

Conservation of Corroded Metals: A Study of Ships' Fastenings from the Wreck of HMS Sirius (1790)

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The study of corroded metal objects recovered from historic shipwrecks provides conservators with a unique opportunity to examine the effects of salts, water movement, depth of burial, and the level of dissolved oxygen on the degradation of a wide range of artifacts. Normally, the chronology of shipwrecks is well defined, and this helps quantify the rates of deterioration that occur. Previous work in the Materials Conservation Laboratory of the Western Australian Maritime Museum at Fremantle has concentrated on the identification of corrosion processes and how, by studying the deterioration of these objects, conservators can improve their techniques for stabilizing such artifacts (North 1976:253-58; MacLeod 1987a:25-40).

In the field seasons of 1985, 1987, and 1988, a team of maritime archaeologists led by Graeme Henderson of the Western Australian Museum's Department of Maritime Archaeology recovered a variety of metal artifacts from the wreck of HMS Sirius. The wreck is located on a coralline reef off Norfolk Island, which lies at 29.48° south latitude and 167.59° east longitude, about 1,500 km from Sydney and 1,000 km from Auckland, in the south Pacific Ocean. The copper, brass, and bronze objects recovered—including nails, bolts, sheathing, and other fittings (Figs. 1-3) were all worn and had apparently been used in the construction of the Sirius.

FIGURE 1.

*Clinch rings from
the HMS Sirius.*



FIGURE 2.
Bronze sheathing
tacks *from* the
HMS Sirius.



FIGURE 3. Brass belt
buckles *from* the HMS Sirius



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HISTORICAL BACKGROUND

HMS Sirius was originally named the *Berwick*. It was built in 1780-81 as a Baltic trading vessel, but in 1781, while the ship was still in dry dock at Christopher Watson's shipyard at Rotherhithe on the Thames, it was purchased by the British Admiralty. The Admiralty intended to make the *Berwick* the flagship of the First Fleet, to serve in establishing settlement in the newly founded colony of Australia. Initially, however, the *Berwick* was fitted out as an armed storeship for service to North America and the West Indies. After being coppered in early 1782, it sailed for Nova Scotia and New York. In 1783 the *Berwick* returned to England, where it was docked for repairs before sailing to the West Indies. Finally, in 1786, after undergoing a comprehensive refit, the ship was renamed HMS Sirius and set sail on its First Fleet voyage to Australia.

The *Sirius* was wrecked at Kingston on Norfolk Island at noon on March 19, 1790 (Fig. 4). Due to a change in wind direction, the ship was driven against a reef while unloading cargo and passengers. Other ships that went down in the rough surf off Norfolk Island include the *Mary Hamilton*, sunk to the west of the *Sirius*'s principal stranding site in 1873; and the *Renaki*, a three-masted auxiliary schooner thrown up on the reef in 1943. The site of the *Rapid* which sank in 1811 near the NW Cape, Western Australia, is more sheltered than that of the *Sirius*, and objects recovered from the former were used for corrosion comparisons. The *Mary Hamilton* went down west of the principal stranding site of the *Sirius*, causing some contamination of a portion of the site, although testing results reveal differences between the artifacts of the two vessels. The *Renaki* was wrecked in an area so distinct from that of the *Sirius* that site contamination did not pose a problem; the few remains of the schooner that were not salvaged are clearly identifiable.

Because of where the *Sirius* was stranded, most of the ship's supplies were salvaged in 1790, and the bulk of the shipwreck remained intact for almost two years thereafter. This fact clearly attests to the skill and strength of the ship's construction, considering the area's rough-breaking seas. To this day, large ships cannot tie up at wharf on the island because of the treacherous waters, and all cargo must be unloaded in deeper water and brought ashore with small boats.

The artifacts from HMS *Sirius* are scattered around the main site, which is located some 70 m offshore. The undersea terrain in this area is a very gently sloping plane of hard calcareous rock in water varying in depth from 1.5 to 4.5 m. The wreck site itself consists of flat beds of overlying coralline reef materials with a series of gullies and depressions in the seafloor. The configuration of the island and the particular location of the wreck site means that submerged objects are subjected to the effects of continuously breaking surf. During a storm, the wave action is sufficient to shift a 1.5 ton concrete plinth 30 m across the seabed. The ship's submerged remains primarily consist of about two hundred concreted cast-iron ballast blocks, a few

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FIGURE 4 "The Melancholy loss of His Majesty's Ship *Sirius* wrecked on Norfolk on Friday Noon 19th March 1789 taken from the Flag Staff on the Beach." Water colour by George Raper 1790



anchors, and one remaining carronade. Smaller artifacts are either trapped within the coralline corrosion matrices or under the ballast. The warm seawater (20.80 ± 1.96 °C), a mean annual salinity of 35.77 ± 0.04 ppt, and dissolved-oxygen levels of 7.7 ± 0.3 ppm constitute a highly corrosive environment for these objects.

