Object: Bronze phiale
Cultural attribution/provenance: Persian / Achaemenid period
Dimensions (HxWxD, inches): 5.25" diameter at widest point, 2.25" tall
Medium: bronze
Current/past owners: Center for Near Eastern Archaeology, La Sierra University
Accession number: LSU0067
Markings: none
Date of examination: 4/9/2017
Conservator: Kasey Hamilton

Object Description:

The object is a medium sized, shallow copper alloy (bronze) bowl with a flared rim, similar in form to Achaemenid phialae (wine drinking bowls). The bowl is covered with accreted material (possibly burial deposits) and various corrosion products. The overall color of the bowl at present is a dull green (from the corrosion products) with several areas covered in beige deposits. The underlying base metal is visible in a few areas on the exterior of the bowl, and appears relatively smooth with a thin layer of iridescent purple corrosion on the surface. In smaller areas where this purple corrosion is absent, a brown/copper-colored base metal is visible.

Materials and techniques:

The bowl is a copper alloy, identified as bronze via X-ray fluorescence (see Testing & Analysis). The form is simple, with a shallow bowl and a broad, flared rim. The form is similar to other metal drinking bowls (*phiale*) of the Achaemenid style (Melikian-Chirvani, 1993), but appears to lack additional ornamentation or decoration (see Appendix I).

The bowl may have either been formed by casting, or raising from a sheet. Raising from a sheet seems more likely considering the simple form, and may be further supported by the XRF data. The bowl would have been formed by hammering the sheet out over the rounded head of a

stake. The bowl would likely have been annealed during this process in order to release the stress generated during coldworking. Following hammering, the bowl may have been planished in order to achieve the smooth surface. Little evidence of metalworking is visible due to the encrusted burial deposits and corrosion product. Metallographic analysis of the microstructure may help to further understand how the object was made, but was not conducted at this time.

Condition:

The object is in fair condition overall. Various accretions are present throughout the surface of the object. These accretions are light beige and sandy. They are loosely bound to the substrate, although some areas are more compact while others are powdery. Additional lighter beige/white accretions are visible in a few areas throughout. Similarly, these are either powdery in nature or appear somewhat more compacted.

A variety of corrosion products are present on the surface. While the corrosion products differ slightly in terms of hardness, all seem to be soft enough to cut with a microscalpel. These corrosion products include a dark green corrosion layer (possibly malachite, $Cu_2CO_3(OH)_2$) that extends over approximately 90% of the surface. This dark green corrosion appears to have formed over another corrosion layer that is more red/brown in color (possibly cuprite), which may be contributing to the overall darkened appearance of the green. In areas where this corrosion crust has been lost, a thin layer of iridescent purple corrosion product (also possibly cuprite) appears to have formed over the base metal. In some areas, there appear to be gaps or void spaces that exist between the thin purple (cuprite) and dark green (malachite) layers.

There are at least four distinct areas where wart-like corrosion pustules have formed. These areas have been indicated in Figures 1, 2 and 4. In these areas, some of the warts/pustules appear cracked. The warts appear somewhat similar to bronze disease, a condition affecting copper alloy artifacts in which copper chloride corrosion is formed. This type of corrosion occurs due to the presence of chlorides, water and oxygen. A cyclic reaction proceeds in which oxidized copper reacts with chloride ions to produce nantokite (CuCl), forming above the original base metal. The cyclical reaction continues as long as water and oxygen are present, forming additional nantokite and/or the copper trihydroxychlorides paratacamite, clinoatacamite and atacamite (Scott, 2002). These corrosion products may occur either in pits or on the surface of the patina in archaeological bronzes. They often appear somewhat powdery, ranging from blue to green in color.

Warts or pustules may also be formed during the bronze disease corrosion process. The nantokite layer will exist at the very bottom of the pustule, between cuprite and original metal. Copper carbonate corrosion or copper trihydroxychlorides will form in a raised lump over the nantokite, forming warty corrosion (Scott, 1994). When bronze disease is present, these warts may crack and eventually erupt, exposing the nantokite to air and moisture, further accelerating the corrosion process.

While some warts present on the surface of this object do exhibit some cracking, none have completely erupted. It is possible that the corrosion has formed in this manner and may not be related to bronze disease. Microchemical tests for chlorides were completed in an effort to determine whether or not bronze disease is present (see Testing & Analysis). Lighter colored, plate-like green corrosion is present surrounding the previously mentioned warts, particularly at the bumpy area on the interior of the rim. There are also areas of dark blue corrosion product in these regions (possibly azurite, $Cu_3(CO_3)_2(OH)_2$). There are a few regions where a powdery, light blue corrosion product is present, both on the interior and exterior of the bowl (Fig. 2-3). However, these areas of powdery corrosion exist separately from the warty corrosion. For this reason, it was initially thought that the areas of warty corrosion was not indicative of bronze disease.

Two areas of hardened waxy material exist on the bottom of the bowl. This material fluoresces a yellow-green color under ultraviolet light (λ_{ex}=365nm). It is likely remnants of a wax product that was applied in order to anchor the object to its display base.

