

PRELIMINARY STUDIES OF SOME BASE AND PRECIOUS METALS FROM THE *QUEEN ANNE'S REVENGE*

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ABSTRACT

Metal-bearing artifacts recovered from the wreck site of the *Queen Anne's Revenge* have been subjected to various oxidizing and reducing conditions during the nearly 300 years that they lay on the sea floor. The base metals respond to these conditions by forming corrosion layers of oxides and hydroxides under oxidizing conditions and layers of sulfides under reducing conditions. These phases alter the surfaces of the metals but also then serve as protective layers that preserve the underlying metal from further corrosion or dissolution. The precious metals are represented by numerous small placer gold grains that have been recovered. They contain gold-rich rims that are characteristic of a placer origin, but it is not yet possible to determine the site of original extraction. Preliminary lead isotopic data confirm a European/Mediterranean origin, consistent with the ship having been constructed in France.

INTRODUCTION

Recovery efforts from the first several seasons of work on the *Queen Anne's Revenge* (*QAR*) site, have yielded an array of artifacts, many of which are composed in whole or in part of base and precious metals (Lusardi, 1999). The pieces themselves aid in interpreting the activities on board the ship, help to trace the course of its journey, and may assist in confirming the identity of the ship as the *QAR*. The metals of which many artifacts are composed may offer other useful information including the localities from which metals were initially extracted, the conditions under which the artifacts have lain for nearly 280 years, and some general, but potentially widely applicable, data on the corrosion/ preservation of metal artifacts. Certainly, characterization of corrosion products is an important initial step in planning the procedures to be employed in conservation efforts.

Only a very small proportion of the metal artifacts of the *QAR* have been retrieved, and as many as one million separate items may ultimately be recovered. Samples already available

range over the length and breadth of the wreck site and have been found from the surface of the sediment to depths of approximately five feet in the sediment. They range from iron barrel hoops, anchors, and nails, to brass nautical devices, to lead shot and stripping, to pewter plates and a syringe, to gold grains. Hence, the metal artifacts are probably representative of most of the materials that will ultimately be excavated. Recognizing that this is only a preliminary report, the authors do feel that the observations reported here (and briefly given in some oral presentations, Craig and others 2000) will remain valid and may help in the study and interpretation of artifacts yet to be recovered. Some of the observations made here should be applicable at other sites because the conditions of burial at the QAR site are similar to those at many other shipwreck sites.

BASE AND PRECIOUS METALS AT THE QAR SITE

The discovery and recovery of metal-bearing artifacts at underwater wreck sites is always fortuitous and always subject to the vagaries of the waters in which they reside. In contrast to some mineralogical and geological studies where one can plan and conduct orderly investigations based on expected directions of water or earth movement, submarine wreck sites are haphazard jumbles of materials whose original spatial arrangements can only be surmised after artifacts have been carefully recorded, recovered, cleaned (sometimes this is not useful from the mineralogist's perspective), studied, and interpreted. The wreck site has been sampled from the outside (top and flanks) inward so that materials are not damaged or allowed to move or corrode unnecessarily. Thus there is always the possibility that deeper parts of the debris mound may contain some specific materials that were held in unique sites on the vessel or contain materials that have been subjected to a different set of preservation conditions than those on the top. At the time of this manuscript preparation, the metal-bearing objects recovered include the following:

Iron - cannon, barrel hoops, nails - range from

well preserved to completely converted to hydroxides

Copper — small pieces of sheeting, alloyed in brass, and in some pewter

Zinc — in brass surveying and map reading instruments

Lead — shot of various sizes, sheets to reduce leaks in hull, small tack-like nails,

Tin — pewter plates in a variety of sizes, medical syringe

Mercury — alloyed with gold and silver in ornamental clasps, inside a medical syringe

