Characterisation of corrosion products on artefacts recovered from the RMS *Titanic* (1912)

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Abstract

The analysis of corrosion products on a number of bronze, brass, nickel silver and silver plated objects recovered from the wreck of the *Titanic* (1912) has revealed a diversity of speciation. The normal range of copper (II) hydroxy chlorides such as paratacamite and atacamite was found, along with the dull green $Cu_7Cl_4(OH).10H_2O$ and the basic chloride $CuCl_2.3Cu(OH)_2$. Traces of nantokite, CuCl, were found in conjunction with the cuprite, Cu_2O. Bronzes tended to produce a mass of corrosion products, which were amorphous light blue, white, to light brown tin compounds, which were contaminated with traces of copper, lead and zinc corrosion products. Brasses were found to produce large amounts of the blue hydroxy chlorosulphate connellite, $Cu_{19}Cl_4SO_4(OH)_{32}$. An aluminium corrosion product has tentatively been identified as metabasaluminite $[Al_4SO_4(OH)_{10}]$. The sulphate ions appear to play a more significant role in the formation of oxidation products compared with shallow and sub-tropical wreck sites. The degradation products recovered from modern materials such as aluminium provide an insight into the corrosive forces, which operate under high pressure and in cold water. Selective corrosion phenomena have resulted in some significant conservation challenges but understanding the decay mechanism materially assists the conservator in determining the most appropriate form of intervention.

Keywords

shipwreck artefacts, RMS *Titanic*, leather, brass, aluminium, nickel silver, corrosion, water pressure

Introduction

The tragic collision of the world's most prestigious luxury liner with a massive iceberg, just before midnight on 14 April 1912, has provided the perfect laboratory to study corrosion of modern and traditional shipbuilding materials at extreme pressures and cold temperatures. The loss of the "unsinkable" *Titanic* on its maiden voyage from Southampton in the United Kingdom to New York in the United States took place 650 kilometres off the coast of Newfoundland. In what is the worst disaster in the history of modern transport, 1523 people lost their lives. The wreck site was located at a depth of 3.8km by a titanium-hulled submarine owned by IFREMER, the French oceanographic Institute on the 1st of September 1985. A total of 3600 artefacts have been recovered from the debris field, located between the two major sections of the wreck, since recovery operations began in 1987. The corrosion products on the artefacts provide invaluable clues about the nature of physical and chemical processes in extreme stress conditions [1]. Materials salvaged from the *Titanic,* which have been subjected to pressures of 380 atmospheres for more than three-quarters of a century at average temperatures of 1–2°C, can provide useful data on the fate of materials in this unusual burial environment, which has relevance to conservation management of modern shipwrecks, specially those containing the remnants of their nuclear powered propulsion systems and have sunk in very deep water.

The intense cold, complete absence of light and low oxygen levels at the ocean bed where the *Titanic* was found has slowed down the deterioration of the ship and many other artifacts. However, some significant corrosion has occurred. Metals suffer electrochemical attack caused by slight differences in energy between the sections exposed to flowing seawater and those that have been buried in the marine sediment. Despite the depth and the cold and the generally low level of dissolved oxygen, bacteria are omnipresent and capitalise on the readily available source of iron, from the corroding ship, to promote their growth and the concomitant effect on the overall corrosion mechanism. These bacteria, along with the vast majority of respiring organisms, use iron complexes in their mitochondria, which are the primary powerhouses of animal cells. The lack of light and the extreme pressures normally means that the deep ocean sites are close to being a nearly sterile environment,

however the consumption of most of the wood on the site clearly indicates that marine organisms are opportunistic and will capitalise on new food resources suddenly "dropped on their doorstep". The only wood to survive in this environment had been buried in the sediments.