Analysis of the corrosion properties and materials performance of the various alloys of the recovered artifacts was undertaken for two purposes, one of history and one of materials science. The primary historical purpose was to establish the quality of the materials used in the construction of the Sirius; several accounts indicate that it was poorly built, whereas the archaeological evidence supports the contrary. The second purpose of this research was to learn how a very aggressive shipwreck site degrades different materials, and what conservation problems this presents to the conservator (MacLeod 1989b:227-29).

EXPERIMENTAL METHOD

Eight samples of copper sheathing, a brass bolt, and bronze sheathing nails were examined metallographically and electrochemically after they had been sectioned and embedded in Araldite D (Ciba-Geigy's two-part epoxy resin, which is cured with an amine catalyst). Surfaces were prepared by grinding with wet and dry carborundum paper to 1,200 grit and polishing with diamond paste to $0.25 \mu\text{m}$; the etchant was 2 wt % ferric chloride in ethanol. Some objects were sectioned in several places with a number of longitudinal sections (LS) and transverse sections (TS) representing the tail (shank), body, and head regions of the fittings.

Drilled core samples (360 ± 100 mg) were analyzed at a commercial laboratory (ANALABS) using atomic absorption techniques. Core samples were taken in an attempt to overcome the problems associated with analysis of archaeological metals (Caley 1964:1-15). Results are listed in Table 1.

Table 1.
Composition
of fastenings
and sheathing
from HMS
Sirius (1790)

Type	Copper sheathing	Copper sheathing	Copper sheathing	Brass Bolt	Sheathing tack	Clinch ring	Eroded tack	Sheathing nail
Sample	<i>SI357</i>	<i>SI 465A</i>	<i>SI491</i>	<i>SI15</i>	<i>SI465</i>	<i>SI254</i>	<i>SI 228A</i>	<i>SI 228B</i>
Cu	99.4%	99.4%	98.9%	67.7%	91.1%	99.10%	91.47%	90.0%
Sn	25.6	15.3	75.9	402	7.69 %	1010	8.16 ⁰ / ₀	8.00 %
Pb	1750	1710	99	6670	520	1000	2720	4680
Zn	48	16	28	31.5%	108	120	257	7680
As	2410	2550	8260	460	6390	4380	<200	<200
Sb	300	302	185	92.7	216	183	52.9	49.3
Bi	500	525	1130	173	2240	935	265	1020
Ag	177	665	49	161	680	394	400	530
Ni	190	185	350	275	850	300	180	185
Fe	44	76	104	370	170	220	460	5130

Copper values are calculated by difference. Results are in ppm unless otherwise stated. Due to the small size of some samples it was not possible to accurately determine the amount of arsenic. The symbol < denotes values less than the detection limit.

Vickers microhardness measurements on the polished sections were made using a Tukon model 300 operating on a 600 g load with a x 20 objective. All the sections were examined under the scanning electron microscope (SEM) at the Commonwealth Scientific and Industrial Research Organisation's Division of Mineralogy, using the back-scattered electron/low-vacuum mode before and after the corrosion experiments. Semi-quantitative elemental analyses were made using energy dispersive analysis by X rays (EDAX) attached to the JEOL scanning electron microscope (JSM2) after calibrating the instrument with standard bronze, brass, and copper alloys (Robinson and Nickel 1979:1322-28).

