation.

There is green corrosion unevenly scattered across about 90% of the surface. Artifact 17/3096 (fig. 2) is a circular gorget. It was

originally about 4 cm in diameter with four 'D-shaped' holes pierced through it. The holes would have been near the center arranged symmetrically, like the holes of a button. This piece also has a film material attached as a backing. The copper is unevenly scattered with green corrosion over about 80% of the surface.

Unfortunately, the treatment and storage conditions of the pieces since their excavation are undocumented. The repair materials, however, were probably applied before 1930 when the collection was purchased from the Academy of Natural Sciences in Philadelphia (McGee 2007). The NMAI collection is based on that of George Gustav Heye, who applied the accession numbers to each object in black ink. The accession numbers are clearly visible on top of the repair material in figure 6, indicating that it was already in place when they were brought into the collection. Since the application of the repair materials, the adhesive and backing film have discolored and distorted. Because their condition and treatment has not previously been documented, the origin of the corrosion is unknown. It could be from burial or storage, such as acetic or nitric acid released from the repair materials or other pollutants from the storage environment.

XRF will be employed to attempt examination of the major and minor elements in the copper. The portable XRF should be sensitive enough to identify whether the copper is pure enough to be considered native. In addition, the examination of cross-sections of unassociated fragments with SEM-EDS can provide further insight into the elemental

composition of the copper. Because these fragments are not associated with the two artifacts being examined in this study, they will be examined to provide more general information about the development of corrosion on the artifacts. Examination of the metallographic structure of the cross-sections will also provide information about the metallurgical techniques used to create the artifacts. Because previous studies have found that only hammering and annealing have been used in the manufacture of these types of artifacts, we should not find any evidence of smelting and casting.

In addition to analysis of the metal components, this study aims to provide information about the materials that have accumulated on the surface of the two objects since their excavation. These materials include a resinous adhesive/coating, organic/plastic film backing, and corrosion products. The characterization of these materials—especially if they are found to be detrimental to the artifacts—will be used in making decisions about and possibly making an argument *for* their treatment. No studies have been carried out to analyze conservation materials used specifically on native copper artifacts, however, there have been studies on the identification of modern synthetic materials using FTIR and GC-MS (Learner 2000). An examination of the corrosion products will help determine what is causing the corrosion. It is possible that the corrosion is from centuries of burial, post-excavation storage conditions, or degradation of the repair materials. Copper corrosion has been discussed in many articles and books, although there is a particular focus on copper alloys and of those mostly bronzes. There is not much discussion about the corrosion of purer coppers, such as native copper. The basics of copper and its corrosion are discussed in detail in Scott's book, *Copper and Bronze in Art* (2002). The use of Fourier-transform infrared spectroscopy and Raman spectroscopy for pigment identification may be useful for this aspect of the examination as copper corrosion products are often used as pigments.

The analytical techniques were chosen by: their appropriateness of the technique to the application, the extent that it was possible to sample, and ethical concerns regarding sampling. Only materials that were likely to be removed through treatment and were not a part of the original manufacture were sampled; this included the resin, plastic film, and corrosion. Destructive analysis was carried out only on disassociated fragments, millimeters in diameter, which could not be returned to the original artifact.

3. Experimental Procedures

As the objects could not leave the NMAI's Cultural Resources Center (CRC) in Suitland, MD, sampling was carried out on location and the samples were analyzed later with the instrumentation at Winterthur's Scientific Research and Analytical Laboratory (SRAL). The author collected samples for analysis on December 13-14, 2006 with assistance from Kim Cullen Cobb (see Appendix A for sample locations). XRF analysis was carried out with the portable instrument at the CRC on February 27, 2007 with Catherine Matsen and Cobb. The procedures and instrumentation used in this study are outlined in the order in which they were performed.

Fourier Transform Infrared Spectroscopy (FTIR):

Samples, on the order of micrograms, were prepared with a Nikon SMZ800 microscope and Sony Trinitron monitor by flattening them with a steel roller tool onto a diamond cell. An area on the diamond cell was left clear to subtract from the background. The Nicolet Magna-IR 560 Spectrometer with Nicolet Plan IR Microscope in transmission mode at ½ mm fixed aperture was used to characterize the organic repair materials and corrosion products. This instrumentation gathers data in the spectral range of 4000-500 cm^{-1} (with spectral resolution of 4 cm^{-1}) with a collection time of approximately 2 minutes using 120 scans to reduce the signal/noise ratio using OMNIC E.S.P. 6.1a software. The software package provides tools for automatic correction of the baseline and access to the IRUG, Aldrich, Gettens, and Hummel libraries of searchable spectra. During analysis, a known sample of cupric nitrate was collected as a reference, because one did not exist in the various libraries.