Gold — small free grains, small ornamental clasps

Silver — alloyed with gold in small ornamental clasp

All of the samples were likely subjected to varying conditions of oxidation and reduction while they lay buried in the sediments near Beaufort Inlet for nearly 280 years. The metals may act as geochemical indicators of the conditions within the sediments by developing different kinds of surficial corrosion minerals. Under oxidizing conditions, copper or lead may form oxides or hydroxides, whereas, under reducing conditions, these metals readily form sulfides. Whether the surficial corrosion phases remain of one type or shift back and forth as the result of changing oxidation - reduction conditions, the corrosion phases generally serve valuably as an "armor" protecting the underlying metal. For example, metallic lead is moderately soluble and would dissolve away if long exposed to fresh or saline waters. However, the surficial coatings of the hydroxycarbonate, hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) that form under oxidizing conditions or the sulfide galena (PbS) that form under reducing conditions, provide protection. The solubility of the corrosion phases are nearly always very low - otherwise they could not form - and therefore they serve as very effective protective capsules. The brief discussions and the illustrations presented below are restricted to the base and precious metals and are intended to give "snapshots" into the natures of the base and precious metal-bearing phases and the types of minerals forming as a result of the corrosion. The discussion attempts to be broad but not detailed nor complete.

BASE METALS

Lead

Lead is widespread at the *QAR* site in the form of lead shot ranging from approximately 2 mm to more than 20 mm in diameter (Figure 1).

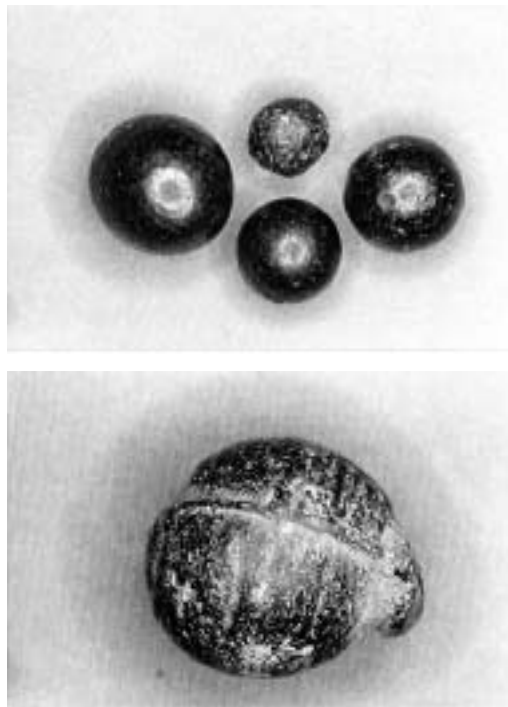


Figure 1. Lead shot recovered from the wreck site of the *QAR*. (a) 2 to 4 mm shot of the type found widely dispersed at the wreck site. (b) An 8 mm lead shot on which is clearly visible the mismatch of a two part mold.

In portions of the *QAR* site, distinct horizons consist almost entirely of scattered lead shot. In some of the buried portions of the site, the lead shot and the interstitial sand are cemented into solid masses (Figure 2). Lead is well known for its ability to persist in marine environments and has a long history of recovery from wrecks more than 2000 years old in many parts of the world. The lead at the *QAR* site reveals two different modes of corrosion. Under oxidizing conditions, the lead rapidly begins to form an oxide and then to form the hydroxycarbonate, hydrocerussite. This phase occurs on the surfaces of many grains as randomly oriented platelets



Figure 2. Cemented mass of lead shot and interstitial sand. This material has been extracted as solid masses which are cemented by a mixture of lead oxides, hydroxides, and sulfide (See also Figure 5).