Electrical connections were soldered to the metal sections prior to encapsulation in resin. The corrosion potentials were measured using a Titron silver-silver chloride reference electrode (saturated with KCl), which was calibrated against a platinum electrode in a quinhydrone solution at pH 4.0. (Voltages are all relative to the Ag/AgCl unless otherwise stated.) The seawater temperature in the laboratory studies was 24 ± 1 °C. Dissolved-oxygen measurements were taken using an Imperial Chemical Industries (ICI) oxygen meter (411) after correction for the salinity of the seawater (35.67 ppt). The seawater was filtered after collection from the ocean, but no preservatives were added. The current voltage curves for polarization-resistance measurements were recorded using a Princeton Applied Research (PAR) potentiostat with a platinum auxiliary electrode and an XY recorder; the data were collected over a range of ± 25 mV around the corrosion potential (E_{corr}) with the voltage scanned at ± 1 mV per second. The effects of dissolved oxygen and stirring on E_{corr} were determined using a combination of E_{corr} and polarization measurements. Tafel slopes were determined on the same samples used in the polarization studies. The measurements were made in a specially designed polarographic cell that allowed side mounting of the metal sections.

Corrosion Potentials and Polarization Resistance

When copper and its alloys are immersed in oxygenated seawater, they will corrode at a rate that is dependent on their chemical composition and microstructure and on the amount of dissolved oxygen in the water (Gilbert 1982:47-53; Bjorndahl and Nobe 1984:82-87). In aerated solutions, the E_{corr} is the voltage of a corrosion cell consisting of the anodic (oxidation of metal) and cathodic (oxygen reduction) half-cells. The way in which the corrosion rate changes with the voltage of a corrosion cell is very complex, but it can be simplified in two extreme sets of conditions. At voltages close to the corrosion potential, the metal obeys Ohm's law, since there is a direct relationship between the voltage and the current, according to the $E = iR$, where E is the voltage, i is the current, and R is the resistance. In other words, there is a linear relationship between ohmic resistance and the voltage. At applied voltages several hundred millivolts removed from the E_{corr} the increase in corrosion rate with applied voltage has a logarithmic rather than a linear response. The characteristic slope is called the Tafel slope. Corrosion in the Tafel region is often characterized by the presence of a passivating film on the surface of the metal.

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The corrosion rate (current) at the E_{corr} can be calculated from the rate at which the current varies with small variations in the potential. For voltages within 30 mV of the E_{corr} , the polarization resistance (R_p) is calculated from the slope of the current voltage plot via the expression:

$$\left(\frac{\partial E}{\partial i}\right)_{\partial E \rightarrow 0} = R_p$$

The corrosion rate (current) is inversely related to the polarization resistance by the expression:

$$R_p = B/i_{\text{corr}}$$

The constant B can be calculated via Faraday's laws relating to weight-loss data, or it can be determined from analysis of electrochemical polarization data. In physical terms, the value of B can be obtained from the Stern-Geary (1957) relationship,

$$B = \frac{b_a b_c}{2.303 (b_a + b_c)}$$

where b_a and b_c are the anodic and cathodic decadic Tafel slopes, as described above. The values of B depend on the composition of the objects and the types of corrosion products on the surfaces.

The Tafel slopes of the various fittings tested fell into two groups, one of which had characteristic values of 52 ± 5 mV, while the other had values of 39 ± 2 mV. The former is typical of cathodic Tafel slope values for concreted bronzes, and the latter is characteristic of machined samples. The individually calculated values of B were used to determine the corrosion currents, shown on table 2, using the above relationships. The anodic Tafel slope (b_a) of the samples varied from 42 to 85 mV. These calculated corrosion currents are based on measurements of R_p after twenty-one days of exposure of the samples to seawater. As such, they are approximately one order of magnitude too high for the bronzes and should be regarded as initial corrosion rates rather than average long-term values (Taylor and MacLeod 1985:100-4). In contrast, the copper corrosion currents fall within the normal range of long-term corrosion rates (Lush and Carr 19.79:1079-88).

RESULTS AND DISCUSSION :

CORROSION POTENTIALS

The sectioned copper alloys were immersed in fresh seawater (pH 8.18), and the corrosion potential was monitored for a period of three weeks. All the samples showed significant changes in the corrosion potential as the polished surfaces reacted with the seawater during the first ten days. The bronze sheathing tack (228B) shifted by more than 200 mV, whereas the copper sheathing samples and the clinch ring showed anodic shifts of only 20 mV over the same period. During the monitoring of E_{corr} , the level of dissolved-oxygen in seawater was varied to see how sensitive the metals were, since the microenvironment at the site may be significantly different from the microenvironment, which is fully oxygenated.*