In transmission mode FTIR, the sample absorbs electromagnetic radiation causing changes in vibration energies, which are characteristic of the functional groups present in the material. Spectra are generated from the characteristic motion, including stretching and bending of molecular bonds. Due to the wide peaks produced with FTIR it is often possible to only establish a class of compounds for organic materials through the identification of major functional groups. Inorganic materials, excluding oxides and sulfides, can be more definitively identified. The fingerprint region (1500-500 cm^{-1}) can contain peaks characteristic of specific compounds with a class; however, it takes a

practiced scientist to interpret this data, because mixtures or impurities common in natural materials can complicate the data by causing peak shifts.

Dispersive Raman Microanalysis (Raman):

A Renishaw inVia Dispersive Raman Microscope with 514nm (Argon) laser source was used for qualitative analysis of the copper corrosion. The corrosion sample was placed on a microscope slide, which was placed on the microscope stage under the 20x objective, and the door closed around the stage to eliminate surrounding light sources. The laser was used in the 4000-100 cm^{-1} spectral range with a resolution of 3 cm^{-1} at 10%, 20%, and 50% laser power. Three scans were collected, each with a 20 second exposure time. The generated spectra (saved in .spc format) were interpreted with “Galactic Grams” software and compared to reference spectra from the UCL website (Gibbs 2007) and spectra collected from known materials.

In Raman spectroscopy light energy at a specific wavelength excites molecules in the sample that exhibit polarizability from the ground electronic state to a ‘virtual state’. Some of the molecules fall back to a different energy level in the ground electronic state and lose energy, or exhibit a Stokes shift. This energy difference can be measured and converted to yield spectra that are unique to the compound. In the spectra the x-axis represents the wavelength and the y-axis represents the intensity.

Gas Chromatography-Mass Spectrometry (GC-MS):

A Hewlett Packard HP 6890 series gas chromatography system with a HP5973 mass selective detector and a 7683 automatic liquid injector was used for gas chromatographic separation and mass spectrometric analysis of the repair materials and degradation products that could not be adequately characterized with FTIR. GC-MS can identify compounds based on retention time and mass spectrum for each component. In GC the components of a sample are separated by their affinity to the stationary phase or the mobile phase. Due to the accurate reproducibility of GC, it is possible to identify components by comparing retention times to a library of reference standards. As the components are eluted, they are ionized in a vacuum accelerated in an electric field, separated based on the m/z ratio and then detected by an electron multiplier. Mass spectrometry is highly sensitive and can provide structural information making this a powerful tool for our use.

The sample, on the order of micrograms, was placed in a capped heavy-walled vial (100-300 μ L) and ~100 μ L of 1:2 MethPrep II reagent (Alltech) in benzene was added. The vial was then warmed at 60°C for 1 hour. The sample was used directly for injection into the GC/MS with an inlet and transfer line temperature of 300°C. The injection hardware cleans itself and injects the sample automatically to ensure even and consistent sample size. Analysis was carried out using the RTLMPREP method on the GC-MS (Petersen 2007, AL4696).

Energy Dispersive X-Ray Fluorescence (XRF):

A handheld TRACeR III-V energy dispersive x-ray fluorescence spectrometer was employed for qualitative and quantitative elemental analysis of the copper. This instrument can detect low-energy elements, as low as sulfur ($Z \geq 16$) and as high as plutonium ($Z=94$), in a matrix and in concentrations ranging from 100% to parts-per-million. A rhenium tube acted as the x-ray source, with an acceleration voltage of 40 kV at 2.4 μ A. The collection time ranged from 50-200 seconds. For this type of analysis no sample or sample preparation is necessary; the object can be analyzed as is. To collect data, the artifact to be analyzed was placed against the measurement window and the trigger depressed. PXRF software gathered the spectra with the x-axis representing the characteristic energy levels of the emitted x-rays (e.g. $K_{\alpha 1}$, $K_{\beta 1}$) and the y-axis representing the intensity. The Cu1orig.cfz program provided by the manufacturer was used as the standard for quantitative analysis.

This type of spectrometry is based on the theory that incident x-rays will strike inner shell electrons and eject them from the atom. When a higher energy electron falls to fill that vacancy a characteristic fluorescent x-ray is given off. The fluorescence is detected and converted to an interpretable spectrum so that major and minor elements can be identified by their characteristic energy levels marked on the spectra with vertical lines.

