ENVIRONMENTAL EFFECTS ON SHIPWRECK MATERIAL FROM ANALYSIS OF MARINE CONCRETIONS

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ABSTRACT

From the analysis of corrosion products and concretions which form on metal objects, much valuable information can be obtained for the maritime archaeologist and materials scientist regarding the past conditions at a shipwreck site. Techniques used include isotopic analysis of $^{18}O/^{16}O$ ratios in barnacles to determine water temperatures and microprobe analysis of metal corrosion products. Variations in pH and redox potentials can be gleaned from detailed analysis of the complex concretion matrices.

INTRODUCTION

By their very nature, historic shipwrecks act as time capsules of man's activities and the artefacts recovered by maritime archaeologists serve as examples of contemporary technology in wood, metals and ceramics as well as giving tangible reminders of the life of the ship's company. The nature of sites varies from the extremes of anaerobic fresh cold-water environments of the *Wasa* (1628) (Arrhenius et al. 1973) to tropical aerobic sites such as found for the *Batavia* (1629) (Worth 1976:253). The extent of preservation of bone, wood and metal is dependent on such variables as salinity, temperature, oxygen content and the interrelated factor of marine growth.

Analysis of marine concretions and the entrained corrosion products can give much information to the conservator and materials scientist regarding the site conditions that have prevailed since the vessel foundered. Normally data on parameters such as temperature, pH and redox potentials are only available for a very limited period of the site history because of financial constraints on field work, the remote nature of many locations and the fact that shipwrecks often pre-date European settlement in Australia. The work reported in this paper is based on information from the wreck of the American China Trader *Rapid* which sank on 7 January 1811 near Point Cloates on the Exmouth Peninsular ($22^{\circ}44'S$, $113^{\circ}41'E$) some 1100 km north of Perth. The material was recovered during two major excavations in 1979 and 1980. (Henderson 1981:124).

BARNACLES AND WATER TEMPERATURE

One of the main factors determining the corrosion rate of metals and the deterioration of organic materials is the temperature. The temperature not only alters the rate of the chemical reactions involved in degradation of the artefacts but also has a pronounced influence on the rate of colonisation of marine organisms on biologically inert substrates. It has been shown (Killingley 1980:759) that the calcareous exoskeleton of barnacles acts as a recording device of the ambient temperature since the oxygen 18 to oxygen 16 isotope ratio in the $CaCO_3$ of their skeletons is sensitive to changes in temperature and to variations in the $^{18}O/^{16}O$ ratio of the ocean. Some barnacles were found on lead sheathing (Fig.1) and on some leather-covered rigging which was uncovered at a depth of approximately 50 cm in the sediment. The

5cm

Figure 1 A sectioned view of *Megabalanus tintinnabulum tintinnabulum* found on leather sheathing from rigging on the *Rapid* (1811). The growth lamellae are clearly seen.

presence of a thick lead-sulphide film on the metal sheet indicated that the barnacles had been under anaerobic conditions for a considerable period. The barnacles were identified as a tropic species, *Megabalanus tintinnabulum tintinnabulum*, and had apparently colonised the vessel on or near the wreck site. Samples of calcium carbonate were removed from the sequential growth lamellae of the two samples and were isotopically analysed (MacLeod and Killingley 1982). The results are shown in Figure 2 where the isotope ratio $\delta^{18}O$(PDB)$^o/_{oo}$[a] is plotted against the distance from the base of the sheath (terminal edge). There is an initial increase in $\delta^{18}O$ in the direction of shell growth reflecting decreasing water temperature which passes through a maximum (positive $\delta^{18}O$ values), and then the isotope parameter begins to fall back towards the initial value. Because barnacles do not exactly follow the equilibrium palaeotemperature equation (Epstein et al. 1953: 1315) the temperature scale was calibrated using some barnacles which had grown under conditions of known temperature and salinity. The equation used for the barnacles was

$$t^oC = 22.14 - 4.37 \ (\delta_c - \delta_w) + 0.07 \ (\delta_c - \delta_w)^2$$

where δ_c is the measured value of $\delta^{18}O$ for the calcite and δ_w is $0.3^o/_{oo}$ for water salinity of $35.5^o/_{oo}$.
The barnacles from the *Rapid* showed a temperature variation from $21.5-26.0^oC$ over the period of growth. It seems likely that the barnacles in sample 1 attached themselves to the *Rapid* in January 1811, shortly after the vessel had foundered, since the initial isotopic temperature of 24.5^oC agrees with on-site measurements made in January