The solutions were saturated with pure oxygen (14 ppm) or with air (8.2 ppm) or degassed with instrument-grade nitrogen to give a reading of 0 ppm. Three distinct types of response were observed. The E_{corr} of the sections of the bronze sheathing tack moved anodically by 9.0 ± 0.4 mV/ppm, and the brass bolt moved by 4.8 mV/ppm O_2 , while all the copper fittings and the copper sheathing tacks (465 and 228A) moved by 2.4 ± 0.5 mV/ppm O_2 . The latter samples also showed no increase in corrosion potential above the air-saturated, dissolved-oxygen level. These results indicate that, above this concentration of oxygen, the rate of corrosion is controlled by the anodic oxidation of copper metal. For the copper samples, the anodic shift of 24 mV per tenfold increase in oxygen concentration corresponds closely to the theoretical response of the oxygen half-cell of 29 mV. The corresponding values for the brass and bronze fittings are much higher than the theory would suggest, but they are consistent with the observations of others who saw shifts as great as 160 mV per decade for pure tin (Butler et al. 1969: 715-38). The ratios of the E_{corr} sensitivity of the alloys to oxygen are 4:2:1 for the bronze, brass, and copper fittings, respectively. These ratios are the same as the number of electrons commonly involved in the oxidation of tin, zinc, and copper.

Although the wet-chemical analyses listed in Table 1 show the overall composition of the alloys, it is readily apparent from the SEM EDAX analysis of the corroded surfaces that wide variations exist between the composition of the surface layers and the inner sections of some of the cast-bronze sheathing tacks. Apart from the brass bolt (SI 15), all the other materials from the *Sirius* site showed a similar dependence of E_{corr} and the size of the voltage shift when the seawater was deoxygenated. The response of the fittings to the change in levels of dissolved oxygen is given by the relationship:

$${}^O_2 E_{\text{corr}} = 0.236 {}^N_2 E_{\text{corr}} - 99 \text{ mV}$$

The apparently anomalous behaviour of the brass bolt is not really surprising, since it came from a part of the wreck site that had been contaminated with material from another ship. Inspection of the analysis in Table 1 shows that this anomalous bolt has a composition essentially identical to a modern, yellow, low-leaded brass (Miner and Seastone 1955:2-325). When compared with artifacts recovered from vessels of similar age to the *Sirius*, the low level of impurities in this fitting adds further weight to the conclusion that the bolt did not originate from the flagship of the First Fleet (MacLeod 1987b:280-91). The bolt most probably comes from the wreck of the *Mary Hamilton* (1873).

COMPOSITION AND CORROSION RATES

Bronzes

Several fittings were sectioned in sequentially to gain an understanding of how differences in microstructure and composition affect the rate at which different parts of the same object corrode. It has *

always been a major problem in stabilizing corroded artifacts to reliably determine what sort of variation is possible within one object. Results from the corrosion of the square-headed bronze sheathing nail (228B) illustrate the point. The corrosion current increases linearly with increases in the surface concentration of tin (Fig. 5), according to the equation:

$$i_{\text{corr}} = 0.886 x + 1.44$$

where x is the wt % tin in the sample and the corrosion current is expressed in $\mu\text{A}/\text{cm}^2$. The effect of the increased tin concentration is also seen in the corrosion potentials of the fastenings in oxygenated seawater: the lower the tin content, the more negative the E_{con} , and the lower the corrosion rate.

It should be noted that the corrosion data above relate to the fully oxygenated site of HMS *Sirius*. The sensitivity of the bronzes to dissolved oxygen has previously been noted (MacLeod 1985:10-13). A difference appears to exist between these studies of the *Sirius* fittings and the data from studies of long-term corrosion of artifacts recovered from other less aggressive sites. Interestingly, the corrosion of archaeological bronzes on land sites is similar to that of bronze objects found in marine sites with a low level of oxygenation.

From the SEM EDAX analysis of the surfaces of the corroded sections of the 228B bronze sheathing tack, it is clear that significant amounts of antimony are present in the tin-rich phases despite the total content amounting to only 0.00493 wt %. Tin and antimony readily form intermetallic compounds that are less reactive than the parent, tin-rich areas (North and MacLeod 1987:90-91). Increased amounts of antimony in the $(\alpha + \delta)$ phase of the bronze effectively promote interdendritic corrosion of the sections that have higher tin concentrations, as seen in Figure 6. In addition, increased amounts of antimony in the bronze fittings decrease the sensitivity of the corrosion potentials to changes in the value of E_{corr} when the seawater is deoxygenated. These observations confirm the theory that very small amounts of impurities, such as antimony, can have a major effect on corrosion performance.