Since the discovery of the wreck of *RMS Titanic* in 1985 by Robert Ballard and his team [2], the public has become familiar with pictures of the ship festooned with drapes of rust, that are referred to as *rusticles*, which have grown to between twenty to thirty centimetres over the past ninety years. Scanning electron microscopy (SEM) studies have confirmed that the brittle shell, approximately 100–200 mm thick, has a smooth dark red outer surface, which is covered with microspheres of lepidocrocite [^{3} FeO(OH)]. The inner surface is covered by a reticular framework of spherical aggregates of goethite [± FeO(OH)] along with other species such as the iron(II) carbonate [$FeCO_3$] siderite [3]. There were also significant amounts of an iron silicate deposit which has tentatively been identified as hisingerite [$Fe_2Si_2O_5(OH)_4.2H_2O$] and the source of silicon is most probably associated with the siliceous skeletons of diatoms which were embedded in the bacterial iron web of the rust flakes [3]. Since the massive remains of the original vessel dominate the corrosion chemistry of the site, an understanding of the way in which iron is corroding is vital to in gaining an understanding of all the other interactions on the site. One critical physical chemical issue is the lack of the normally protective calcareous concretion since the prevailing conditions of the very cold temperatures and great pressure conspire to prevent the deposition of calcium carbonate. Since decreasing temperature and increasing pressure both result in an increased solubility of calcium carbonate, it is most unlikely that a set of circumstances will arise on the *Titanic* where the steel plates will become protected by "normal" concretion formation. Without this physical barrier to dissolved oxygen, the exposed metal readily produces the *rusticles* and recent photographs indicate that the *rusticles* are growing at a rate of the order of 10cm/yr and this may indicate an accelerated rate of decay owing to increased visitation of the site [4].

A series of corrosion samples were made available during conservation of the objects from the *Titanic* that was being undertaken in the LP3 Conservation Laboratories in Semur-en-Auxios. Observations made on the original condition of the artefacts were recorded by Stephane Pennec during field operations in the Atlantic Ocean. This data formed an invaluable reference and provided a check on any issues associated with mineralogical changes after excavation and prior to conservation treatment being commenced. Sets of corrosion matrices from the Titanic were examined using a range of techniques, which included optical microscopy; automated powder diffraction (APD) and Fourier transform infrared spectroscopy (FTIR). The elemental analyses were done using a scanning electron microscope equipped with an energy dispersive X-ray analyser (SEM/EDXRA). Photomicrographs were taken using an optical microscope. The results are discussed in detail under the individual assemblages and the laboratory reports have had the Chemistry Centre of Western Australian prefixes of 94T removed from the identifying codes for simplicity of reference. The LP3 Conservation laboratory numbers that identify the artefacts are also noted in parenthesis. It should be noted that the mineral phases and chemical composition relate to the nature of the artefacts when examined in the laboratory in France, some six months after the artefacts had been recovered from the wreck site.

Corrosion products from a silver-plated serving dish

The sample 45–1 came from a silver plated nickel silver serving dish (87/0199), which was 25.5 cm in diameter and 2.5 cm in height, and the corrosion product matrix was composed of various forms of copper chloride hydroxide with some cuprite [Cu_2O]. The upper dull green patches were composed of mainly of paratacamite [$^3 Cu_2(OH)_3Cl$], and the oxidised and partially hydrolysed copper chloride hydroxide [$Cu_7Cl_4(OH)_{10}(H_2O)$], which would have been formed via the original copper(I) chloride corrosion products, was also found along with copper chloride hydroxide [$CuCl_2.3Cu(OH)_2$]. The lower bright green patches over the red cuprite [Cu_2O] were composed mainly of copper chloride hydroxide [$CuCl_2.3Cu(OH)_2$] and paratacamite. A trace of nantokite [CuCl] was detected with the cuprite. Some of the x-ray diffraction lines were consistent with the presence of atacamite [$Cu_2Cl(OH)_3$]. The silver plate had become disbonded from the object where the underlying corrosion of the nickel silver (Cu/Ni/Zn) alloy was most severe. The results of the SEM analysis are show in Table I, which shows the dominance of copper and chlorine in all the phases and the bright green deposit, which was rich in nickel and zinc, had poorly defined morphology, which did not allow it to be clearly identified. The intensity of the green deposit is due to the presence of nickel(II) corrosion products since the zinc(II) corrosion products are colourless.

