APPENDIX 5

Archaeo-metallurgy: 49-SIT-963

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1. Analysis and Metallography of Copper Sheet from Sitka, Alaska (#R5032)
2. Analysis and Metallography of Copper Sheet fragments from the NEVA Survivors' Camp (#R5032/5284-85)
3. Analysis and Metallography of Copper 1 *Kopek* Coins (#R5253-59)

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1. Analysis of Metal Artifacts from Suspected Neva Survivor Camp

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By
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Introduction

The *Neva* was built in England in 1800, originally named the Thames, and sold to Russia in 1803 and renamed. The ship weighed 372 tons and measured 110' 6" in length. The ship's hull was sheathed in copper around the time it was sold to Russia. On January 9th, 1813, the *Neva* ran aground and sank on its way to Sitka, Alaska, less than 100 miles from its destination. Twenty-eight of the original 73 crew and passengers made it to shore and established a camp where they lived for nearly a month before being rescued (McMahan 2016). Excavations were undertaken at SIT-00963, the location believed to be the *Neva* survivor's camp in 2015 and 2016. Several features were excavated and numerous historic period artifacts were recovered including copper nails, copper sheet, lead musket balls, gun flints, iron axe heads and other metal artifacts of either iron or copper (McMahan 2017). A collection of 13 individual pieces of metal corresponding to 8 separate catalog numbers (Tables 1 and 2, Figures 1-10) recovered from this site were forwarded to Purdue University and analyzed using a combination of x-ray fluorescence, optical microscopy, and scanning electron microscopy, for basic materials identification, and if possible, determine whether these materials are likely to be associated with an early 19th c. shipwreck.

Figure 1. UA2015-237-0271 nautical instrument/carpenter's divider leg.

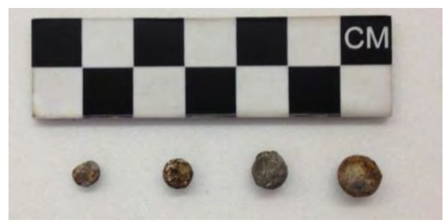

Figure 2. UA2015-237-260 lead shot.

Figure 3. UA2016-063-026 chape (scabbard tip).

Figure 4. UA2015-237-88 triangular copper fragment.

Figure 5. UA2015-237-87 copper sheet (microscopy sample).

Figure 6. UA2015-237-93 copper sheet.

Figure 7. UA2015-237-196 copper sheet.

Figure 8. UA2016-063-078 copper sheet fragment (microscopy sample). Fragment 1 in Table 1.

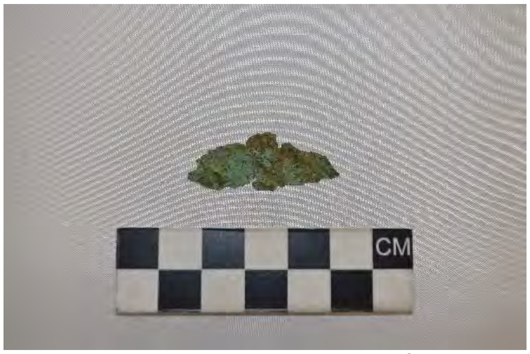

Figure 9. UA2016-063-078 copper sheet, fragments 2 and 3 in Table 1.

Figure 10. UA2016-063-078 copper sheet, fragment 4 In Table 1.

Methods

X-Ray Fluorescence

After initial inspection of artifacts the next step in analysis was acquiring compositional data non-destructively. To accomplish this a hand-held (portable) Bruker Tracer III-SD x-ray fluorescence (PXRF) spectrometer with rhodium target x-ray tube and silicon drift detector was used to determine major and minor elemental concentrations. All readings were taken using an Al Ti filter at 40 keV and 10mA for 100 seconds with the instrument in desktop configuration with small sample table. This allowed each artifact to be placed directly on top of the x-ray window where the beam spot size is 6 x 8 mm. The quantitative results shown in weight percent in Table 2 were determined using a custom-made calibration file created by Robert Speakman (University of Georgia, Center for Applied Isotope Studies) and Cooper, composed of 62 copper and copper alloy standards. Artifacts were not cleaned prior to analysis.