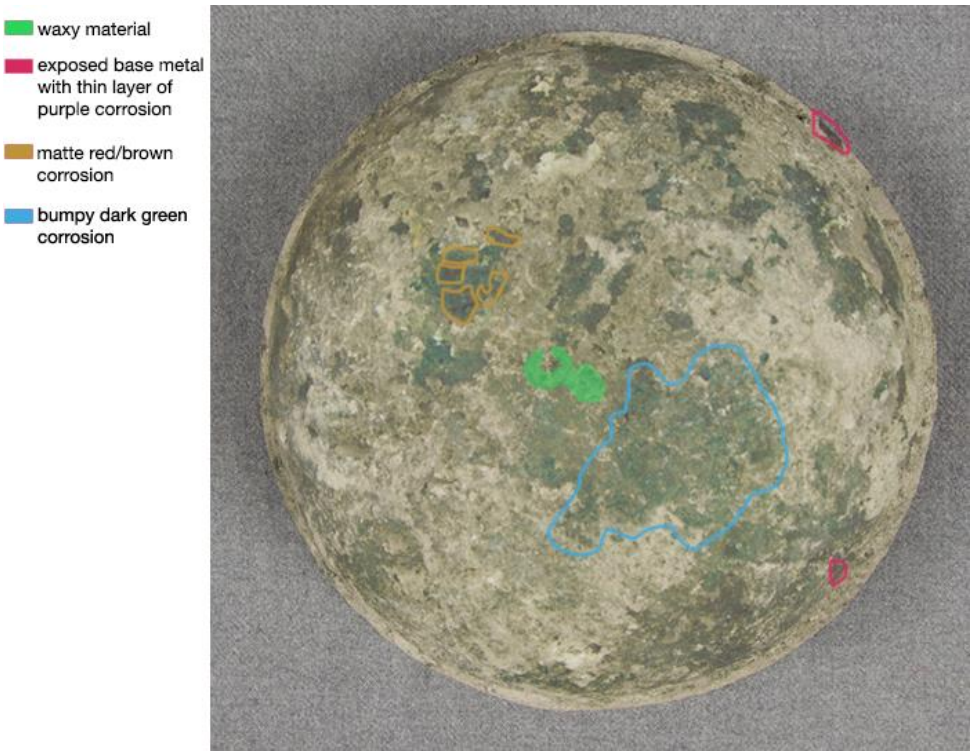


Figure 1. Annotated image, base of bowl.

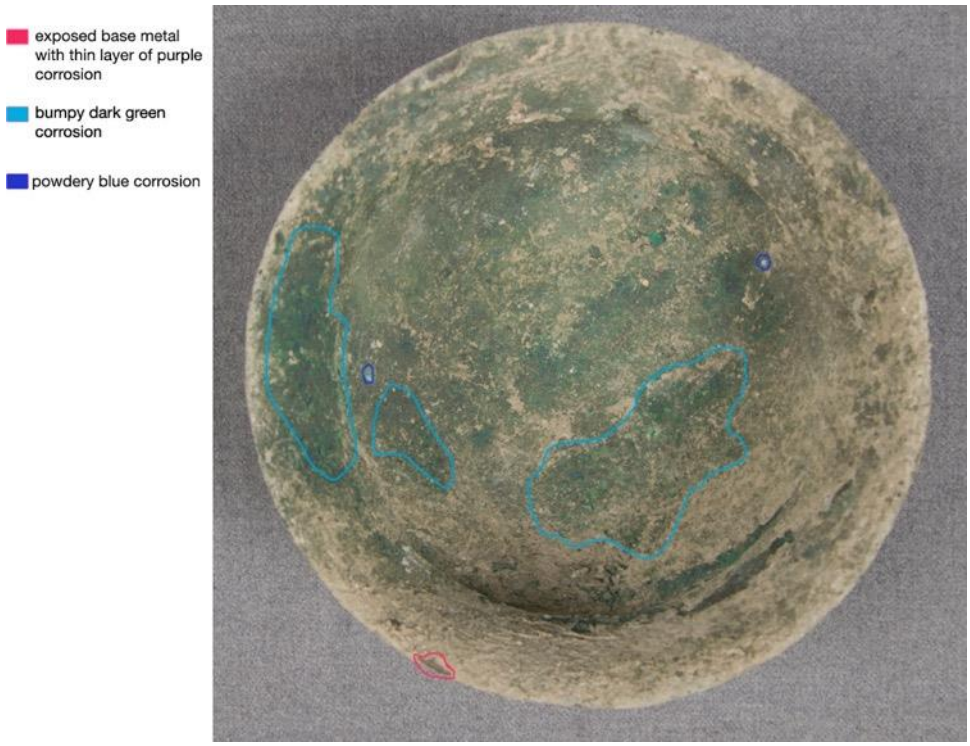


Figure 2. Annotated image, interior of bowl.