(a) $\delta^{18}O$ (PDB)$^o/_{oo}$ is defined as
     $\delta^{18}O$ (per mil) = [$(^{18}O/^{16}O)$ sample/$(^{18}O/^{16}O)$ standard - 1] x 1000
     and is related to PDB, an international standard (Craig 1957:133)

1979 and with literature data. The minimum of 21.5°C, which typically occurs in August/September, was found at mid-growth in the barnacles and from then the temperature began to increase following the normal seasonal progression.
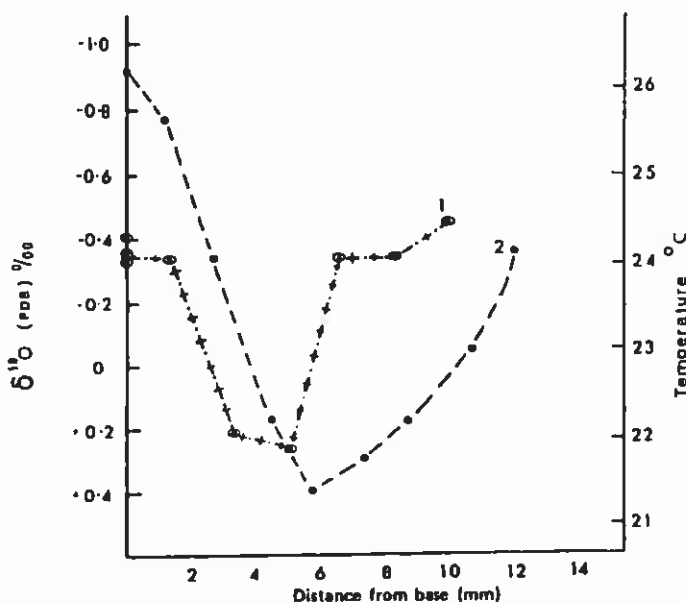

Figure 2 Plot of the $\delta^{18}O$ values found in growth lamellae of two sets of barnacles recovered from the wreck of the *Rapid*. The calibrated temperatures corresponding to the $\delta^{18}O$ values are shown on the right hand ordinate.

Both samples of the barnacles died at a time of increasing temperature; the final growth showing temperatures typical of those between December and February. Since the barnacles were firmly attached to the lead sheeting and the leather, they must have had a significant change in their substrate environment to cause their death at an age of between seven months and a year. Such marked changes could have resulted from salvage attempts or cyclonic activity at the end of 1811 or early in 1812.

CONCRETIONS AND CYCLONES

When metals corrode in aerobic environments the nature of the corrosion products is often markedly different to those found on the same metals which have been recovered from anaerobic or polluted environments. Aerobic corrosion products are typically metal oxides, hydroxides, hydroxy chlorides, sulphates and chlorides whereas metal sulphides readily form under anaerobic conditions. Copper and silver artefacts found on the *Rapid* site exhibited both types of corrosion products and their occurrence was closely correlated with their location on the wreck and the depth of sediments in which they had been buried. Polished sections of corroded silver coins (Fig.3) were examined using an electron microprobe and a scanning electron microscope which showed up a series of bands in the corrosion product layer that separated the remaining metal from the sea. The solid metal was 94.5% silver, 5.5% copper, while the composition of the bands varied
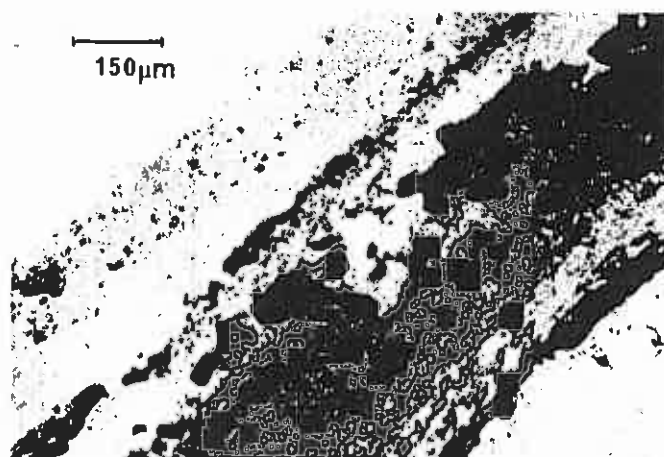
Figure 3 An optical micrograph of a polished section of a silver coin from
the *Rapid*. The uncorroded metal is in the upper left hand corner.
The banded nature of the corrosion products is clearly seen.

from the silver chloride chlorargyrite (AgCl) to the silver sulphide
acanthite (Ag_2S). Smaller amounts of the copper corrosion products
cuprite (Cu_2O) and chalcocite (Cu_2S) as well as small amounts of the
mixed silver copper sulphide jalpaite ($Ag_{1.55} Cu_{0.45} S$) were found in
the concretion. A schematic representation of the bands is shown in
Figure 4 where the composition (atom %) is plotted against the thick-
ness of the corrosion product layer. There is a thin layer of silver
chloride adjacent to the residual metal then a band of the silver
sulphide acanthite (Ag_2S) is followed by another band of silver chlo-
ride. The outermost layer is composed of silver sulphide and this
showed up as a dense grey-black layer on the surface of the coin when
it was excavated from the wreck site.