Microscopy

Two copper sheet fragments (UA2015-237-87 and UA2016-063-078) were examined microscopically using both optical microscopy and scanning electron microscopy. Sample preparation required the removal of a small piece (< 1 cm square) from each artifact using pliers. Samples were then hot mounted using bakelite at a temperate of 150°C. Mounted specimens were then polished using a progression of course to finer grits starting at 400, then 600, 800, 1200, 2000 and finishing with diamond paste. Samples were polished for 30 seconds at each step and washed thoroughly with soap and water between each polishing step. Samples were then soaked in an etchant consisting of 50% distilled water and 50% Nitric acid for 30 seconds in order to highlight metal grain boundaries. Because the copper artifacts were extremely thin, a proper polishing cycle was not possible to prevent grinding off the entire sample.

Discussion of Results

X-Ray Fluorescence

XRF is essentially a surface characterization technique best suited for bulk compositional analysis where the analyzed surface does not differ significantly from the inner portion of the object because the x-ray beam penetrates from a few microns to a few millimeters depending on the sample (Dussubieux and Walder 2015; Smith 2012). Additionally, corrosion processes post-deposition can result in localized depletion and by default, on the surfaces of copper alloy metals. Analyses of historic brasses from archaeological contexts using laser ablation- inductively coupled plasma mass spectrometry, scanning electron microscope electron dispersive spectroscopy (Dussubieux et al. 2007), and instrumental neutron activation analysis (Moreau and Hancock 1999) have noted that corroded surfaces were significantly depleted in Zn, a process known as dezincification.

Because these artifacts have a patina and in some cases are partially corroded, and were analyzed without cleaning, the results of surface analysis regardless of how precise may not accurately reflect the original composition of the object. However, all of the copper artifacts analyzed, except for the chape are relatively thin, especially the sheet fragments which are <1 mm thick. For these thin artifacts the penetration of x-rays goes through the entire artifact. Our results (Table 2) are useful for identifying the presence of relatively pure copper and copper alloys in this collection of material.

The copper looking artifacts analyzed here are essentially pure (un-alloyed) copper, except for two. UA2015-237-93 stood out from other copper sheet fragments in that it had nearly 4% lead. Even with the difficulty accurately quantifying lead no other sheet copper fragments had more than 0.11 wt % lead. Otherwise the composition of all of the sheet copper fragments was similar. UA2015-237-88, described as a possible knife tip, has essentially the same composition as the thinner sheet copper specimens. This pointed fragment was either part of a larger object made of copper similar to that of sheet copper in composition, or it might be an ad hoc tool fashioned out of copper sheet by survivors of the wreck. The four pieces of shot were analyzed and confirmed to be lead (see Fig. 11).

The other artifact that is not pure copper is the scabbard chape, which is a quaternary alloy consisting of mostly copper but with appreciable amounts of lead, zinc, and some tin. Such alloys have been commonly used in Europe since the Middle Ages for a variety of decorative work (Day 1998). The chape also shows a high level of iron and the presence of manganese. The presence of both elements have been associated with the use of calamine or smithsonite, carbonate ores of zinc, in the production brass (Carradice and Cowell 1987, Pollard and Heron 1996). However, the iron results for the chape are too high (7-8.5%) to be accounted for entirely by its presence as an accidental impurity. In a study of 27 Roman military copper-alloy artifacts from Israel the iron content of brass was generally much less than 1% with a single specimen having 1.7% (Ponting 2002). The high iron results here are most likely a result of the object having been analyzed without cleaning.

The problem with accurately and precisely determining the composition of this particular object is due in part to the large quantity lead. Because lead does not dissolve when alloyed with copper (Scott 1991) it will be present in the final alloyed product as globules, which makes characterization from one or even two analyses difficult.

Additionally, the calibration file used to convert spectral data to weight percent data is lacking in standers with high amounts of lead. As a result, although the lead results in this study are off, which in turn leads to the results for other elements being off as well, we are confident in identifying this has a quaternary alloy (Cu-Pb-Zn-Sn), or heavily leaded tin brass.