Table I. SEM and EDAX analysis of corrosion products from a silver plated nickel silver dish

Sample Description	Major	Minor	Trace
Dull green	Cl, Cu	–	Fe
Bright green	Cu, Cl	Ni, Zn	–
Copper red	Cu, Cl	–	Fe, Si, Ni

Unless specific identification is made, no comments are need to explain the trace amounts of iron and silicon in the samples since they are associated with adventitious iron corrosion products and siliceous ooze from the marine sediments. The lack of specifically identified mineralogical phases containing zinc and nickel may be due to poor crystallisation processes i.e. the kinetics of corrosion favour the formation of a series of amorphous compounds.

Bronze corrosion products

Some corrosion products that had come from a nickel cooking pot (93/0035) were analysed as sample no 45-2 that had come from the area on the upper surface of the 15.4 cm diameter, 15.1 cm high pot, where it was clear that once there had been a handle as there were three extant rivets that had once attached the handles to the object. The corrosion matrix was composed of poorly crystalline fragments of mainly tin with traces of copper, zinc, lead, sulphur, chlorine and sodium. Some of the fragments were iron stained. No phases were identified by x-ray diffraction since the corrosion matrix was essentially an amorphous assemblage of debris from the surface of the degraded bronze fitting. An overall view of the samples is seen in photomicrograph shown in Figure 1. The lack of a clearly defined morphology is consistent with the nature of tin corrosion products, which even when recovered from subtropical waters, tend to produce an amorphous mass of corrosion products, which can only occasionally be fully characterised by X-ray diffraction [5-7]. The totally mineralised and corroded bronze handle came from a nickel cooking pot, which explains the presence of both the other alloying elements of nickel and zinc as minor components of the corrosion matrix. The generally greater solubility of zinc corrosion products over the corresponding

Table II: SEM analysis of corroded bronze handle on a nickel cooking pot

Sample Description	Major	Trace
Light blue	Sn	Cu, Zn, Pb, S, Cl, Na
White	Sn	Cu, Zn, Pb, S, Cl, Na
Light brown	Sn	Fe, Cu, Zn
Green	Cu, Cl	

copper species explains why no specific zinc minerals were identified in this matrix. The pot was stamped "E. DEHILLERIN 18 RUE COQUILLRE PARIS" in a vertical text run up close to the rim.

It is interesting to note that the presence of zinc corrosion products in the tin oxidation matrix may be an indication of a mixed tin-zinc-leaded bronze as the parent alloy of the object. The presence of sodium and chloride in trace amounts simply reflects the retention of some sea salts in the matrix. The dominance of the corrosion matrix by amorphous tin corrosion products is mainly a reflection of the effect of the low temperature in failure to bring about sufficient energy to promote dehydration and crystallisation of the hydrolysed tin corrosion products. The total loss of the metal from the handle is a strong indication of the galvanic coupling of the exposed massive surface area of nickel, which was 76 times the surface area of the two bronze handles. It has previously been reported that under conditions of low levels of dissolved oxygen, bronzes are subjected to thermodynamically controlled corrosion in which the tin-rich phases are selectively corroded [8-10]. The galvanic coupling to the nickel vessel would have only exacerbated this susceptibility to corrosion. Given the absence of any identifiable sulphide minerals in the matrix, it is most likely that the sulphur present is in association with sulphate corrosion products.

Figure 1. Amporphous bronze corrosion products from a cooking pot handle.