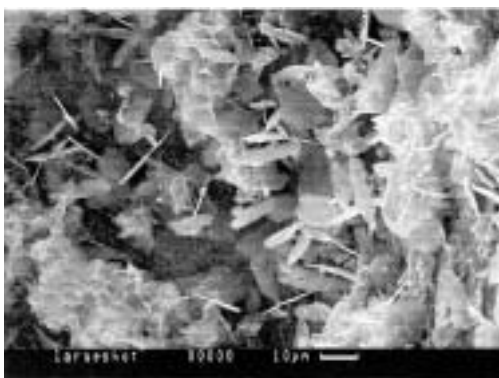


Figure 3. Plate-like crystals of hydrocerussite that have formed by reaction of a grain of lead shot with sea water. Once this surface forms, the underlying lead is protected from further reaction with the sea water.

as shown in Figure 3, but may also occur as beautiful sphere-like masses as shown in Figure 4. Under the reducing conditions preserved at depth in the sediments, the release of sulfur by sulfate reducing bacteria allows for the formation of galena (PbS). The piece of lead shot shown in Figure 5 has thin coatings of lead oxide and hydroxycarbonate overlain by a zone in which the galena resides interstitially among blades of aragonite. All of this was over-grown by thin layers of pyrite (FeS₂) which is also present as small necklace-like beads around many quartz grains. The combination of galena, pyrite, and aragonite needles serve to cement the masses together as is visible in Figure 2.

Tin

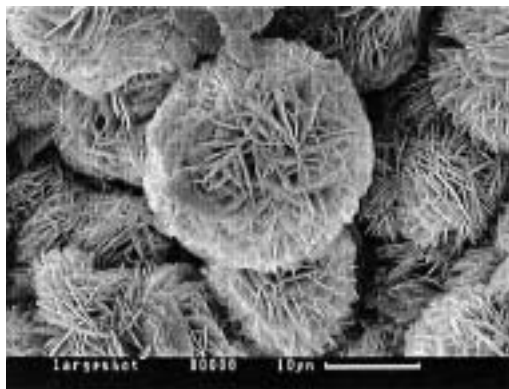


Figure 4. A sphere of hydrocerussite platelets that has formed along a margin where the lead shot molds did not match perfectly (see Figure 1b). The mismatched edges provided protection during recovery and handling of the specimen.

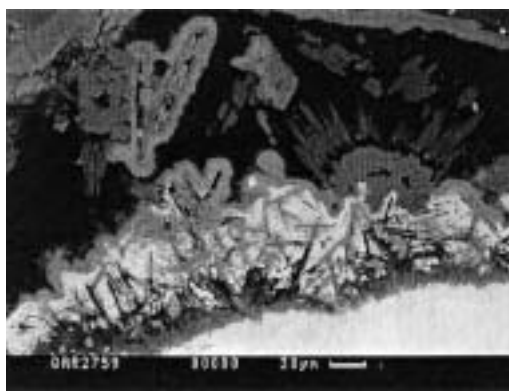


Figure 5. Back scattered scanning electron image of the margin of a lead shot grain from a cemented cluster as shown in Figure 2. There is a narrow zone of lead oxide and hydroxide overlain by a zone with galena interstitial to aragonite needles. This is all overgrown by a layer of pyrite. The various layers and the interlocking texture have cemented the mass together.

There is, of course, also the potential of using the lead isotopic ratios in determining the provenance of the metal. Preliminary data available, courtesy of A.K.Sinha, are consistent with lead sources in Europe and the Mediterranean as would be expected from the *QAR*.

Tin has found extensive use over the past several thousand years because it resembles silver, has been relatively inexpensive, is easy to work, and is reasonably resistant to corrosion under normal conditions. Pewter is basically a tin-based alloy but may contain varying amounts of a variety of metals. Early pewters commonly contained significant amounts of lead, but this was largely phased out by the late 1600s. The other most common metal in pewter is copper which may range from traces to tens of percents. Pewter artifacts from the *QAR* include several sizes of plates and a medical syringe.