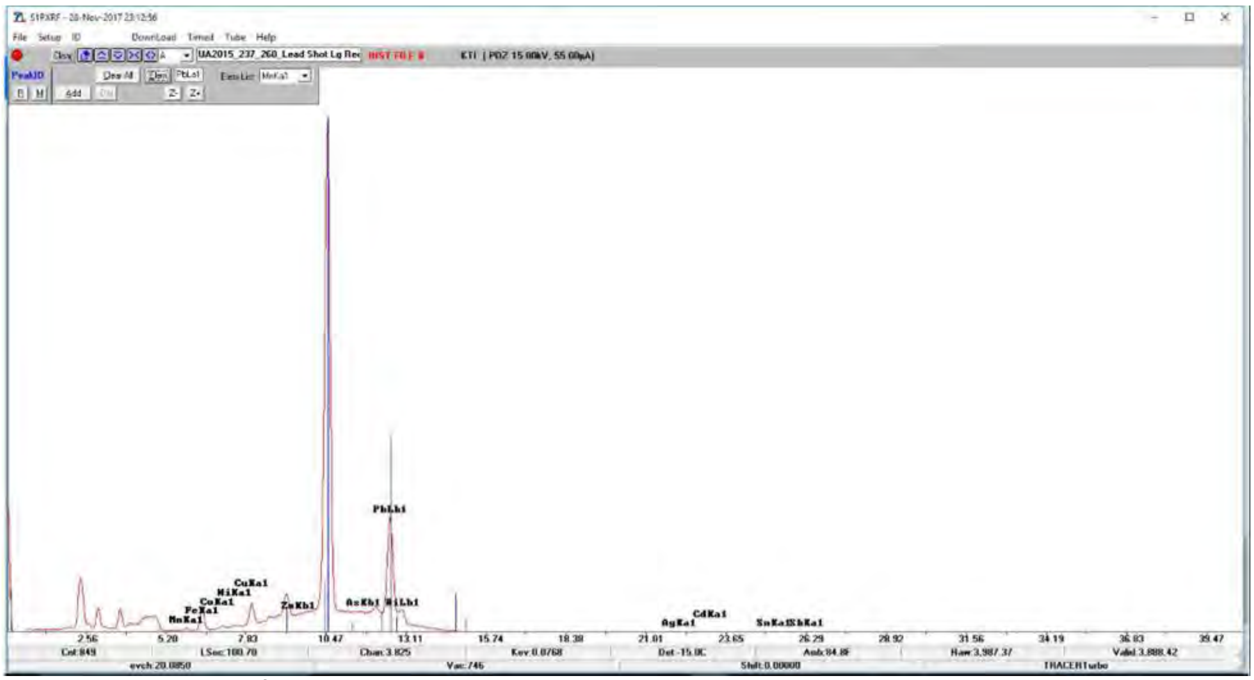

Figure 11. PXRF spectrum for lead shot.

<u>Microscopy</u>

The as-polished surface of both samples viewed using optical microscopy display pitting and larger areas of corrosion. Sample UA2016-063-078 exhibits an equiaxed grain structure without a specific orientation and annealing twins (Figure12). Etching heavily corroded much of sample UA2016-063-078. As a result only sample UA2015-063-87, which was slightly thicker, was additionally viewed using scanning electron microscopy. This analysis corroborates the initial finding of both fragments have a microstructure consisting of equiaxed copper grains with no specific orientation, and both show evidence of annealing twins (Figure 13).

This combination of equiaxed grains and annealing twins provides evidence of annealing. Annealing is a heat treatment where a metal is heated to an elevated temperature for an extended period of time to relieve stored stresses and increase ductility for better formability purposes. Annealing twins are formed during cooling as individual metal grains regrow and reorganize into a more stable crystal structure. The implications of these finds will be discuss below.