The degradation matrix from a **brass pendulum lamp** (93-0037) some 24 cm long, 13 cm width and 11 cm in height was identified as sample no. 45-3 and was composed mainly of a poorly crystalline blue connellite [$Cu_{19}Cl_4SO_4(OH)_{32}$] seen in Figure 2 and an unidentified white zinc compound with minor amounts of quartz and an unidentified brown copper compound. The SEM data is consistent with the clear material being an amorphous silica deposit and with the parent brass alloy having been a low level leaded brass, since the lead only appears in the matrix at the trace level. It should be noted that in normal seawater lead has a significant solubility owing to the formation of soluble $PbCl_x^{(x-2)-}$ species and so it may not necessarily be trapped in the corrosion matrix [11]. However, analysis of the *rusticles* shows that lead degradation products, associated with the red-lead primer and general lead-based paints used on the hull of the *Titanic*, indicates that lead has limited migration on the site since the basic plumbonacrite [$Pb_{10}O(OH)_6(CO_3)_6$] and also some galena [PbS] was found on iron-coated minerals which were dispersed within the bacterial matrix of the *rusticles* materials recovered from hull plates along with the original minium [Pb_3O_4], the main component of the original red lead along with the inert paint filler barite or barium sulphate and calcite[3].

The lead oxide hydroxy carbonate plumbonacrite has been reported on lead artefacts recovered the wreck of HMS *Sirius* (1790), which lies in turbulent shallow reef-strewn waters off Norfolk Island [5], and so it is entirely likely that the mineral observed on the *Titanic* wreck may well relate to conversion of the underlying red lead during the sea trials and the outward voyage of the vessel.

Table III: SEM analysis of a leaded brass pendulum lamp

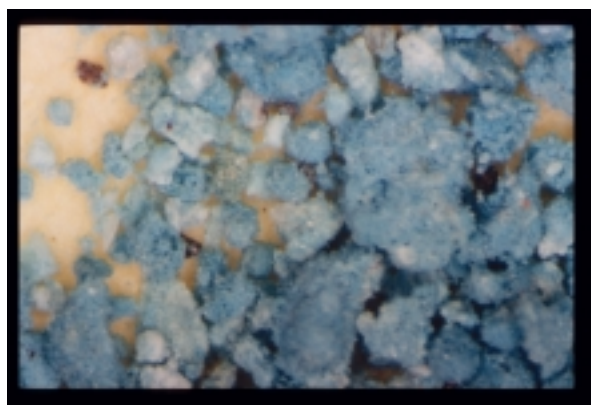| Sample Description	Major	Minor	Trace
Blue	Cu	Cl, S	Zn, Pb, Si, Ca, Al
White	Zn	Ca, Na	S, Ni, Pb, Si, Al
Brown	Cu	Cl, Si, S	Ca, Zn, Fe, Sn, Pb
Clear	Si		