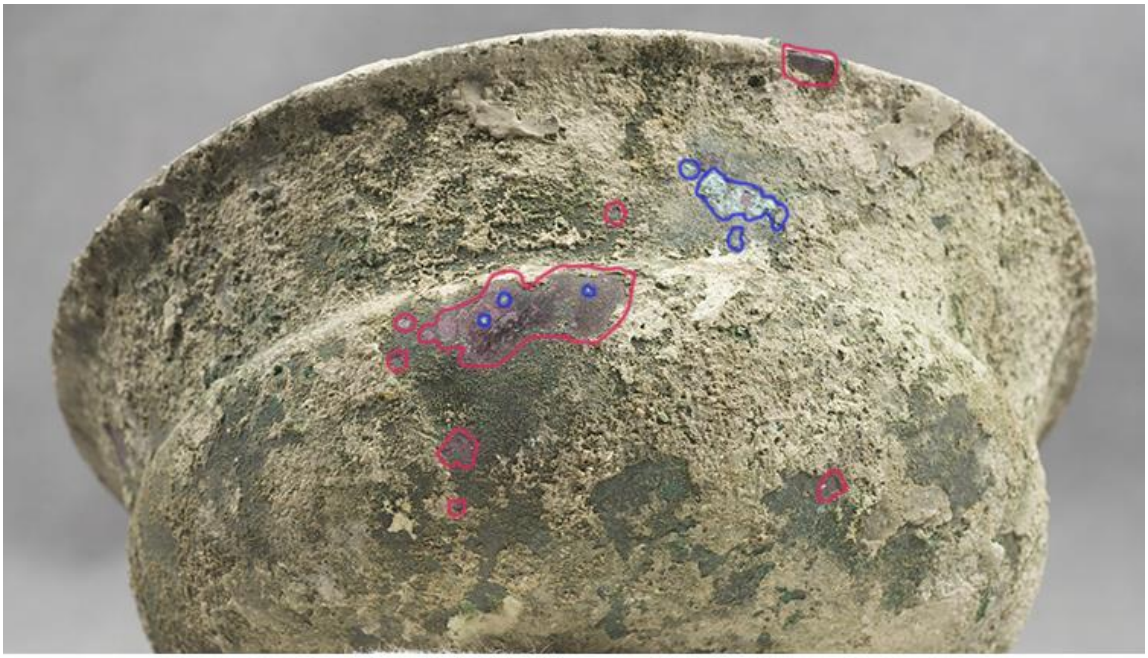


Figure 3. Annotated image, side of bowl.

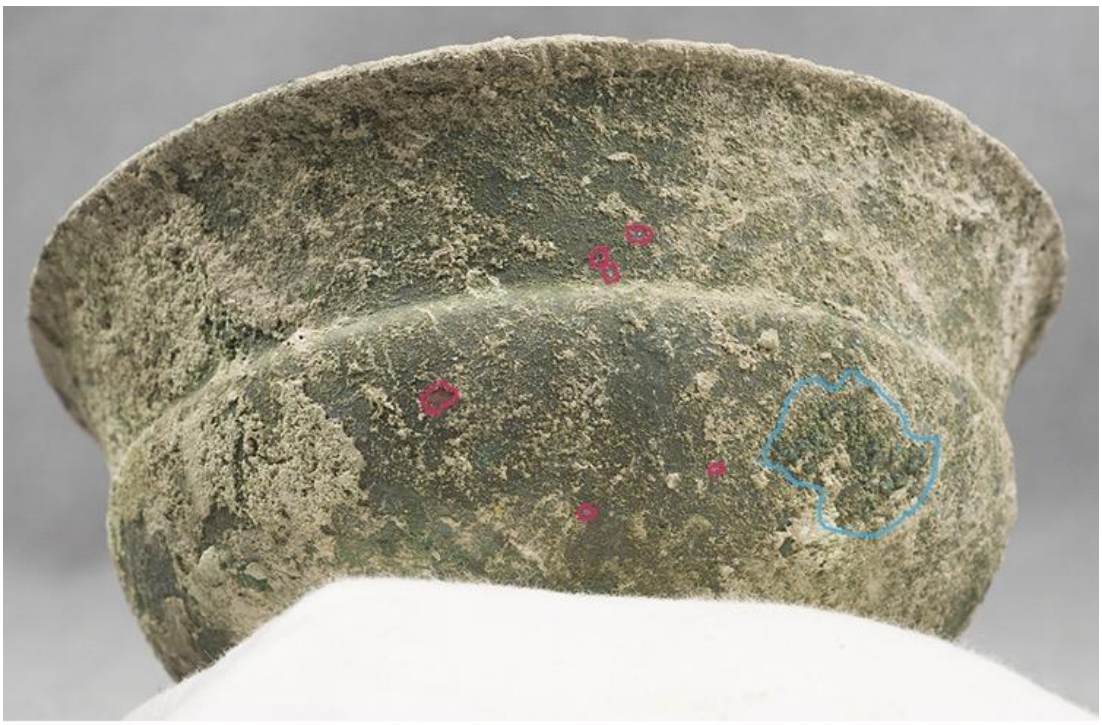


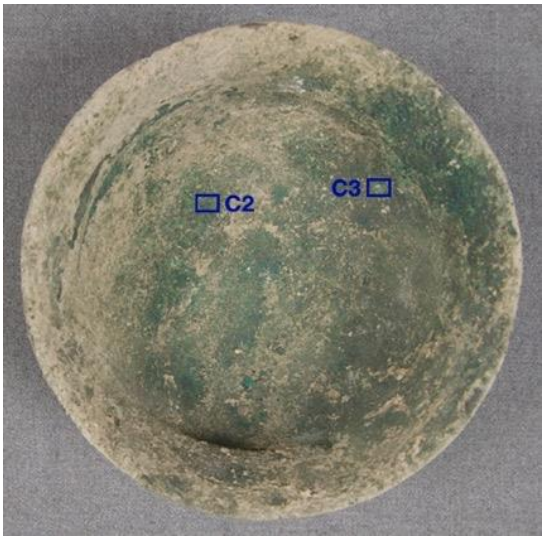
Figure 4. Annotated image, side of bowl.

Condition Summary:

Object is structurally sound with accreted burial deposits and copper corrosion products overall, including some areas of bumpy or wart-like corrosion that does not appear related to bronze disease.

Testing & Analysis:

Three areas were sampled and tested for chlorides, using a silver nitrate microchemical spot test (Odegaard, Carroll, Zimmt, 2015). Small samples were removed from the areas indicated in the figures below, and placed in small test tubes. Approximately 5 drops of deionized water was added to each test tube, followed by 2 drops of nitric acid and 1 drop of silver chloride. A known positive (NaCl) was also tested. In the presence of chloride ions, a white precipitate will form.



Figures 5, 6. Areas where samples were taken for chloride spot tests.

Table 1. Results of microchemical test for chlorides.

Sample	Description	Result	Observations
C1	Powdery, light blue	+	Solution appears cloudy white, however no distinct precipitate is visible.
C2	Dark green corrosion from bumpy area	-	No change occurred. Solution remains colorless.
C3	Powdery, light blue	+	Solution appears cloudy white, however no distinct precipitate is visible.