The microstructure in samples UA2016-063-078 and UA2015-063-87 is comparable to what was found by De Rosa et al. (2015) in their analysis of brass ship sheathing, which was formed into sheets in a rolling mill. Though their sample was sheet brass, both it and our sample were formed similarly, as copper and copper alloy sheet was manufactured with the use of rolling mills in the 18th and 19th centuries, whether rolled cold or hot. However, the brass sheathing analyzed by De Rosa and colleagues was most likely formed through a combination of slow rolling and low heat (Jones 2004:98-99). As hot rolling copper results in annealing twins (Mishin et al. 1997), the two copper sheet samples examined were potentially hot rolled, although cold rolling cannot be ruled out.

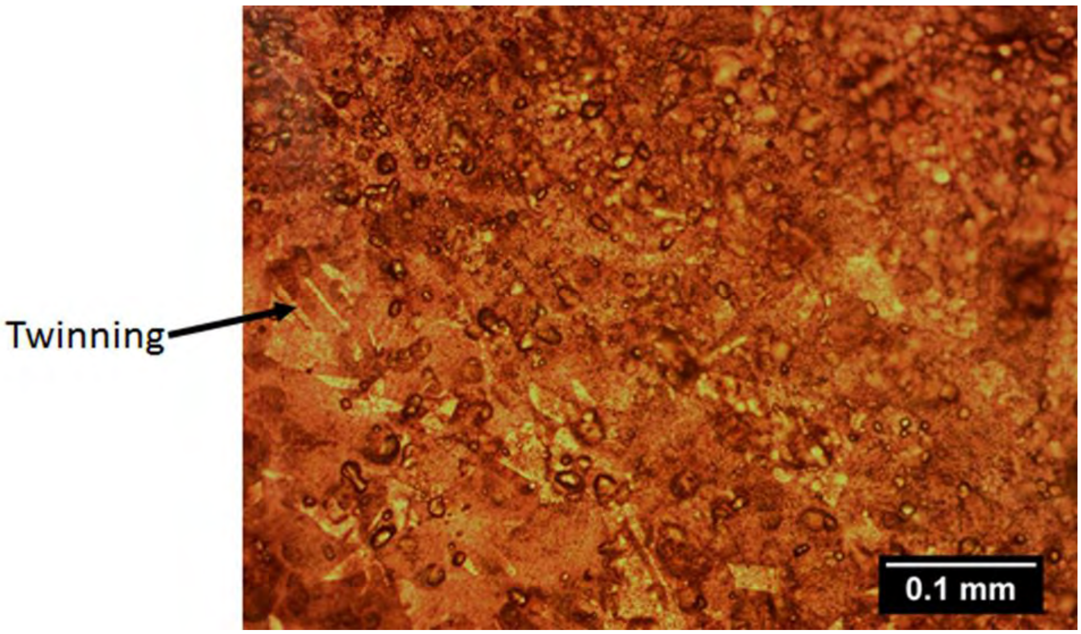

Figure 12. Optical microscope image of UA2016-063-078 (fragment 1) after etching. An equiaxed grain structure is seen as well as annealing twins.