Figure 2. Lump of poorly crystalline connellite from a brass pendulum lamp.
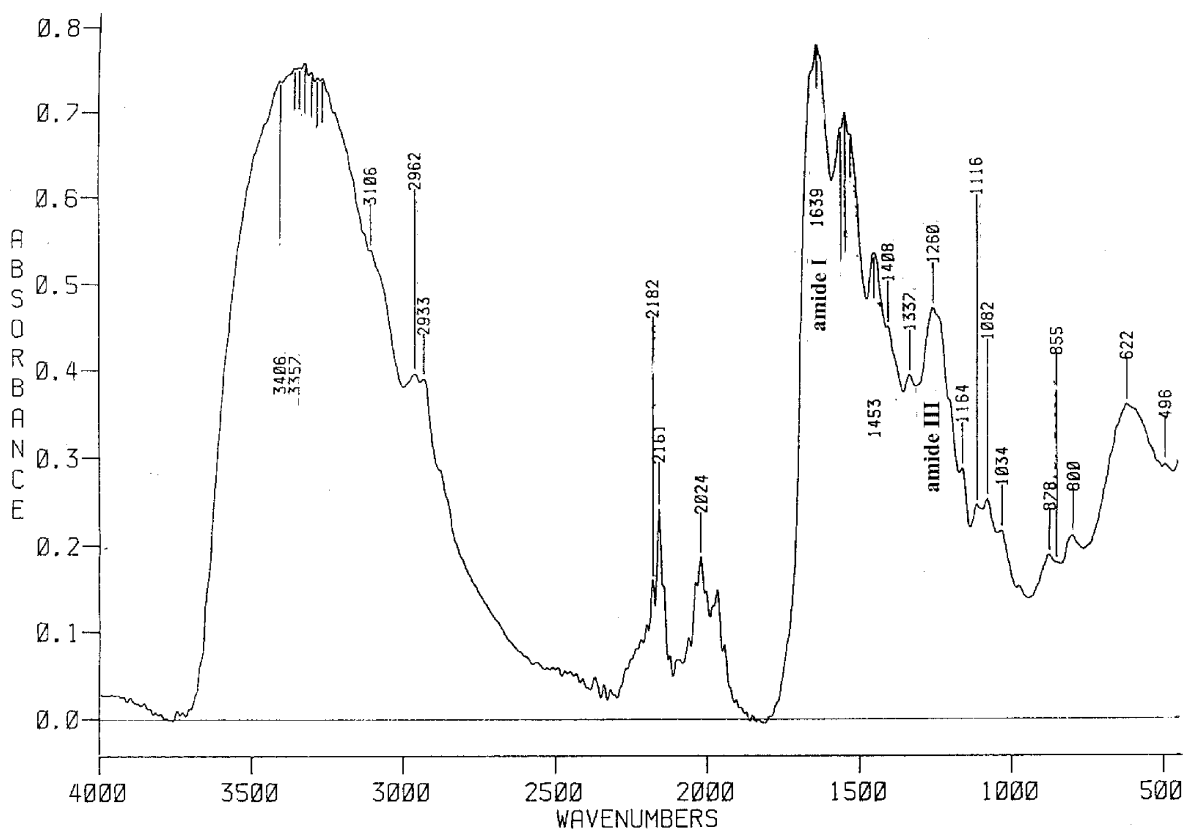
Iron-impregnated leather

The next sample of corrosion products involved analysis of the matrix, which was covering some leather from a **suitcase** (93/0058) which had been found on the debris field, between the two major remaining sections of the hull and superstructure. A section of the leather, matrix 45-4 was removed from the suitcase and examined by Fourier Transform Infra Red Spectroscopy (FTIR) and the spectra is dominated by absorbances associated with the host leather matrix (see Figure 3). The interstitial spaces between the leather fibres were filled with lepidocrocite [$^3FeO(OH)$] and some goethite [$\pm$-FeO(OH)] as seen in Figure 4, which are the same iron minerals as found in the *rusticles*. The SEM analysis showed that both calcium and silicon were present as trace components in both iron(III) phases and that the black matrix contained trace amounts of phosphorus. Whilst no specific phases containing the calcium and silicon were identified, it is likely that calcium silicates are present in the matrix of the iron corrosion products. The presence of trace amounts of phosphorus is perhaps an indicator of the presence of minerals such as vivianite, $Fe_3(PO_4)_2.8H_2O$ that has been commonly found on iron artefacts, which have corroded under low oxygen environments [5]. Despite more than eighty years on the bottom of the Atlantic Ocean the overall condition of the leather is very good. The presence of well defined absorbances in the amide I (1660–1610cm^{-1}), amide II, proline and amide III (1270–1210cm^{-1}) regions are indicative of well preserved leather. Indicators of degradation are seen in the reduced absorbances in the region 2970–2900cm^{-1} which indicates that some of the fatty acids and oils have been lost [12]. The spectrum also indicates that some denaturation and defibrillisation of the collagen fibres has also taken place (see Figure 4). This information was of great assistance to the conservators in ensuring the successful treatment of the waterlogged leather.