Most of the plates reveal no knife marks and several contain impressions that appear to have been formed by enclosing burlap bags. Accordingly, it is believed that most of these plates were not actually in use but rather were being carried for barter or sale. Some of the plates bear legible hallmarks indicative of manufacture in London near 1700; the provenance of others is unknown. The plates display variable behavior during burial in that some were completely folded over, whereas others apparently broke in a brittle manner instead of bending. The pewter objects are generally only lightly corroded and are readily recognizable when recovered, in contrast to iron objects that are commonly completely encrusted with oxides and carbonates. Preliminary electron microprobe analysis of some small representative fragments of the pewter plates reveal that some plates are nearly pure tin whereas others contain 10 or more percent copper. In these latter samples, the copper is not uniformly dispersed but rather occurs as irregular clots (up to 10s of microns across) within a matrix of tin. We do not yet have sufficient data to be able to correlate the malleability of brittleness of the plates with specific textures, but it is likely that some chemical or textural difference controls the behavior. The tin of the pewter apparently slowly reacts with sea water forming thin black sooty layers of tin oxides, hydroxides, and chlorides commonly referred to as “tin pest” (North and MacLeod, 1987). Preliminary data reveal numerous small scale complexities that will be addressed in a

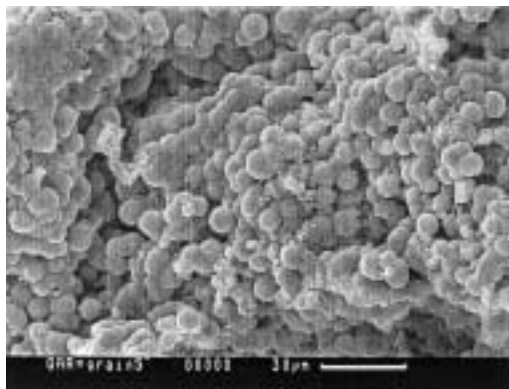


Figure 6. Botryoidal mass of tin sulfide (believed to be herzenbergite, SnS) that formed inside a pewter medical syringe. Sulfur produced by sulfate reducing bacteria reacted with the tin of the pewter in the confines of the syringe to produce a crust of sulfide.

later paper.

The pewter syringe has yielded some interesting tin sulfides (Figure 6) and some mercury (discussed below). The presence of the tin sulfides indicates very reducing conditions, at least in the interior of the syringe. The sulfur is believed to have been generated by sulfate reducing bacteria in the sediment, and the tin presumably came from the interior of the syringe. The small botryoidal tin sulfide masses have not yet been specifically identified but other corroded samples of the pewter have been found to contain small amounts of herzenbergite (SnS); accordingly, we believe that these masses are also herzenbergite.

Mercury

Although no specific mercury compounds have been identified, mercury concentrations of up to 10,000 parts per million were found in the sediment that was extracted from the syringe. The use of mercury compounds to treat a variety of medical conditions in the early 18th Century is well documented. Hence, we believe that the mercury may be a residual material left from medical treatments that were administered with the syringe.

Copper

Most of the copper at the *QAR* site occurs in the form of brass which exhibits the typical development of a greenish patina as expected in the marine environment; this material has not been studied in detail as yet. Some small pieces of copper sheeting of unknown use have been recovered. The copper has been oxidized along the margins and has apparently been corroded to form copper oxide (probably cuprite, Cu_2O).

PRECIOUS METALS

Gold

Gold has been found as free grains in the sediment of the *QAR* site and in one small metal clasp. Approximately 100 loose gold grains (Figure 7a) ranging from less than 1 to 10 mm have been recovered to date at the *QAR* site.