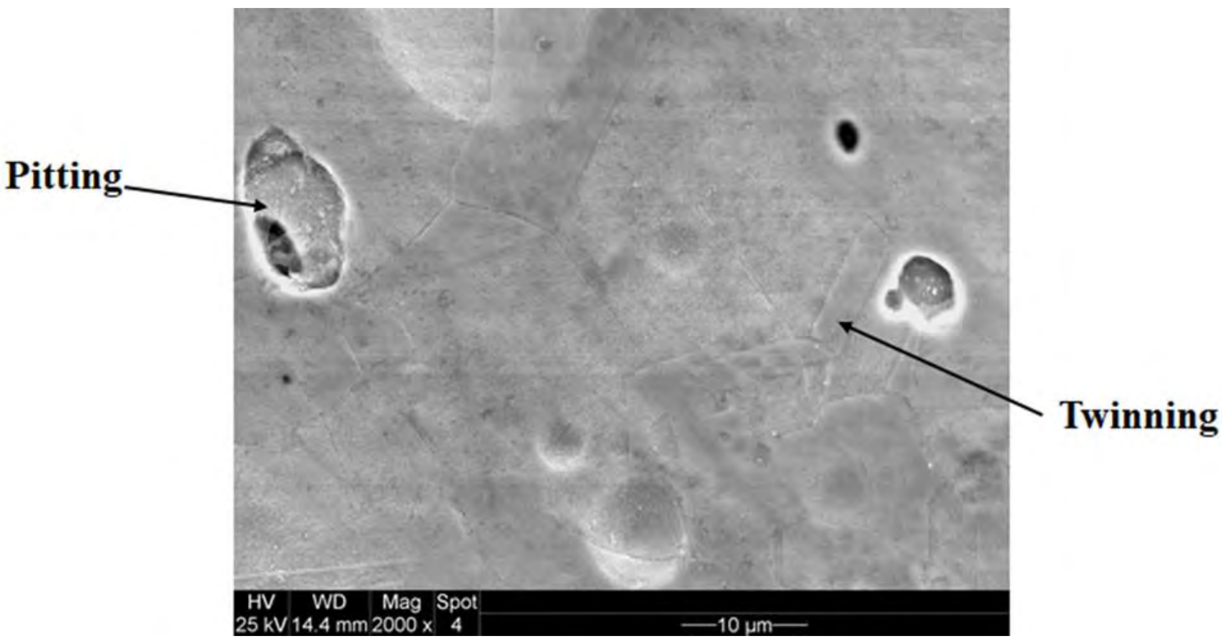

Figure 13. Scanning electron microscope image of UA2015-237-87 copper sheet fragment 2 at 2000x.

Notes on Copper Sheathing

The use of metal, specifically lead, to sheath wooden sailing vessels goes back at least 2000 years in the eastern Mediterranean. Lead was also used on Spanish ships in the early 16th century and this innovation had reached England by the middle of that century. The use of lead sheathing was officially approved for the Royal Navy by an Act of Parliament approximately 100 years later in 1670. The use of lead sheathing was finally halted in 1770. Experimentation with copper sheathing by the British Royal Navy and others begun in the early 18th c. After the notably successful experiment in copper sheathing conducted using the British Royal Navy's *Alarm* it became common in the ship building industry (Bingeman 2000).

Copper sheathing prevented structural damage caused by wood boring worms and also decreased the drag caused by barnacles and seaweed thereby increasing speed and maneuverability. Its use increased rapidly during the decades after its introduction as metallurgical innovations resulted in improved metal alloys for both sheathing and fasteners (Bingeman 2000; Knight 1973). Muntz metal, patented by George Muntz of Birmingham, England in 1832 specifically for sheathing the hulls of wooden ships was a brass with an stated ratio of 60:40 Cu:Zn, though the actual could vary from 63:37 to 50:50. Muntz metal was more commonly used after 1850 (Day 1991). Analyses of eighteenth and nineteenth century sheet copper used for ship sheathing demonstrate that relatively pure copper with 99%–100% copper by weight were commonly used (Craddock and Hook 1990; Atauz et al. 2006).

As noted in by Bingeman and colleagues (et al. 2000) a ship might have sheathing with a variety of compositions due not just to variation in composition of copper products, but also because it was common to remove a sheet of copper once it became wasted, but not to replace all of the plating. As a result, at any given time a ship might have sheathing of a variety of different compositions. Notably, there were no high Zn, i.e. brass examples found in the copper sheet material analyzed here.

Conclusions

A collection of metal artifacts were analyzed using a combination of techniques resulting in the material identification of four pieces of lead shot, three relatively pure copper sheet fragments, a triangular copper point, one sheet fragment of leaded copper, a copper carpentry or nautical measuring instrument, and a leaded tin brass scabbard chape. While the analyses described here cannot by themselves prove or disprove the identity of the site in question as that of the *Neva* survivor's camp, the composition of these metal artifacts is consistent with what would be expected from an early 19th c. European sailing vessel.

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Table 1. Artifact Data.