Nickel Silver Corrosion products

Corrosion products from a series of **silver-plated nickel-silver vegetable dishes** (93/0093.1-7/7) were identified as matrix 45-8. The silver metal surfaces came away from the totally mineralised nickel-silver parent metal alloys. The stack of dishes

Table IV: SEM analysis indicated the following composition of the phases found in the matrix:

Sample Description	Major	Minor	Trace
Metal	Ag		Cl, Cu
Top (bulk)	Ag	Cl, Cu	Zn, S, Ca, Mg
Metal back (bulk)	Ag	Cu, Ni, Zn	Cl, Fe, S, Si
Dark green	Cu, Cl	Fe, Zn, Ni	Si, Ca, Ti, Al
Blue	Al	S	Cu, Zn, Ca, Na
White	Ca		Si

Titanic leather with lepidocrocite

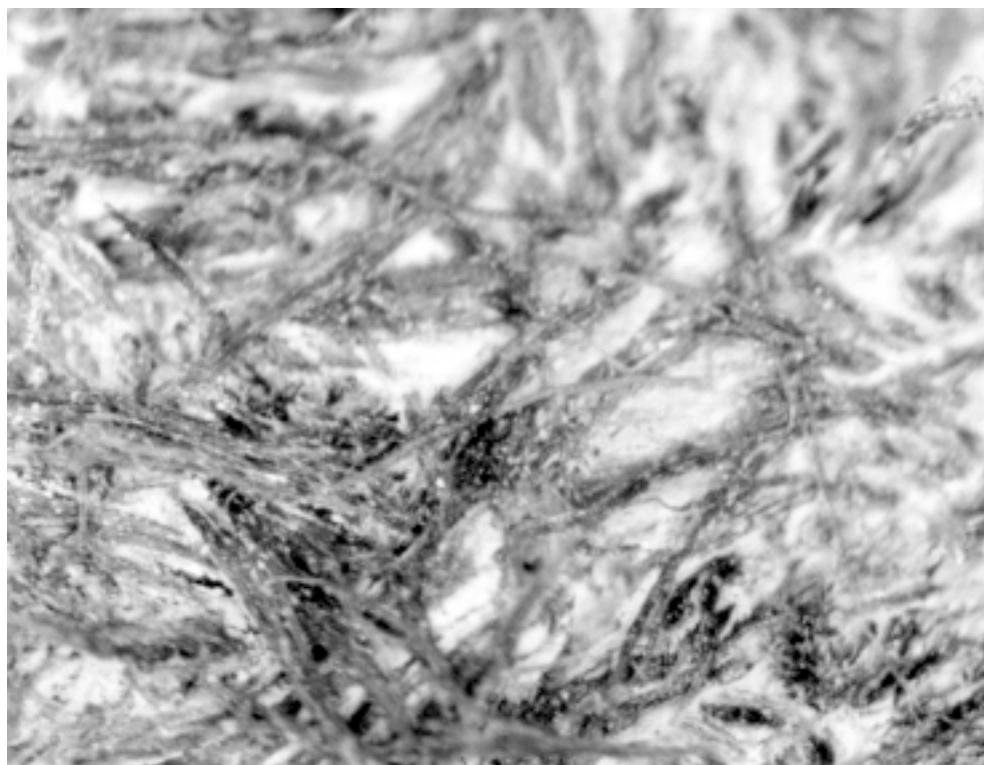Figure 3. FTIR spectrum of iron-impregnated leather recovered from a suitcase.

Figure 4. Macro photograph X 60 94T45-4 Titanic leather showing interstitial spaces between leather fibres filled with lepidocrocite and some goethite.

were 28 cm long, 18.5 cm wide and 11 cm in height and the matrix contained pieces of pitted silver plating with specks of red cuprite, along with a green copper chloride hydroxide (possibly atacamite) and blue unidentified aluminous compound. Fine lines in the XRD pattern indicated the possible presence of minor amounts of aragonite and malachite. The complex corrosion matrix of the once attached silver metal is seen in photomicrograph in Figure 5.