Metallographic Cross-section Microscopy:

Unassociated fragments from one object were mounted in Buehler Epoxicure resin (no. 20-8130-032) cured with an epoxide hardener (no. 20-8132-008) following the manufacturer's instructions. The resin was ground to reveal the sample with Buehler silicon carbide grinding paper for metallography in 400 and 600 grit. Followed by

polishing with 6 and 1 micron Buehler Metadi[®] Supreme polycrystalline diamond suspension on a polishing wheel using an appropriate polishing cloth and Struers DP-lubricant. The cross-sections were examined with a Nikon Epiphot 200 microscope with a metallographic stage ranging from 100-1000x and images captured with Nikon ACT-1 software before and after etching with alcoholic ferric chloride (120 mL ethanol, 30 mL HCl, 10 g ferric chloride) in bright and dark field, with Normarski prisms, crossed polars, and a first order red compensator.

Energy Dispersive Scanning Electron Microscopy with X-ray Microanalysis (SEM-EDS):

The mounting resin of the cross-sections was cut down, mounted to a carbon stub with carbon tape (distributed by structure probe inc. supplies), and coated with carbon paint (a colloidal graphite in isopropanol) around the sample to increase conductivity and reduce charging. The uncast sample was applied directly to the carbon tape. An ABT 60 Topcon scanning electron microscope with EDAX 9900 energy-dispersive x-ray analyzer with a liquid N₂ cooled SiLi detector, beryllium window, and tungsten filament gun source (electron beam generator) was used to analyze the metallographic cross-sections. The backscatter mode, which shows the relative atomic numbers of the elements present projected on a CRT monitor with the heavier elements appearing whiter, was used to focus in on the sample. The accelerating voltage was set to 20 kV with a stage height of 22 mm and 20° tilt towards the x-ray detector. Spot elemental analysis was carried out on areas ranging from 10-100 microns across. The data was interpreted with Evex NanoAnalysis software to produce spectra with the x-axis displaying characteristic energies of emitted X-radiation and the y-axis indicating counts and standardless internal quantitative data. SEM-EDS analysis allows for elemental analysis, as well as topographical information of the sample with secondary electron imaging. Backscattered electron imaging and x-ray mapping can create an “elemental map” of the sample surface to help understand changes in the composition of the artifact.

Cresol Red Testing:

After identifying the repair material as cellulose nitrate, it was monitored for the release of nitric and nitrous acid with cresol red. The cresol red paper was prepared by mixing a solution of 0.04% w/w cresol red in water, soaking filter paper with the

solution, and allowing it to dry. Pieces of the paper were placed on and near the cellulose nitrate repair material and left for one week in a storage cabinet covered with blackout cloth. Strongly acidic vapors react with the cresol red indicator dye in the paper to change their color (Odegaard 2000).

4. Results

Sample Number	Sample Description	Analytical Instrument	Results
170151_1	String of adhesive	FTIR	Cellulose nitrate
170151_2	Adhesive with corrosion	FTIR	Cellulose nitrate
170151 #1	Artifact surface, some corrosion	XRF	Cu, trace of Fe
		XRF w/ vacuum	Cu, trace of Fe and Ca
170151 #2	Artifact surface, some corrosion	XRF	Cu, trace of Fe
		XRF w/ vacuum	Cu, trace of Fe and Ca
170151 #3	Artifact surface, some corrosion	XRF	Cu, trace of Fe
		XRF w/ vacuum	Cu, trace of Fe and Ca
173096_1	Green corrosion with adhesive	FTIR	Malachite, trace of cellulose nitrate
		Raman	Malachite
173096_2	Repair film	FTIR	Cellulose nitrate
			Malachite, trace of cellulose nitrate
173096_3	Repair film with corrosion	FTIR	Cellulose nitrate
		GC-MS	Inconclusive
173096_4	Repair film with green corrosion	FTIR	Cellulose nitrate and malachite
			Malachite, trace of cellulose nitrate
173096 #1	Artifact surface, some corrosion	XRF	Cu, trace of Fe
		XRF w/ vacuum	Cu, trace of Fe and Ca
173096 #2	Artifact surface, some corrosion	XRF	Cu, trace of Fe
		XRF w/ vacuum	Cu, trace of Fe, Ca, K, Ba
173096 #3	Artifact surface, some corrosion	XRF	Cu, trace of Fe
		XRF w/ vacuum	Cu, trace of Fe and Ca
170123_1a	Etched cross-section of fragment	SEM-EDS	Cu, trace of Fe and Cl around perimeter, Cl in mineralized area
170123_1b	Etched cross-section of fragment	SEM-EDS	Cu, trace of Fe and Cl around perimeter, Cl in mineralized area
170123_1c	Uncast sample and cross-section of fragment	SEM-EDS	Cu, minor Fe, Cl, Si, S, Mn, Ca, Si and possibly Al, P
		FTIR	Cellulose nitrate
		Raman	Cuprite
170123 #1	Artifact surface	XRF	Cu, trace of Fe
170123 #2	Artifact surface	XRF	Cu, trace of Fe
170123 #3	Artifact surface	XRF	Cu, trace of Fe

Table 1: Summary of results from FTIR, XRF, SEM-EDS, Raman, and GC-MS.