No reaction was observed for sample C2. However, both C1 and C3 (areas of powdery blue corrosion) appeared to react slightly, as the solution turned cloudy white. The samples obtained

were small - the powdery nature of the corrosion product made it somewhat difficult to transfer to the test tube. The literature suggests that if there are few Cl^- ions present, only a white haze will form (as opposed to a strong precipitate). This is likely the case here. The results of this test indicates that the powdery blue corrosion product may be a copper chloride. The absence of chlorides in C2, taken from one of the warts in an area of bumpy corrosion, may be further evidence that the warts are not related to bronze disease.

X-Ray Fluorescence

X-Ray Fluorescence (XRF), a nondestructive elemental analytical technique, was carried out to examine the elemental composition of the material present. Readings were taken with a Bruker-Tracer III-SD instrument with a rhodium x-ray source and silicon drift detector. Readings were collected at 40 kV, 11 µA, 120 sec, using a Titanium-Aluminum (yellow) filter appropriate for use during the analysis of metal objects. Spectral data was acquired and interpreted using S1pXRF software.

A reading was collected from the largest area of exposed base metal, noted in Figure 7. XRF analysis revealed major copper peaks, and minor peaks for tin and lead. These results indicate that the metal is bronze with trace amounts of lead. Lead is often added to bronze in order to improve wettability and flow of the molten metal during casting. Had the object been fully cast, a stronger lead signal may be expected. It is possible that the lead present may have been added to improve casting properties when the molten metal was poured out into a sheet.

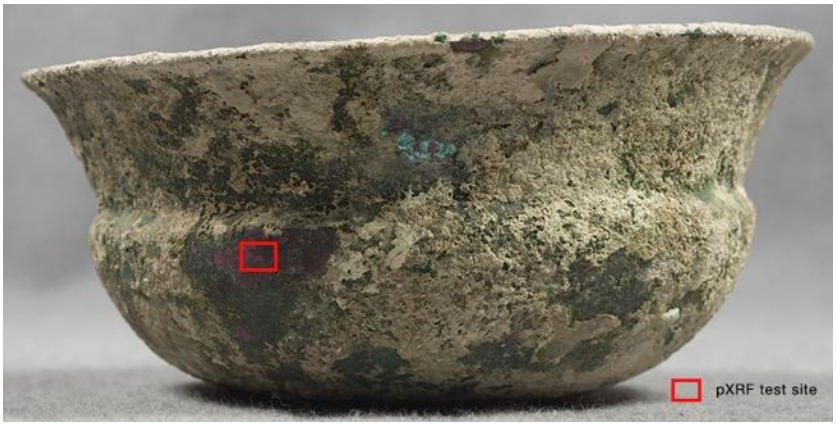


Figure 7. Area where pXRF analysis was performed.

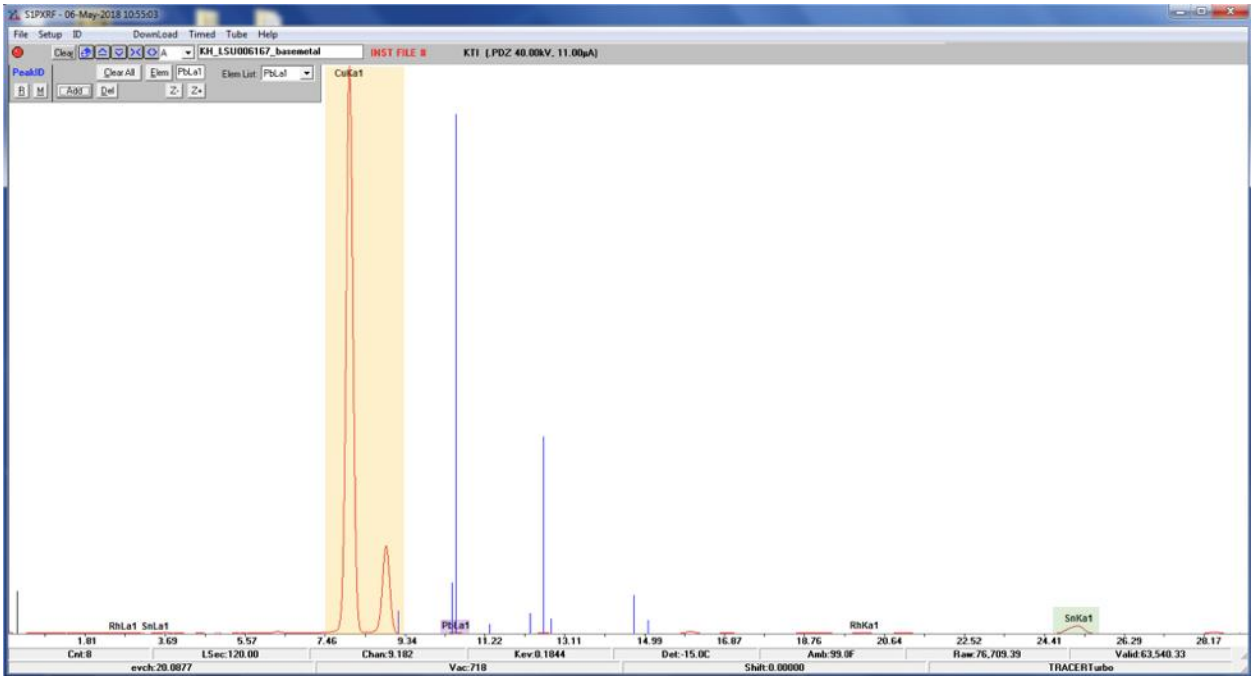


Figure 8. pXRF spectra indicating large peaks for copper (highlighted in orange), and small peaks for lead (purple) and tin (green).