Since the base metal was a copper-nickel-zinc alloy the presence of copper, zinc and nickel as minor components on the 200 mm thick silver film is expected. The silver metal had curled and buckled into disconnected fragments as the tension created by the electrodeposition around the curved sections of the dish was released through the corrosion of the underlying base metal. The lack of any silver chloride on the surface of the silver metal is indicative of the way in which the nickel-silver alloy had been preferentially corroded to leave the metallic silver in its parent state. Given the low overvoltage for oxygen reduction on metallic silver, the advanced state of decay of the underlying alloy is not unexpected, despite the low oxygen environment on the wreck site. The difference in the kinetics of oxygen reduction are significant since the 28 mV overvoltage (·) for silver is a lot less than the 68 mV for copper, 108 mV for nickel and 134 mV for zinc [13]. This means the surface coating of silver would have resulted in localised corrosion cells in the as-cast dendritic structure of the alloy, which lead to the collapse of the support structure for the electrodeposited layer of silver. The silver coated dishes had major conservation problems, which appear to be related to the incorporation of

nantokite in the inter-dendritic corroded metal. When the objects had been washed in alkaline solutions, post treatment efflorescence of blue-green copper hydroxy chlorides necessitated the use of degassed solutions of 50 vol.% aqueous acetonitrile to remove the entrapped copper(I) chlorides [14].

The aluminium corrosion products appear to be adventitious and their blue colour is due to contamination of the hydrolysis products with copper ions, very little of which is needed to bring about a major colour change. Like many corrosion products of aluminium, they were amorphous [15]. The presence of sulphur in the aluminium corrosion matrix indicates that it is likely that the hydrolysis products incorporate a sulphate ion, given that the electrostatic attraction to set up ion-pairing between the triply charged aluminium ion and the doubly charged sulphate ion will favour the formation of alumino-sulphate complexes. The colourless mineral deposit with calcium and silicon present may simply be a contaminant of a calcium silicate complex.

Corrosion products from an electrical clock

A copper-alloy support base for a big electric clock (93/0094) some 231 cm long, 23.5 cm in diameter and 6 cm in thickness, gave a complex matrix of corrosion products. The sample of corrosion products no. 45-9 also contained fragments of an unidentified blue aluminous glass, coated with a white flaky aluminous compound. The blue vitreous aluminous compound contained a minor amount of silicon, which was absent in the white aluminous compound. The white compound was poorly crystalline and has a structure close to metabasaluminite [$Al_4SO_4(OH)_{10}$]. There was a green
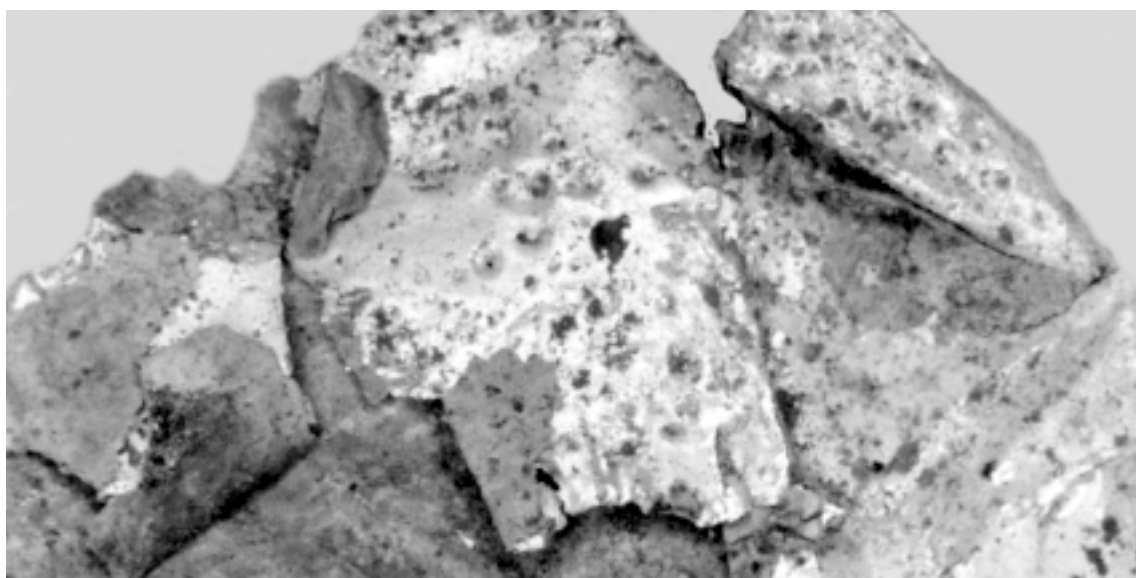