The sensitivity of bronzes impurities such as iron can be seen by comparing the corrosion currents, shown in Table 2 for the SI 228A and SI 228b sheathing tacks. Inspection of the

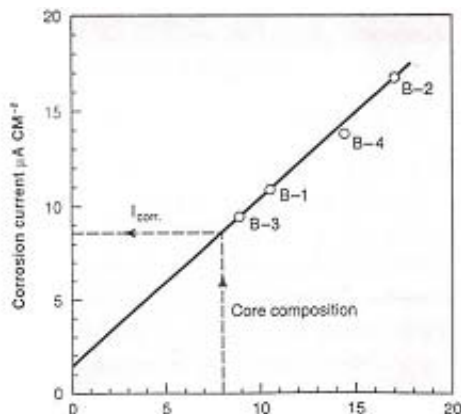


Figure 5. Diagram showing the effect of tin on the corrosion rate of a bronze sheathing tack (SI 228 B)

analytical data in Table 1 shows that 228B has eleven times as much iron as 228A. The effect of this greater concentration of iron is seen in a doubling of the mean corrosion rate of SI 228B compared with SI 228A, which otherwise has a very similar composition. For the sections of SI 228B that corroded the fastest, SEM analysis showed that significant amounts of iron were found in the corroded, tin-rich surfaces.

The variability of the corrosion rates in the bronze fittings is also seen in the microhardness measurements, which show a direct dependence on the composition of the alloys. The bronze sheathing tack (SI 465) showed a linear dependence of microhardness on the amount of tin over the range of 4-10 wt % according to the following relationship:

$$HV_{465} = 41.3 + 10.2x$$

where x is the amount of tin at the point of measurement. The maximum value of 145 is essentially the same as that measured by Samuels (1983) on an identical bronze tack from the *Sirius*. Apart from localized hardness, possibly due to so-called tin sweat and coring segregation, the other cause of the decrease in microhardness from the heads of the nails to the tips is that the nails had all been hammered in use; in other words, the fittings had not been cargo but part of the vessel, and thus they had been work-hardened.

Copper

Corrosion performance of the copper hull fastenings and the copper sheathing was an essential factor in ensuring that the *Sirius* remained a seaworthy vessel. Physical examination of two samples of copper sheathing, SI 357 and SI 491, indicates that they are similar, whereas another sample, SI 465A, is much thicker and appears to be tougher. Analysis of the samples shows that the chemical composition of SI 357 and SI 465A is identical and that the apparently similar material clearly has a different composition from that of the other samples, the latter sheathing being typical of most of the recovered materials.

The main impurities in the copper sheathing are arsenic and lead. One major effect of arsenic in copper is that it causes an increase in the microhardness of the metal during cold-working. Using the average values for each of the sheathing samples and the clinch ring, the following relationship between microhardness and the amount of arsenic was established:

$$HV_{Cu} = 26y + 74$$

where y is the wt % of arsenic in the material. It should be noted that the maximum amount of arsenic in these alloys is 0.826%, which is at the lower end of the range for ancient alloys (Scott, personal communication, 1991).

Since the maximum amount of arsenic occurs in the bulk-sheathing material, it is reasonable to assume that the vessel was covered with good-quality copper sheathing. The thicker sheathing (465A) showed negligible signs of intergranular corrosion and had been extensively worked, as indicated by the presence of annealing twins •

and the oblate Cu₂O inclusions (approximately 30 μm across). The grain size ranged from 50 to 60 μm. Erosion appears to have been the main corrosion mechanism for this material, which was subjected to the most turbulent waters of the wreck site. Localized current flow during the descent of a typical 4 m wave breaking on the site at a water depth of 3 m produces a velocity of 12 ms⁻¹ at an angle somewhat steeper than 45° (Cresswell 1989:46-70). Such flow rates are typical when erosion is an important factor in the rate of copper degradation (Lush and Carr 1979:1079-88).