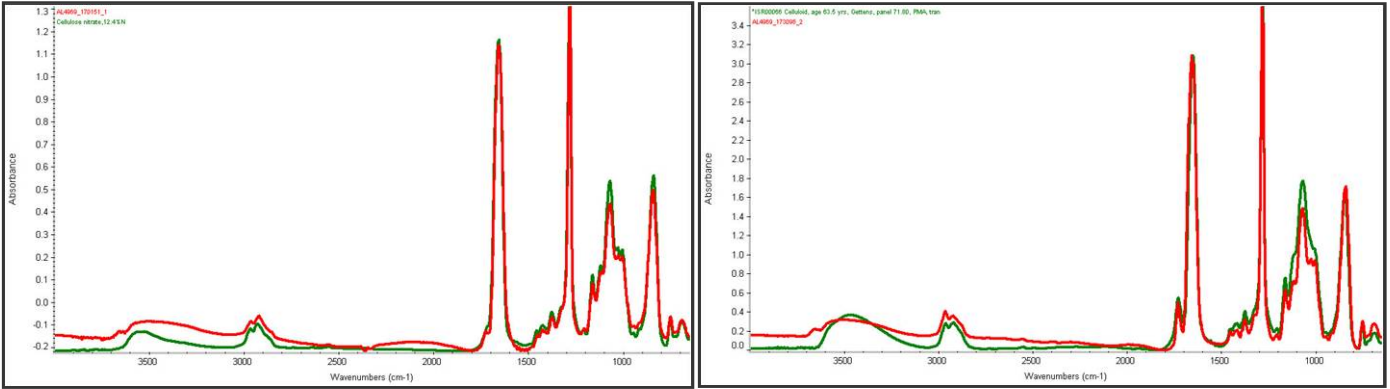


Figure 7a (left) and b (right): FTIR spectrum of adhesive sample 170151_1 in red and reference spectrum of cellulose nitrate in green. FTIR spectrum of film sample 173096_2 in red and reference spectrum of cellulose nitrate in green.

The results of the instrumental analysis are summarized in Table 1. The repair materials, both film and adhesive, were identified as cellulose nitrate with FTIR, as seen in figs. 7a and b. The identification of the repair materials helped focus the subsequent analysis of the corrosion products present on the objects, in that it made the author aware to search for copper nitrates.

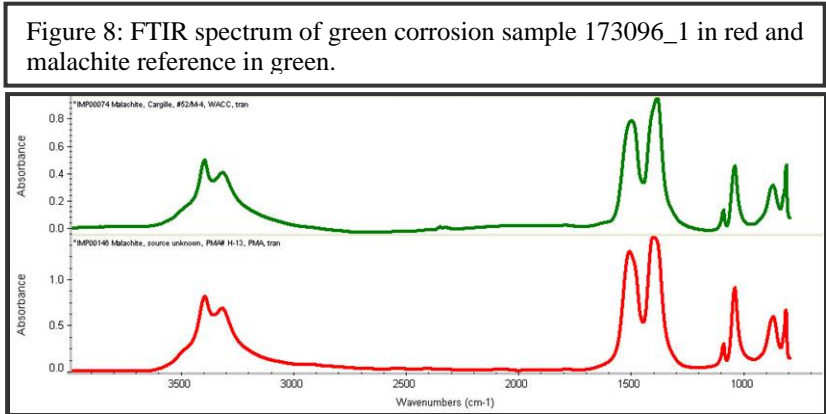


Figure 8: FTIR spectrum of green corrosion sample 173096_1 in red and malachite reference in green.

Figure 9: FTIR spectrum of sample 173096_4, in red, showing a mixture of cellulose nitrate, in green, and malachite, in blue.

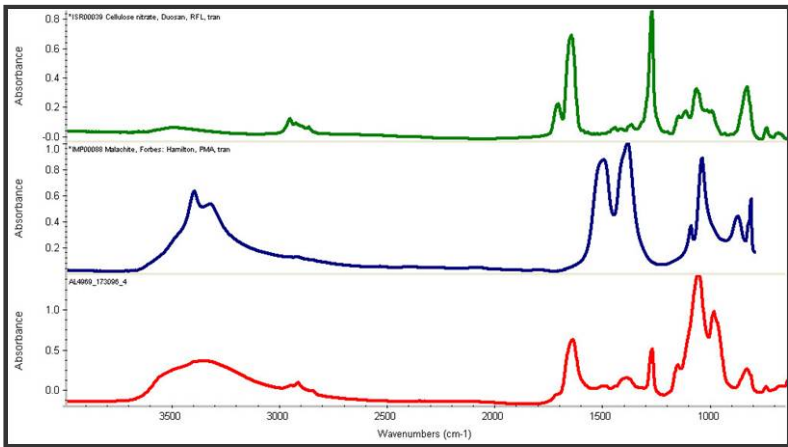


Table 2: Peaks for unknown compared to peaks taken from a reference spectrum from UCL (Gibbs 2007).