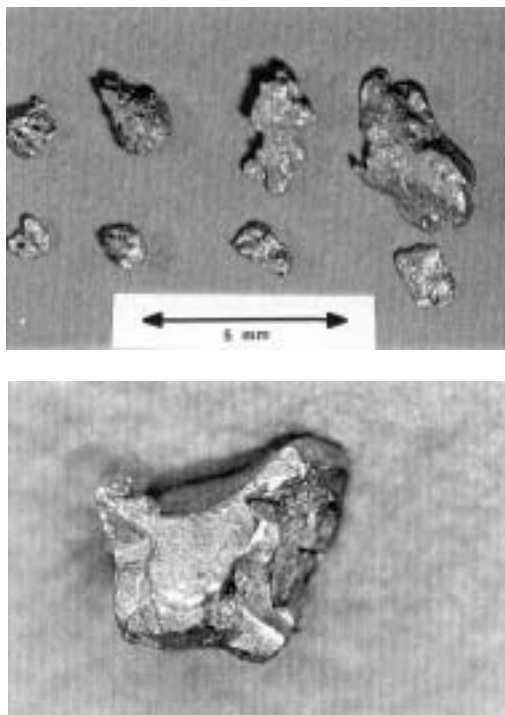


Figure 7.(a) Eight representative placer gold grains recovered from the *QAR* site. **(b)** A 1 mm grain of gold showing partial development of crystal faces.

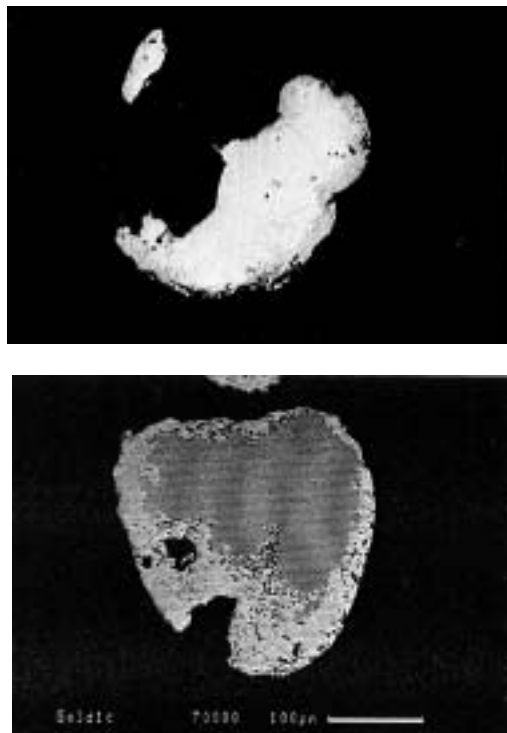


Figure 8. (a) Optical photomicrograph of a grain of placer gold showing the presence of a pure gold rim about a core of gold-silver alloy with approximately 65 percent gold; the grain is approximately 0.3 mm across. (b) Back scattered electron image of a portion of the grain shown in Figure 7a; the gold rich zone is made clear by the higher scattering power of the gold.

Most of these were found associated with lead shot in an exploratory trench that was cut in the northwest part of the site to examine for the presence and nature of artifacts at depth. The discovery was unanticipated and fortuitous, and it is presently impossible to estimate what additional quantity of gold may be scattered about the *QAR* site. Some reports indicated that the *QAR* carried 20 pounds of gold when she went aground, but such a quantity of gold would have been one of the first things rescued from the stricken vessel along with other valuable materials. The origin of the small amounts of gold so far recovered is not known, but the workers on the *QAR* speculate that this may be gold that had been secretly hidden behind beams to prevent theft by the pirates when the ship was comman-

deered by Blackbeard. The original owners were probably unable to return to recover it and Blackbeard did not know of its existence; subsequently, the gold would have been scattered about the *QAR* site as the ship was broken up by waves and the original container (perhaps a leather pouch) decomposed. Wave and current action would have caused some dispersal, but the high specific gravity of the gold would have resulted in its rapid burial in the sand: there was probably little movement afterward. Lead shot, because of its high specific gravity would have behaved in a similar manner; hence the co-occurrence of the materials.