Artifact ID	Object	Wt. (g)	L (cm)	W (cm)	H/Thick (mm)	Notes
UA2016-063-026	chape (bulb)	4.8	3.1	.8		
UA2016-063-026	chape (flat portion)				1.1	
UA2016-063-078 (fragment 1)	sheet	0.4 (post sampling)	2.6	1.4	0.29	From Bag: " COPPER SHEET FRAGMENT (Sheet 4 of Neva Cache) (MDN) 31cm B.S. (in situ) DRT 7/16/16 *sample for microanalysis sent 5/25/2017 - DRT (n=1)
UA2016-063-078 (fragment 2)	sheet	0.3	2.2	1	0.35	From Bag: "MD-N (Shipwreck Cache) Copper Sheet 4 Fragments - 31 cm BS. (n=2), A in Stow and Harland assignment, 1 of 2 pieces broken (possibly after shipping to Purdue, larger of two A fragments
UA2016-063-078 (fragment 3)	sheet	0.3	1.6	1	0.39	From Bag: "MD-N (Shipwreck Cache) Copper Sheet 4 Fragments - 31 cm BS. (n=2), A in Stow and Harland assignment, 1 of 2 pieces broken (possibly after shipping to Purdue, smaller two A fragments
UA2016-063-078 (fragment 4)	sheet	0.4	2.9	0.7	0.47	From Bag: "MD-N (Shipwreck Cache) Copper Sheet 4 Fragments - 31 cm BS. (n=2), long thin piece, F in Stow and Harland assignment
UA2015-237-87	sheet	0.2 (post sampling)	1.8	0.4	0.77	
UA2015-237-88	triangular point	1.8	3.6	0.06	1.83	
UA2015-237-93	sheet	1.2	2.5	1.1	0.83	
UA2015-237-196	sheet	0.3	2.3	0.4	0.63	
UA2015-237-0271	divider leg	12.1	11.9	0.4	3.61	
		Wt. (g)	**Dia. (cm)**			
UA2015-237-260	shot	0.5	0.513			lead
UA2015-237-260	shot	1	0.566			lead
UA2015-237-260	shot	1.9	0.654			lead
UA2015-237-260	shot	2.5	0.849			lead

Table 2. pXRF results.

Artifact ID	Mn	Fe	Co	Ni	Cu	Zn	As	Pb	Bi	Ag	Cd	Sn	Sb	Material
UA2016-063-026	0.17	7.27	-6.75	-0.03	82.94	7.32	-0.89	17.93	-1.00	0.04	0.09	1.10	0.17	quaternary alloy/leaded tin brass
UA2016-063-026	0.5	8.50	-43.42	0.81	94.66	6.38	-2.21	12.55	-0.65	0.48	0.28	0.45	0.39	
UA2016-063-078 (fragment 1)	0.00	0.08	0.02	0.04	97.50	0.14	0.54	-0.17	0.11	-0.06	-0.03	-0.03	-0.02	copper
UA2016-063-078 (fragment 2)	0.00	0.13	0.02	0.06	96.86	0.14	1.04	-0.14	0.15	-0.07	-0.02	-0.02	-0.00	copper
UA2016-063-078 (fragment 3)	-0.00	0.18	0.02	0.07	96.61	0.12	0.98	-0.14	0.19	-0.05	-0.02	-0.02	-0.00	copper
UA2016-063-078 (fragment 4)	0.01	0.64	0.04	0.05	95.64	0.11	0.13	-0.22	-0.02	-0.11	-0.03	-0.05	-0.02	copper
UA2015-237-87	0.00	0.04	0.01	0.04	97.84	0.12	0.36	-0.15	0.02	-0.12	0.02	0.01	0.01	copper
UA2015-237-88	0.02	0.46	0.04	0.15	96.07	0.11	0.09	-0.19	-0.02	-0.10	-0.03	-0.04	-0.04	copper
UA2015-237-93	0.00	0.26	0.03	0.04	91.87	0.16	0.72	3.86	0.09	-0.14	0.00	-0.01	0.00	leaded copper
UA2015-237-196	0.01	0.38	0.04	0.10	96.10	0.07	0.16	0.11	0.00	-0.09	-0.02	0.00	-0.01	copper
UA2015-237-0271	0.00	0.05	0.01	0.09	97.94	0.12	0.16	-0.21	-0.02	-0.05	-0.03	-0.05	-0.02	copper