X-Ray Diffraction

A small sample of powdery blue corrosion was obtained from the interior of the phiale (spot C3, Figure 6) for analysis via X-ray Diffraction (XRD). XRD is an analytical method for the identification of crystalline materials. A small sample is required, which is mounted on a glass spindle using Apiezon N grease. Analysis was completed using a Rigaku R-Axis Spider powder diffractometer, at setting of 50kv, 40 mA using a Cu-α target. Data was processed using Rigaku's 2D software. Diffraction patterns were identified using Jade 8.3, which contains a reference database from the International Center for Diffraction Data (ICDD). The material tested was identified as atacamite (one of the copper trihydroxychloride possibly associated with bronze disease) and calcite, which likely originates from the burial deposits.

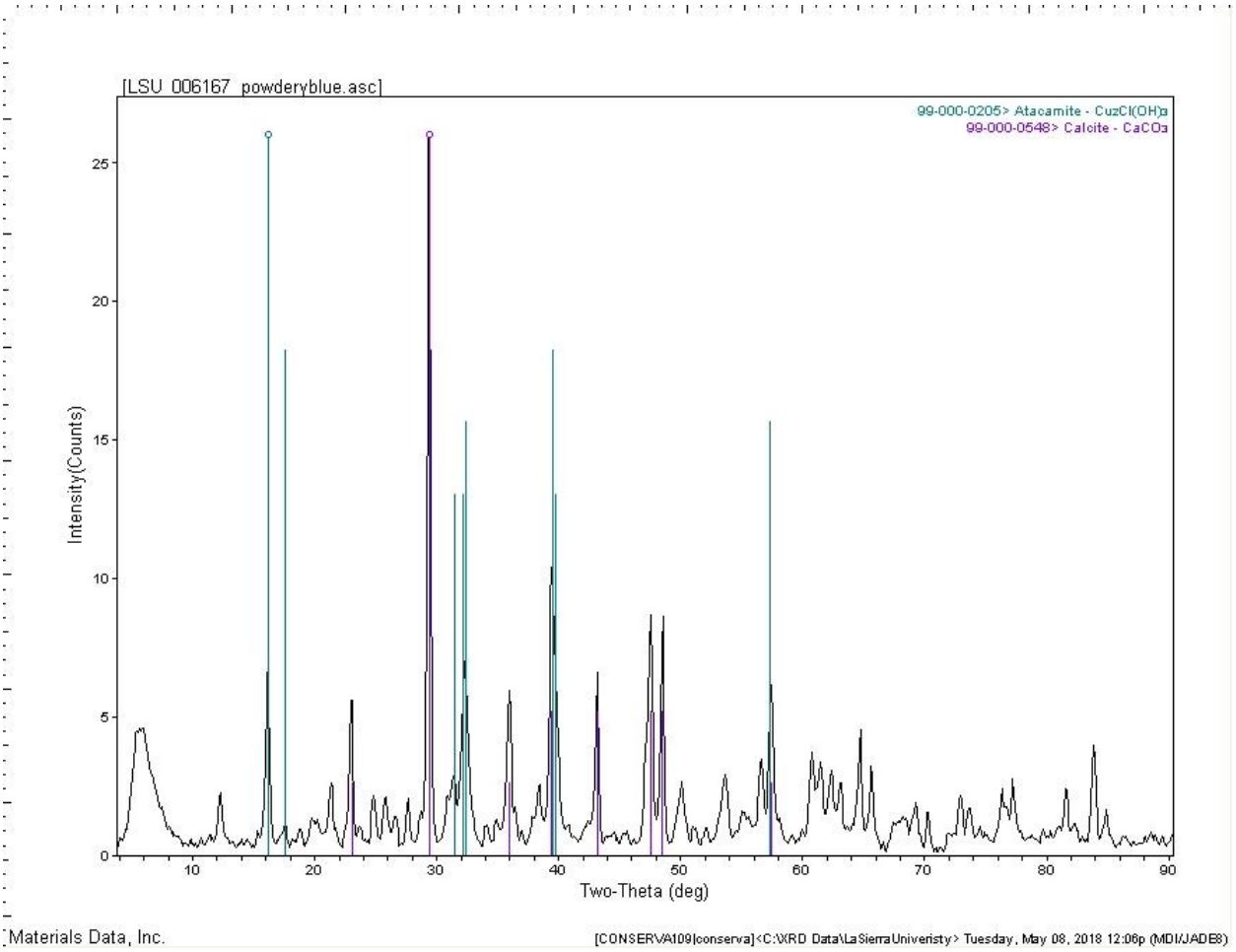


Figure 9. X-ray diffraction pattern obtained indicating presence of copper chloride corrosion (atacamite) and calcite.

Proposed Treatment:

1) Surface clean loosely adhered material using a brush and vacuum.
2) Remove residual wax from the bottom of the bowl using a microscalpel and appropriate solvents (ex: toluene) if necessary.
3) Mechanically clean corrosion products where possible in an effort to reveal the original form.
4) Determine whether or not there are any areas of active corrosion. If so, treatment with a corrosion inhibitor such as BTA or AMT may be recommended.
5) Create custom housing to safely store the object and to act as a buffer from environmental fluctuations.

Treatment:

An attempt to clean loosely adhered material was undertaken using a stiff brush – however it was discovered that the majority of soil was not loosely bound. Remaining wax was removed from the bottom of the bowl using a microscalpel. No solvent was used to further remove the wax, as any wax residues existed on the surface of compacted dirt that would be removed via mechanical cleaning.