Since silver sulphide is markedly less soluble than silver chloride
the latter mineral can only have been formed under sulphide-free aero-
bic conditions such as are found on the sea bed at the wreck site where
the oxygen level was 80% saturation in sea water of $35.6^\circ/oo$ salinity.
A plausible explanation for the alternate layers of silver chloride and
silver sulphide is that the coins were initially lying in aerobic sea
water after the ship sank and they subsequently became buried as the
vessel settled. The site conditions subsequently changed to aerobic
for a period of several years before it returned to being anaerobic.
These major changes in site conditions were probably due to cyclonic
activity which resulted in considerable wave action in an area which is
normally protected from the Indian Ocean swells by an extensive nearby
coral and limestone reef. Severe tropical cyclones occur at irregular
intervals in the northwest of Western Australia and in the past 70
years two major cyclones with destructive winds of greater than 120
km/hr have occurred in the area of the wreck site (Lourensz 1981).
Further measurements on the steady state of corrosion rates of silver
coins in both environments are needed before a definite time scale can
be determined for the occurrence of the cyclones or similar events.

It is noted that copper tends to be concentrated on the seaward
side of the corrosion layers and this may be simply due to the greater
mobility of copper as $CuCl_2^-$ in aerobic and Cu^+ ions in anaerobic
conditions when compared with silver. Where the total weight percent
of the metals and anions shown in Figure 4 is significantly below
95-100% the balance is due to the presence of entrained calcareous
marine organisms and silicious materials. In the areas of concretion,

0.8-1.0 mm and 1.2-1.4 mm thickness, the presence of marine organisms is responsible for the low analysis shown in Figure 4. The distribution curves for calcium carbonate and silica were not included for the sake of simplicity.
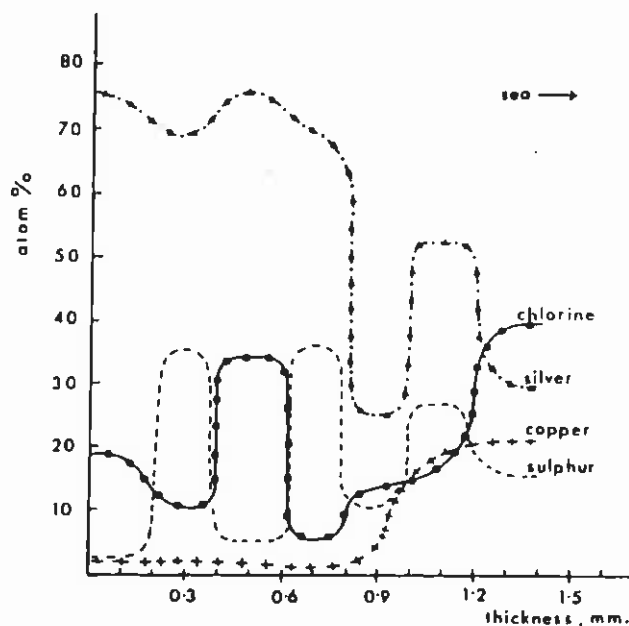

Figure 4 Plot of the distribution of silver, copper, chloride and sulphur in the corrosion product layers found on a silver dollar recovered from the wreck of the *Rapid.*

DISINTEGRATED ARTEFACTS

In the absence of solid metal the concretion analysis can give valuable information on the composition of the original object. If all the components of the alloy have been precipitated within the concretion matrix then the original composition of the metal can be estimated. Analysis for iron must be interpreted with great caution since a large percentage of the carbon in cast iron is lost through the formation of volatile hydrocarbons (North 1976:253).