The copper clinch ring (SI 254) shows twice the corrosion rate of the copper sheathing (SI 357), as listed in Table 2. The reason for this is readily apparent from the differences in their microstructures. The sheathing has a very fine recrystallized structure as a result of extensive working, with typical grain sizes of 35-45 μm. Apparently, the large amount of non-metallic inclusions does not have a deleterious affect on corrosion performance. In contrast, the clinch ring displays severe intergranular corrosion. The small amounts of tin and lead, approximately 0.1 wt %, were apparently concentrated at the grain boundaries and promoted intergranular corrosion (Fig. 7). The iron impurities were also concentrated at the grain boundaries and also appear to be involved in the increased corrosion rate. The normally beneficial effect of arsenic as an inhibitor of intergranular corrosion may have been lost by the even distribution of the arsenic in solid solution.

The surface hardness of the clinch ring was 107 HV, but this rapidly falls to a typical annealed value of 56 ± 12 HV within 1.3 mm of the surface. The mechanical stress of the working of the surface probably increases the corrosion rate (MacLeod and Pennec 1990:732-38). The composition of the clinch ring is the same as the large copper bolt examined by Samuels (1983) and was probably made from the same batch of metal produced by the Swansea copper refinery. The properties of the different alloys provide evidence for the two periods of construction of the vessel, which confirms other archaeological evidence. The two distinct batches of copper sheathing reported in Table 1 probably relate to the ship's initial fitting out (SI 491) in 1781 and to its subsequent refurbishing (SI 357 and SI 465A) in 1786 (Henderson and Stanbury 1988:36-53).

TABLE 2.
Corrosion rates
of copper alloys
from the wreck of
HMS Sirius.

<i>Registration</i>	<i>Type</i>	<i>Corrosion current</i> μA_{cm}^{-2}	<i>n*</i>
SI 465	Bronze tack	3.3 ± 0.3	1.04
SI 228A-1	Bronze tack	3.6 ± 0.6	1.05
SI 228A-2	Bronze tack	8.7 ± 1.1	1.05
SI 357	Copper sheathing	2.0 ± 0.4	1.00
SI 254	Copper ring	4.3 ± 0.1	1.00
SI15	Brass bolt	19.2 ± 4.1	1.31
SI 228B-3	Bronze tack	9.2 ± 0.2	1.05
SI 228B-1	Bronze tack	10.8 ± 0.6	1.07
SI 228B-4	Bronze tack	13.0 ± 0.6	1.08
SI 228B-2	Bronze tack	16.6 ± 1.4	1.10

*n is the number of electrons in the rate-determining step.

FIGURE 6. A scanning electron micrograph of the interdendritic corrosion at the seaward edge of an eroded bronze sheathing tack (SI 228A). Full width of the image is 306 μ m.

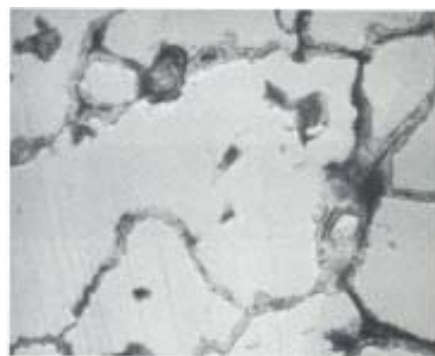
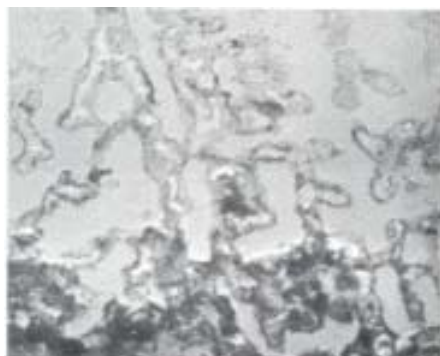


FIGURE 7. A scanning electron micrograph of the intergranular corrosion on a copper clinch ring (SI 254). Full width of the image is 306 μ m.

Brass

Although the brass bolt (SI 15) comes from a different shipwreck, some of the corrosion properties of this important class of copper alloy are worth noting. The microstructure of the bolt indicates that it was either hot-worked or cold-worked and then annealed. Extensive intergranular corrosion is present, with preferential corrosion of the zinc-rich beta phase at the grain boundaries. Microhardness measurements of the head of the bolt show work-hardening of the outer surface to yield maximum values of 149 HV, which fall to 105 ± 13 HV within 2 mm of the surface. The shank is fairly uniform in section with an average value of 80 ± 12 HV. SEM micrographs of the surfaces reveal an uneven distribution of lead in the structure of the alloy. The high corrosion current of $19.2 \pm 4.1 \mu\text{A}$ in the fully oxygenated environment reflects a maximum corrosion rate; if the material had continued to corrode at that rate, it would have ceased to exist in the form in which it was recovered. The extent of corrosion is consistent with a longer-term passivation of the corrosion process.