Mechanical cleaning was undertaken using a scalpel with #15 blade under magnification. The primary objective of cleaning was to remove the beige burial accretions, revealing the dark green corrosion product underneath. Prior to cleaning, purple areas closer the base metal were visible, indicating the presence of a thin layer of cuprite beneath a thicker, dark green (likely malachite) layer. It was decided that cleaning down to the green layer was preferable, as the cuprite layer was extremely thin and easily abraded, leaving the base metal exposed.

Mechanical cleaning tests were conducted on areas of warty corrosion in order to further understand their morphology. The warts appeared to be composed of a voluminous, orange-red cuprite corrosion, covered with the same dark green corrosion layer previously described. Initial cleaning tests revealed that by removing the wart, the thin purple cuprite layer would be exposed. A later cleaning test on another wart lead to the discovery of nantokite beneath the voluminous cuprite corrosion, providing conclusive evidence of the presence of bronze disease. The findings of these cleaning tests lead to the decision not to remove the warts during cleaning, and confirmed the need for treatment using a corrosion inhibitor.

An initial scalpel cleaning removed the fine-grained, loosely bound burial deposits. The more compacted areas of soil presented some challenges. These compacted patches of soil were fairly well bound to the green corrosion layer, and the presence of small gaps between the cuprite and malachite layers contributed to a readiness for the green corrosion layer to spall off during cleaning. Air abrasion was investigated as an alternative cleaning method, and proved to be somewhat effective. 250 micron walnut shells were used as the blasting media, and cleaning was conducted using a pressure of approximately 80 ppi with powder flow 8-9. This method did allow for the removal of some of the more well bound soil, but did still present the risk of spallation.

Consolidation tests were performed to see if introduction of an adhesive (3% B72 in 1:1 acetone:ethanol) between the cuprite and green corrosion layers would provide strength and cohesion between the layers, reducing the risk of spallation during air abrasive cleaning. The

consolidant did not appear to significantly reduce the risk of spallation. Cleaning via air abrasion was carefully continued, avoiding areas where green corrosion layers had already spalled off, until no further soil could be removed at the above pressure and powder flow settings. Despite taking great care during cleaning, small areas of the green corrosion layer had spalled off, often quickly and without warning. In these areas, the cuprite layer remains intact. A final pass of scalpel cleaning was conducted in order to remove any remaining, large grained soil deposit, primarily remaining on the interior of the bowl.

A 0.1M BTA: 0.01M AMT solution in ethanol was selected for treatment, as it has been suggested that this treatment may produce slightly improved results than either corrosion inhibitor on its own (De Alarcón, 2013) due to AMT's effectiveness at low pH. The phiale was first degreased in acetone by immersion for 15 minutes. It was then immersed in the BTA:AMT solution and placed within a glass vacuum desiccator. A vacuum was pulled as the object was closely monitored for any vigorous bubbling which may lead to further spallation of corrosion layers. No bubbles were observed, and the object was determined to be safe under vacuum. The object remained immersed for one hour.

Once removed from the vacuum and BTA:AMT solution, the phiale was examined under magnification for traces of BTA crystals or yellow precipitate that would need to be removed prior to coating. AMT will sometimes form a yellow precipitate following reaction with exposed nantokite. The small area of nantokite that had been exposed during a wart cleaning test was examined, but no yellow precipitate had formed. After the surface had been examined, the phiale was coated by dipping in a 3% Incralac in toluene solution. Incralac is a coating developed for copper alloy objects, and is comprised of B-44 acrylic resin, BTA and a UV absorber. An air puffer was used to help speed drying and mattify the surface.

Custom storage housing was created for the object using single walled corrugated blue board. The bottom of the interior of the box was lined with Volara, and Ethafoam cut outs were inserted at the corners of the box. These cut outs were covered with Volara at points of contact with the phiale to minimize abrasion. The housing does not include a dessicating component, but if desired the entire box could be stored within a sealed bag, along with a dessicating material such as silica gel.

Ideally, the object should be stored in a low RH environment, no greater than 35% RH. Whether or not this is possible, the object should be continually monitored for any changes in

corrosion indicating active bronze disease. Although treatment involved a corrosion inhibitor, and the Incralac coating contains a corrosion inhibitor as well, monitoring is essential to ensure that the treatment has been successful.

The exposed nantokite present on the base of the object should be a good indicator as to whether there is active corrosion. Areas to monitor have been indicated in the attached condition maps of the object after treatment (Appendix III). These areas include both the exposed nantokite, but also the bumpy areas of corrosion. If bumps form in a new location or appear to spread, this would suggest the return of active corrosion. If any new areas of powdery blue-green corrosion form, this may also be evidence for active corrosion.

Materials list:
Walnut shells – 250 micron precision micro-abrasive powder, Part # PD1008-2. (Comco, Inc.)
Paraloid B-72 – ethyl methacrylate (70%) and methyl acrylate (30%) copolymer (Talas)
BTA – benzotriazole 99% (Sigma Aldrich Chemical Company)
AMT – 5-Amino-1,3,4,-thiadiazole-2-thiol (98%), Sigma Aldrich Chemical Company
Incralac – 17% solvent based solution (Conservation Support Systems)
Acetone – reagent grade (Fischer chemical)
Ethanol – alcohol, anhydrous, reagent grade (J.T Baker, Avantor Performance Materials)

Works Cited

De Alarcón, T. (2013) 'A Comparative Study of Corrosion Inhibitors for the Treatment of Archaeological Copper and Copper Alloys', *Anatolian archaeological studies*, (XVIII), pp. 109–119.

Melikian-Chirvani, A. S. (1993) 'The International Achaemenid Style', *Bulletin of the Asia Institute*, (May), pp. 111–130.

Odegaard, Nancy.; Carroll, Scott.; Zimmt, W. S. (2015) *Material Characterization Tests For Objects of Art and Archaeology.* Archetype Pubns.