Unknown	Reference
514 nm	514 nm

The green corrosion was identified a malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) with FTIR, as seen in fig. 8. This identification was confirmed with Raman spectroscopy by comparing the peaks to a reference (table 2). The FTIR spectra showed that the corrosion was occasionally mixed with cellulose nitrate (fig. 9). A reference spectrum for cupric nitrate ($\text{Cu(NO}_3)_2$) did not exist in the available libraries, so one was collected from a known specimen for comparison. The spectra for cupric nitrate, malachite, and unknown 173096_4 overlapped significantly

154	155 s
182	178 s
222	217 m
273	268 m
	354 m
435	433 vs
	509 m
538	553 s
	558 w
722	757 vw
1057	1051 m
1100	1085 m
1493	1492 vs

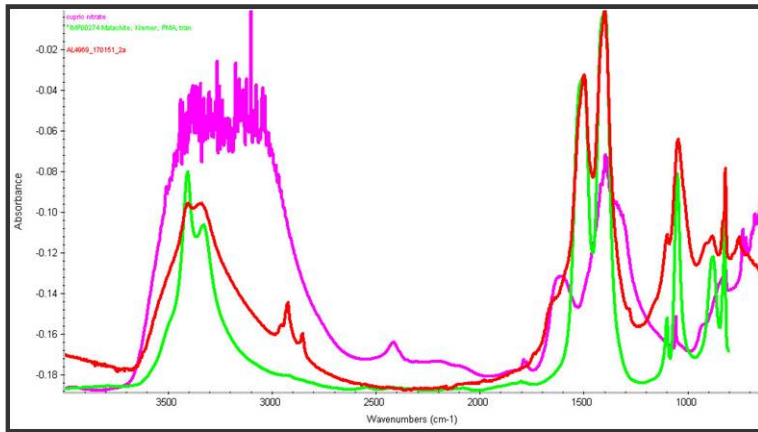


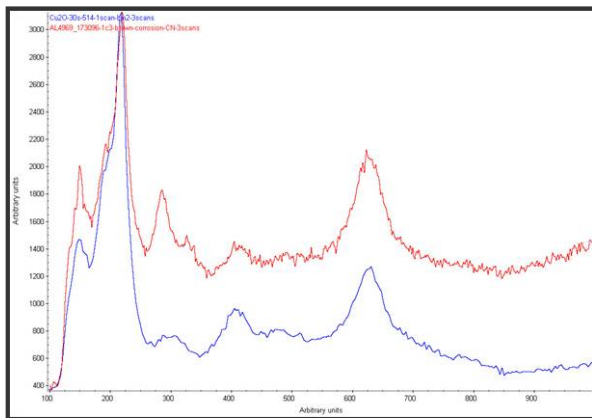
Figure 10: The FTIR spectrum for cupric nitrate, in pink, was overlaid with a reference spectrum for malachite, in green, and the spectrum for sample 170151_2a, in red.

(fig. 10).

The reddish brown corrosion was identified as cuprous oxide, or cuprite, with Raman

spectroscopy (fig. 11). FTIR was not adequate for this identification because it does not detect oxides and the sample was overwhelmed with cellulose nitrate. A reference spectrum also had to be collected for cuprous oxide (Cu_2O), as one was not readily available in conservation or chemistry literature.

Figure 11: The Raman spectrum for unknown 17/0123_1c in red was compared to a reference for Cu_2O in blue.



The portable XRF identified mainly copper and a trace amount of iron (fig. 12). Attempts at quantitative analysis

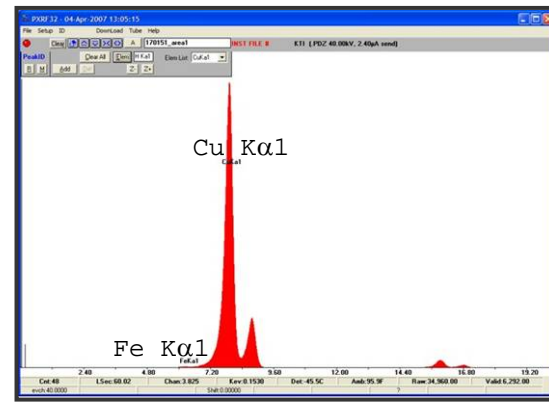


Figure 12: XRF spectrum for 170151 #1.