The gold grains, which are totally free of corrosion or other coatings, are mostly somewhat rounded but one of the grains displays some development of crystal faces (Figure 7b). Several of the grains were mounted in cold-setting epoxy, sectioned, and polished for standard reflected light microscopic and scanning electron microscopic examination. Although some grains are uniform in composition, some of the grains contain a core rich in silver and a surrounding rim of pure gold. This is clearly shown in the optical photomicrograph and the back scattered electron image shown in Figure 8 a and b. These rims are typical of placer gold grains found in many parts of the world but are unknown in gold grains recovered directly from lode sources. Thus, although the mechanism of high-fineness rim development is not entirely clear, the presence of the rims clearly indicates a placer origin gold grains which is entirely consistent with the grain shapes. Figure 9 is an electron microprobe traverse across one of the rimmed gold grains that illustrates the compositional variation and the sharpness of the boundary between the core and the rim of the grain. The compositions of the cores of the gold grains vary from approximately 65 weight percent gold to about 90 percent gold, and the degree of rim development varies from extreme in the sample shown to non-existent in other grains. The core of each grain contains silver alloyed with the gold; this is typical of placer gold throughout the world. Lode gold sites yield grains with rather consistent gold compositions in their cores; the significant variation observed

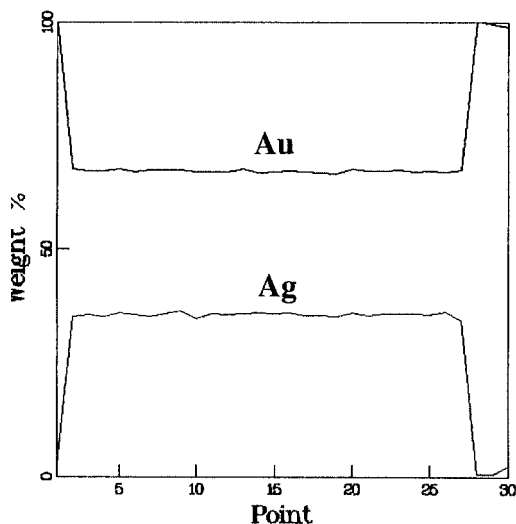


Figure 9. A compositional profile showing the gold (upper curve) and silver (lower curve) contents of a rimmed gold grain. The analytical points, numbered at the bottom, were 2 microns apart and illustrate the sharpness of the boundary between the core and the rim on the grain.

in the *QAR* samples examined, suggests that the gold grains found may have come from multiple sources.

Currently, no feasible way exists to determine the actual sources, but the gold may have been acquired at one or more places along the route. No gold production had been reported in what is now the United States by 1718, but several potential sources were known in Mexico, Central America, South America, and West Africa (Bethell, 1984). It is also possible that the gold had been carried from Europe. If the ship traveled from Europe, to Africa, and then to the Americas as believed, there would have been several opportunities for the taking on of gold, the exchange of gold dust, and the mixing of gold from multiple sources. Gold was a medium of exchange, commonly being weighed out, exchanged, and intermixed with gold dust from other sites.

One small (approximately 1 cm across) five lobed ornamental clasp has been recovered; it is composed of gold and silver with some apparent mercury amalgamation on the surface. The function is not known, but it appears to have

been sewn to some piece of clothing.

Silver

Silver as a free or refined pure metal has not been observed, but silver constitutes a significant proportion of the placer gold grains and is a constituent of the small gold-silver-mercury clasp noted above.

SUMMARY

Base and precious metals constitute significant portions of the artifacts recovered from the wreck of what is believed to be the *Queen Anne's Revenge*. All of the metals, except for the loose gold grains, reveal varying degrees of corrosion as the result of submersion in sea water and sediment for nearly 300 years. The pewter has withstood the corrosive effects of the sea quite well but is being altered slowly to tin oxides where conditions are oxidizing and to tin sulfides where conditions are reducing. Lead is abundant in the form of shot and has developed surface layers of lead hydroxycarbonate where oxidized and lead sulfide where conditions are reducing. Preliminary lead isotope data suggest a European or Mediterranean site or origin that would be completely consistent with a French origin for the ship. Placer gold grains have survived with no visible corrosion effects but display well developed rim structures.

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