Scott, D. A. (1994) 'An Examination of the Patina and Corrosion Morphology of Some Roman Bronzes', *Journal of the American Institute for Conservation*, 33(1), p. 1. doi: 10.2307/3179666.

Scott, D. A. (2002) *Copper and bronze in art : corrosion, colorants, conservation*. Los Angeles: Getty conservation Institute.

Appendix I: Reference Images, Achaemenid Metal Phialae

Bronze wine bowl, Achaemenid style and period. Iran, 6th – early 5th century BCE.
http://www.cais-soas.com/CAIS/Art/international_achaemenid_art.htm

Achaemenid bronze phiale, 6th century BCE

https://www.rubylane.com/item/1142333-1338368/Superb-Achaemenid-bronze-bowl-phial-ca

Achaemenid drinking bowl, copper alloy, 500 – 350 BCE

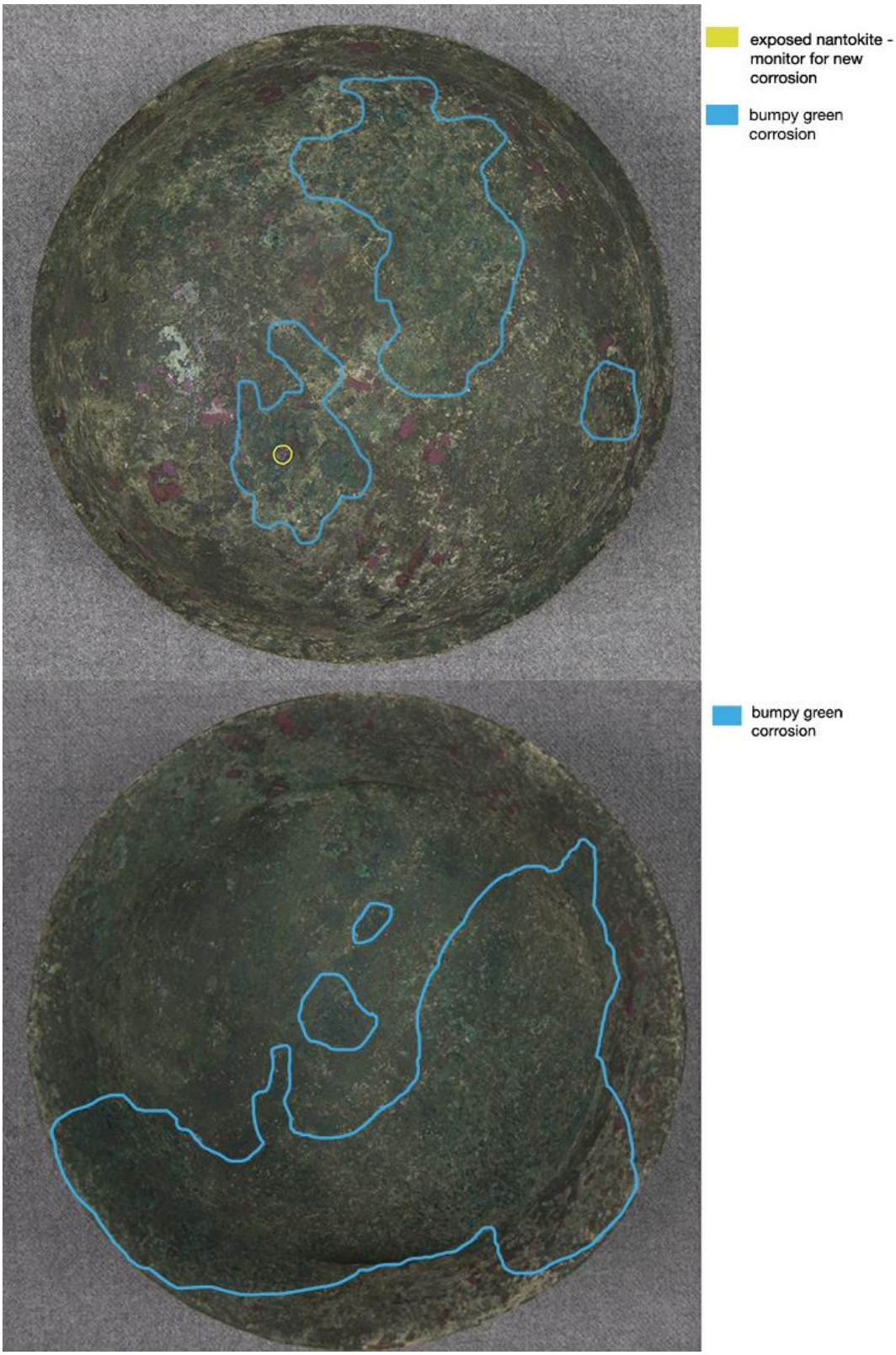
https://collection.britishmuseum.org/resource/?uri=http%3A%2F%2Fcollection.britishmuseum.org%2Fid%2Fobject%2FWCO25518