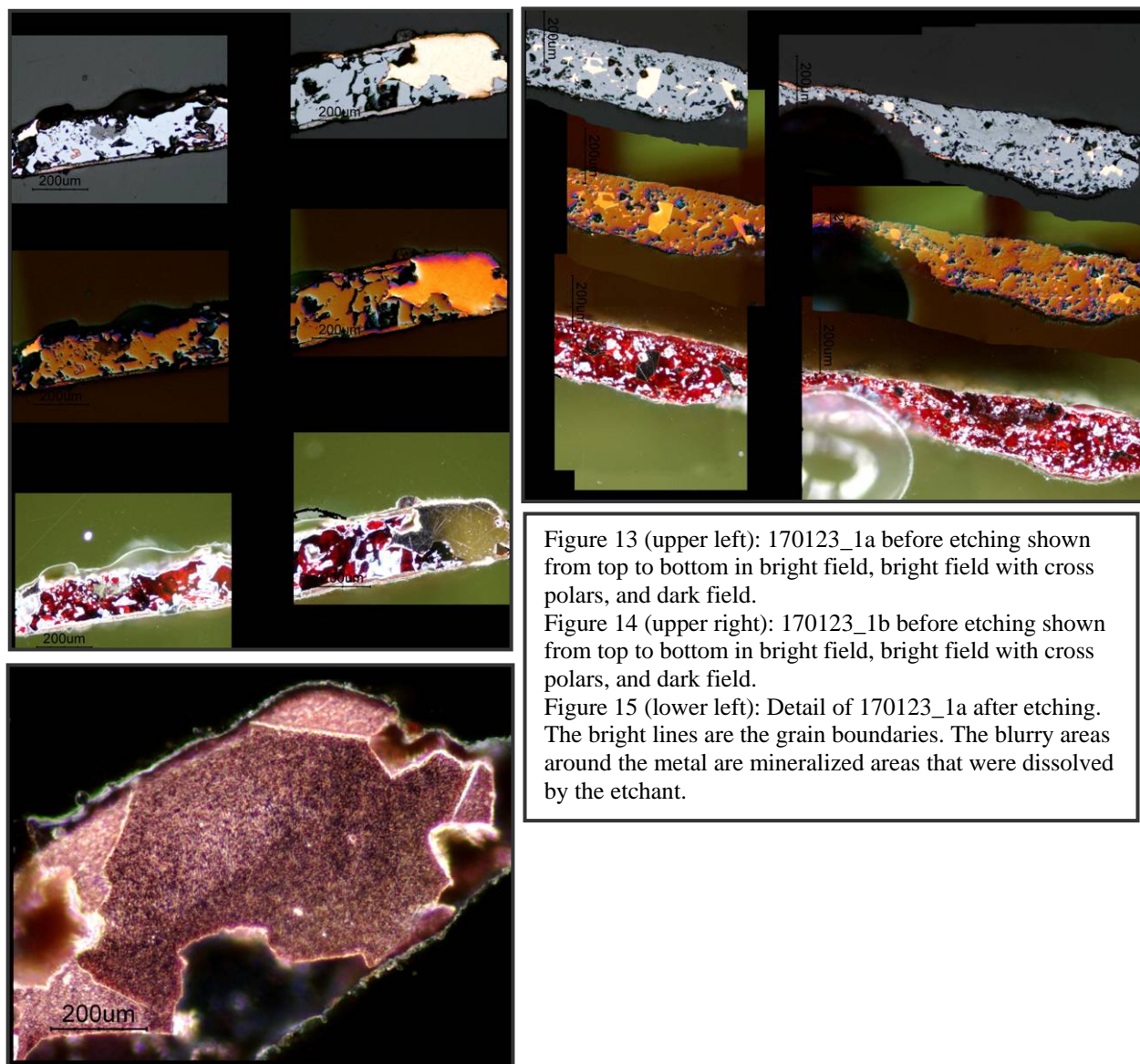


Figure 13 (upper left): 170123_1a before etching shown from top to bottom in bright field, bright field with cross polars, and dark field.

Figure 14 (upper right): 170123_1b before etching shown from top to bottom in bright field, bright field with cross polars, and dark field.

Figure 15 (lower left): Detail of 170123_1a after etching. The bright lines are the grain boundaries. The blurry areas around the metal are mineralized areas that were dissolved by the etchant.

were inconclusive. It was hoped that XRF could provide information about the composition, confirming the use of native copper rather than, for example, European copper. The overall setup and sensitivity of the instrument, however, were not suitable to this type of analysis. The size of the measurement window and presence of other minerals from dirt and mineralization, seen later with SEM-EDS, may have also caused interference.