CONSERVATION OF THE METALS

Having established the corrosion mechanisms for the various fittings from the shipwreck of HMS *Sirius*, one must look at the practical consequences of these observations. The largest difference in corrosion is found in iron artifacts, since they are inherently more reactive than copper and its alloys. A cast-iron carronade from the *Sirius* site, for example, released a total of 26.09 kg (5.36 wt %) of chloride ions during conservation treatment. In comparison, a cannon of similar weight from the more sheltered site of the *Rapid* (1811) released a total of only 4 kg (1.12 wt %) of chloride ions during the same period (MacLeod 1989a:7-16). When the amount of corrosion on the more sheltered site is normalized to account for the shorter period of immersion, the chloride content only increases to 4.6 kg (1.29 wt %). Even after this correction, results show the cannon from the *Sirius* to be four times more corroded than the similar object from the *Rapid* site.

Likewise, the copper, brass, and bronze alloys recovered from the *Sirius* wreck site show higher chloride contents than similar materials from a number of wreck sites off the Western Australian coast. Conservation treatment of the bulk of the copper sheathing on Norfolk Island involved the extended washing for two years in a series of 2.5 wt % sodium sesquicarbonate solutions. During this time, the wash solutions were analyzed for chloride*

ions; the total amount released was 0.07 wt% chloride, which is almost three times the average amount extracted from other wreck sites. The effect on brass and bronze artifacts was even more marked; the average amount of chloride removed under similar conditions was 0.52 wt %, a factor of more than eight times that of average sites (MacLeod 1987c:1079-85).

Measurements of the corrosion potential of artifacts on the site prior to recovery can now be used as a guide to the level of conservation that is probably needed. The in situ E_{corr} value of a copper bolt from the gun carriage of the remaining carronade was -121 mV. This voltage (an inherent indicator of the corrosion rate) is the same as the laboratory measurement of the clinch ring in oxygen-saturated seawater. The consistency of these results may indicate that similar corrosion problems will be found among other artifacts from the *Sirius*. Further studies are needed to confirm the reliability of such indicators.

CONCLUSION

A study of the corrosion characteristics of a series of copper, brass, and bronze fittings from the wreck of HMS *Sirius* shows that bronzes are very sensitive to the amount of dissolved oxygen in seawater. The electrochemical data reveal how differences in the distribution of alloy elements in the same object can lead to major variations in the materials performance of that artifact. The sensitivity of bronzes to the amount of dissolved oxygen indicates that artifacts recovered from low-oxygen microenvironments, such as those found under the concretions associated with iron objects, should be very well preserved without the need of direct galvanic protection. There is, however, a limited range of conditions that provide low-oxygen microenvironments without stimulating the activity of anaerobic bacteria. In addition, copper alloys recovered from sites with a high level of microbiological activity can be extensively corroded as a result of the high concentration of sulfides.

Minor amounts of impurities, such as antimony and iron, have a major influence on the corrosion mechanism of archaeological bronzes. Differences in performance of copper fastenings and sheathing can be rationalized in terms of the influence of arsenic and the metallurgical microstructure. The turbulent and highly oxygenated nature of the HMS *Sirius* wreck site has a direct influence on the extent of corrosion of the artifacts found there. In light of these findings, the conservator should be alert to the special care that is needed to treat such materials.

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Dr. Ian Donald MacLeod received his doctorate from the University of Melbourne, where he studied the electrochemistry of metal fluorides dissolved in anhydrous hydrogen fluoride. During a two-year fellowship at the University of Glasgow, he studied organometallic chemistry. He spent three years at Murdoch University in Perth, where he concentrated on copper chemistry in association with mineral processing. For the past thirteen years, Dr. MacLeod has worked in the Materials Conservation Laboratory of the Western Australian Maritime Museum at Fremantle and is currently head of the Department of Materials Conservation. His research has focused on the problems of conservation and corrosion of metals recovered from historic shipwrecks. He has learned to scuba dive and perform in-situ conservation experiments on iron artifacts on the seabed. In addition to his work with shipwrecks, he has an active research interest in the conservation of aboriginal rock art.

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