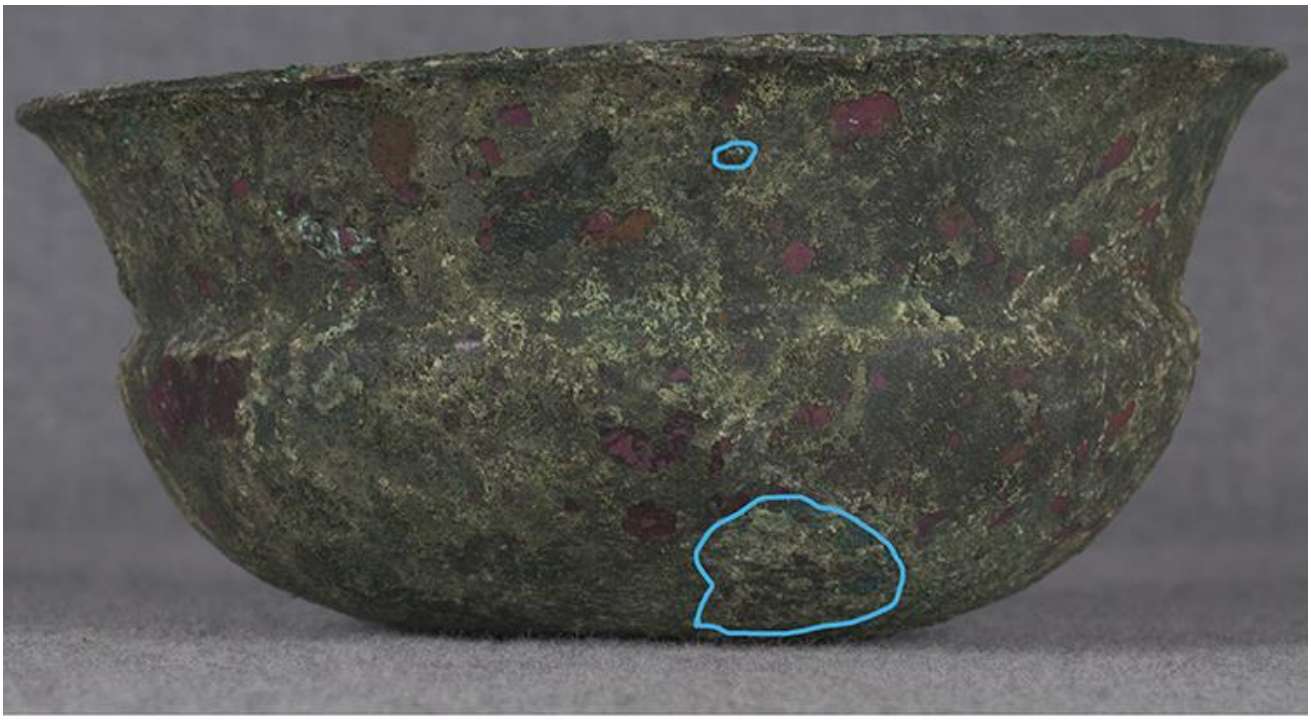
Achaemenid bronze bowl with lotus leaf pattern, ca. 500-320 BCE.

https://www.pegasusgallery.co.uk/products/an-achaemenid-bronze-phiale-with-lotus-design

Appendix II: Before (left) and After (right) Treatment Photographs

Appendix III: Condition Maps (AT photos), Areas to Continue Monitoring





bumpy green corrosion

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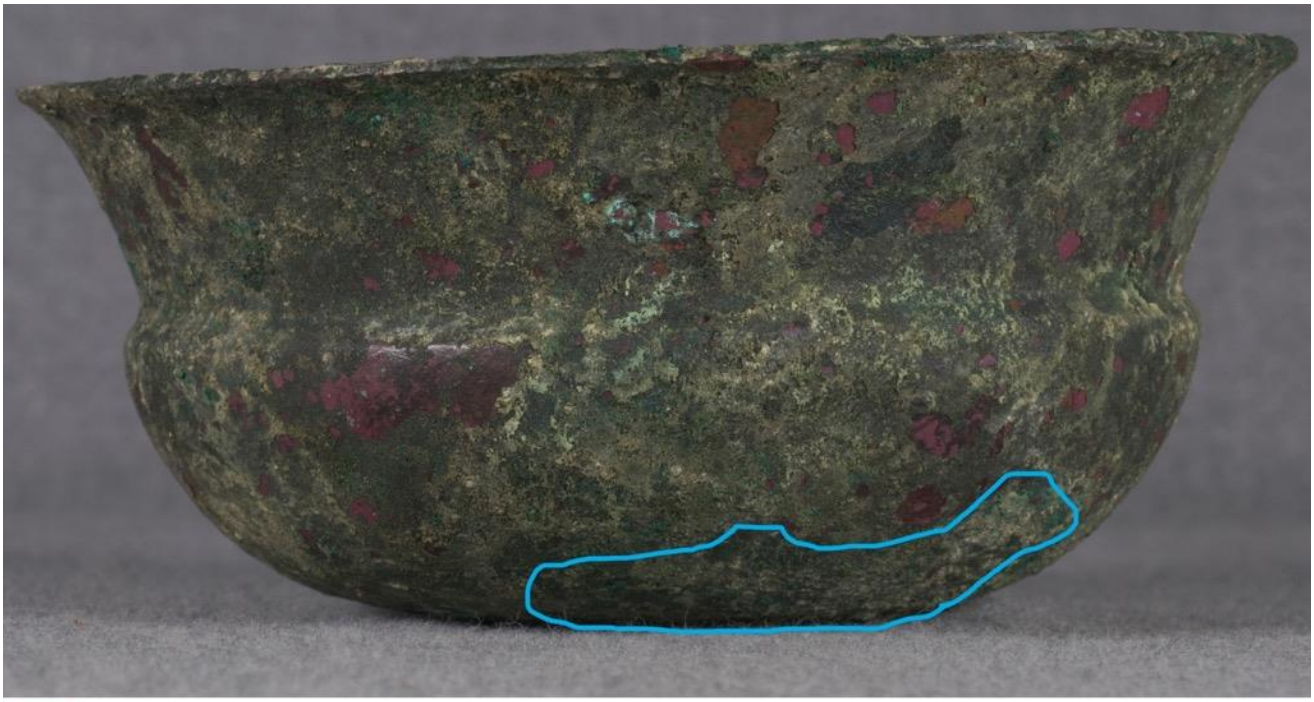

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