The metallographic cross-sections revealed a highly mineralized structure (figs. 13-15). Etching with alcoholic ferric chloride exposed equiaxial grains with no signs of deformation or twinning bands. This grain structure suggests that the artifacts were cold-

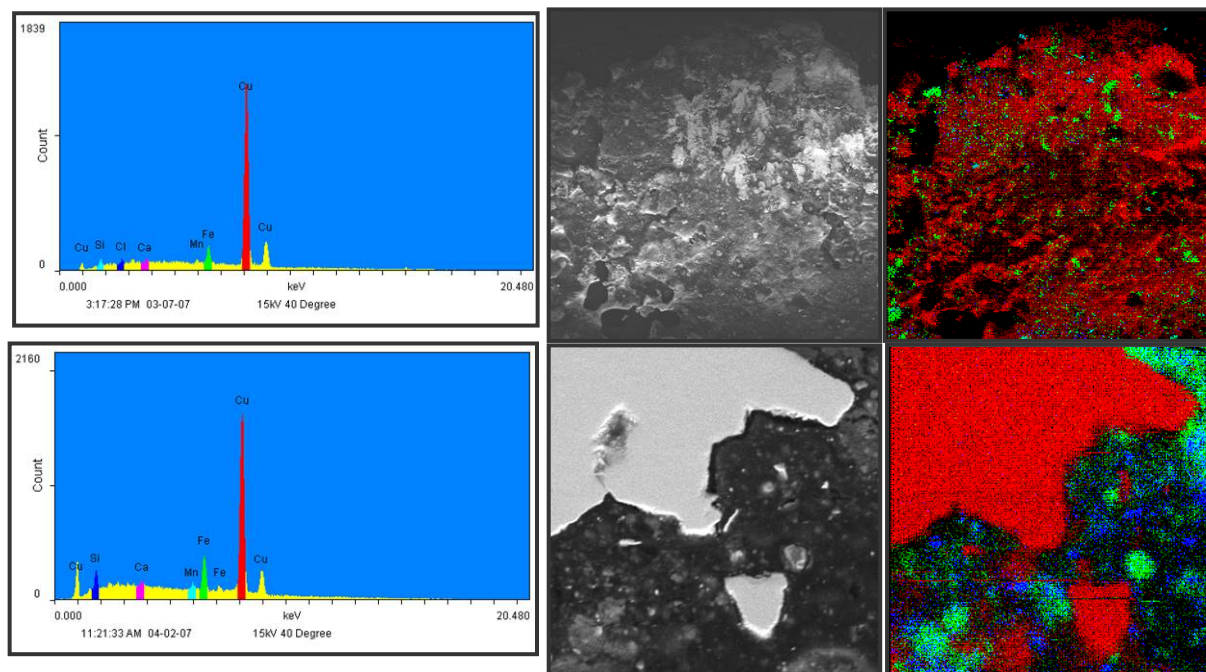


Figure 16 (top): Spot analysis with SEM-EDS (left) of the uncast fragment, 170123_1c, seen in the secondary electron image (center), identified Cu and trace amounts of Fe, Cl, Si, Ca, and Mn. These elements are mapped on the backscatter electron image (right).

Figure 17 (bottom): Spot analysis with SEM-EDS (left) of a cross-section of the same fragment, seen in the secondary electron image (center), identified Cu and trace amounts of Fe, Si, Ca, and Mn. These elements are mapped on the backscatter electron image (right).

worked followed by annealing. When examined with SEM-EDS, the unetched fragment and cross-section exhibited a random scattering of iron, chlorine, calcium, silicon, and manganese on the surface and throughout the matrix of the cross-section (figs. 16 and 17). Spot analysis at the grain boundary versus the center of the grain did not show any difference in composition (fig. 18). For more accurate quantitative and trace-element analysis SEM-WDS is necessary. SEM-EDS of the etched samples revealed iron and chlorine around the perimeter of the sample and chlorine throughout the mineralized areas.

The cresol red test came back negative. In the week that the cellulose nitrate was monitored with the cresol red paper, there was no color change.

5. Discussion

The identification of the repair materials as cellulose nitrate explains the degradation characteristics observed, such as warping and yellowing. According to Horie in *Materials for Conservation* (2005), cellulose nitrate was first used in conservation during the late nineteenth century, soon after its commercial availability. This corroborates the author's dating of the repairs between 1905-06 and 1930. However, beyond the physical deformation of the film, there was no evidence found for further damage to the copper, such as the formation of cupric nitrate. Although there was significant overlapping of the peaks of the FTIR spectra (fig. 10), it was determined that copper nitrate was not present due to: the absence of the peak at 2400 cm^{-1} in the unknown, the identification of cellulose nitrate and malachite in purer samples, and the absence of visual evidence for the bright blue crystals of cupric nitrate. Rather, only malachite and cuprite were identified. The majority of archaeological copper and bronze form a cuprite crust overlaid with malachite (Scott 2002). The extensive mineralization, or corrosion, of the copper fragments might have actually inhibited the formation of copper nitrates, because of the inaccessibility of the copper metal (van Langh 2007).