When iron objects corrode under aerobic conditions they are rapidly covered by concretion and are often found to be completely corroded leaving a black acidic sludge inside the rock hard concretion (ibid.). The original shape of the object is often retained and the primary concretion layers act as a convenient mould from which the overall dimensions of the objects can be obtained. Because of the toxicity of the copper corrosion products it is relatively rare to find copper-based objects completely covered with a dense layer of concretion under aerobic conditions (MacLeod 1982); however, thick adherent layers of copper sulphides will cement marine debris under anaerobic conditions. Material recovered from 0.5-1.0 m in the sediment showed the original nail holes and shape of the copper sheating but no solid metal remained. Analysis of the concretion gave copper 99.77%, lead 0.19%, tin 0.02%, zinc 0.008% (expressed as a percentage of total metal found in the concretion) which is essentially the same as analyses on samples of copper sheathing from the same wreck.

VARIATIONS IN pH AND Eh

Because of the harsh physical environment of many wreck sites (wave surges etc.) it is often very difficult to get accurate measurements of the pH (acidity) and Eh (redox potential) on metal objects, either at the wreck site itself or on board the support vessel, as soon as they have been raised. In the absence of on-site data a good indication of the ranges of pH and Eh, that have existed for the period between the vessel foundering and being excavated, can be obtained through a study of the corrosion products. If basic parameters such as salinity and temperature are known, Pourbaix (Eh-pH) or thermodynamic stability diagrams can be drawn that pertain to the conditions on the wreck site.

Because of aesthetic and numismatic constraints the measurement of pH on silver coin concretions could not be readily obtained, except for surface measurement, which gave a pH of 8.2. On sectioning a corroded coin, crystals of silver (200 μm) were found in a silver chloride matrix close to the seaward surface. The formal Eh required for both silver chloride and native silver to be in equilibrium is calculated to be +0.250 volts at the measured salinity level of 35.6°/oo (Fig.5). Since the conversion of silver chloride to silver does not involve hydrogen ions the redox potential (Eh) is independent of pH in a marine environment. Examination of some coins which had corroded under anaerobic conditions also showed up small silver crystals (12.5 μm) amongst the silver and copper sulphides. Measurements made on sulphide concretions found on copper objects gave a pH range of 6.2 ± 0.1 (MacLeod 1982) which is characteristic of sulphate-reducing bacteria which convert the sulphate ions found in normal sea water to sulphide ions (Baas Becking et al. 1960:264). It is reasonable to assume that a similar pH would exist in the silver sulphide/copper sulphide micro-environment since the same bacteria are active in the same type of sediment. The formal redox potential (Eh) for equilibrium between silver metal and silver sulphide at pH 6.2 is -0.160 volts (Fig.5).
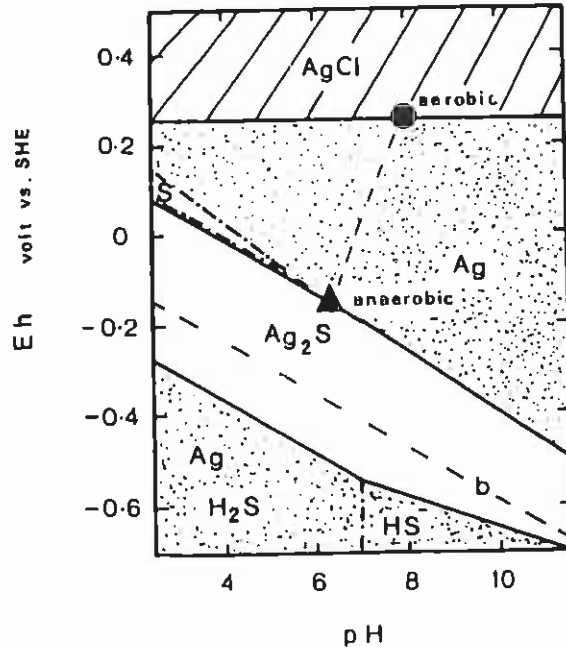

Figure 5

Pourbaix diagram for silver in sea-water of 35.6 salinity, with a total sulphur activity of 10^{-2}M. The line joining the aerobic and anaerobic data points describes the variation in pH and Eh that occurred on the *Rapid* wreck site.

The above data on silver coins serve as an example of how concretion analyses, in combination with on-site measurements on related systems, can give useful information about the variations in pH and redox potential that have occurred on a wreck site. The variation of 410 mV is equivalent to a change in silver activity covering seven orders of magnitude. The activity of many micro-organisms and their interaction with organic materials is Eh dependent and the data obtained on variations in Eh from the coin concretion may be of assistance in determining the mode of breakdown of some 'organic' artefacts.

CONCLUSION

The above examples serve to show how information on ranges of temperature, pH and Eh on the wreck site can be obtained from a study of marine concretions. With a knowledge of these parameters the conservator can often gain a better understanding of the artefacts in their care.

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