Examination of the metallographic cross-sections exposed equiaxial grains with no signs of deformation or twinning bands. This grain structure suggests that the artifacts were cold-worked followed by annealing, which is consistent with the literature. The various elements found with SEM-EDS on the surface of the fragment and within the mineralized area of the cross-section are commonly associated with dirt and are probably

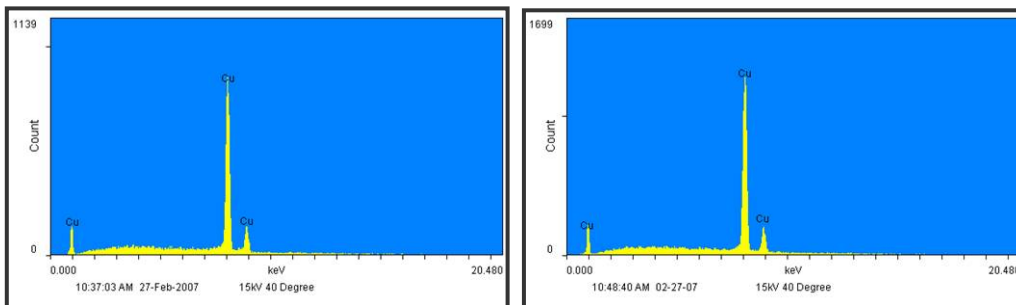


Figure 18: Spot analysis with SEM-EDS in the center of the grain (left) showed the same elemental composition as at the grain boundary (right).

due to the archaeological nature of this artifact. During the mineralization of the copper, elements in the surrounding earth were likely adsorbed onto the corrosion matrix. Analysis of the unetched samples helped to clarify that the chlorine found throughout the mineralized areas of the etched samples came from the ferric chloride etchant and

chlorine in the epoxy resin, rather than an acid bath containing hydrochloric acid. A mixture of acids, including hydrochloric acid, has commonly been used in archaeological settings to strip surface corrosion from metals.

Elemental analysis with XRF and SEM-EDS did not provide conclusive quantitative analysis. And although it was not possible to determine the percentage of copper present, these artifacts do have a very high copper content. This was evident from the strong copper peaks in all elemental analysis. In addition, the metal's composition did not vary significantly at the grain boundary, where impurities are usually concentrated. The iron present during XRF analysis was most likely due to dirt and the mineralization, which was seen around the perimeter and throughout the copper matrix with SEM-EDS.

The negative results of the cresol red test are encouraging, in that the cellulose nitrate is not currently actively degrading. Due to the unpredictable degradation of this material, however, it is not possible to tell what stage of degradation it has reached (Nishimura 2007; Coughlin 2007). Some evidence points to it being in the induction phase, such as it being soft, not brittle and still being intact, while other facts suggest it being past the most catastrophic degradative stage, such as the seventy years in an uncontrolled climate, the negative cresol red test, and the buckling and discoloration.

6. Conclusions

This technical study set out to examine the alterations that have occurred to a group of archaeological native copper artifacts in order to make recommendations for their treatment. No evidence was found for the repair materials causing any other degradation, besides the physical deformation. It is interesting to note that the self-selective group of fragmented artifacts was the most mineralized and brittle and therefore resistant to the pollutants released by the degrading cellulose nitrate. Even just the deformation of the nitrate film and the artifacts, however, is problematic to the long-term preservation of these pieces, as well as their interpretation. The physical deformation may have even caused associated changes to the metallographic structure. Although, due to the high degree of mineralization to the fragmented pieces, there was likely not much metal left to cause a problem.

The final question left by this analysis is whether to remove the cellulose nitrate or not. The negative cresol red test tells us that the repair material is not actively degrading, so there is time to make some decisions. However, due to the unpredictable nature of this material, removing it would be to err on the side of caution. Before doing so, it would be necessary to take three major considerations into account: (1) determining a safe way to remove the cellulose nitrate, which may have a reduced solubility due to its contact with the copper oxides, (2) temporarily support the fragments, which are more brittle than may at first seem, and (3) choose a stable material on which to mount the objects that can conform to their non-planarity and provide adequate support. In the future, it may prove informative to examine other collections with the same repair materials.

For now it is best that the objects remain in a stable environment, even slightly dry and as cool as possible, with good air circulation. This is for the objects themselves, as well as other objects sharing the storage cabinet. It would be prudent to continue monitoring with cresol red paper and maintain as scavenger in the storage area, such as the corrosion intercept already in place. Finally, a treatment system should be devised to remove the cellulose nitrate film from the objects in the future.

7. References

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APPENDIX A:

Sample sites