Figure 5. Micrograph 94T45-8 showing a fragmented pitted sheet of disbonded silver plate. The top surface was covered with minute specks of a copper hydroxy chloride, possibly atacamite, with rusty brown Cu_2O and a light blue aluminous corrosion product. The underside had the same materials on it and dark areas of a Cu-Ni-Zn alloy. Magnification approximately x 9.5.
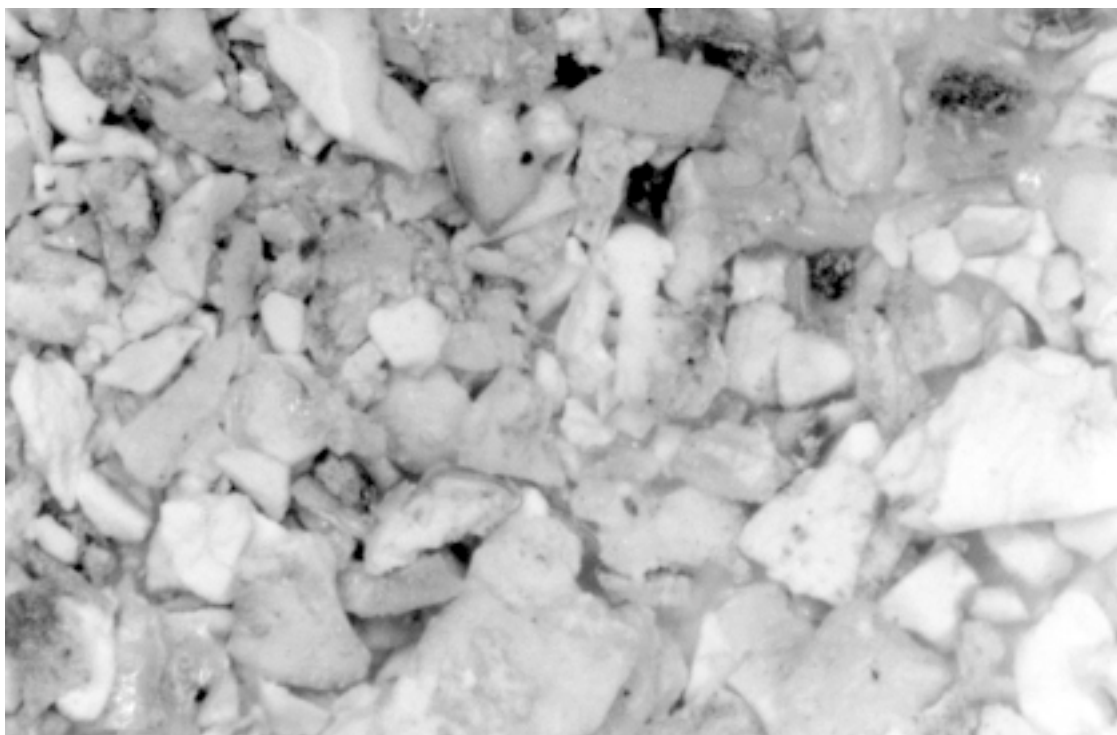
Figure 6. Macrophotograph of corrosion products x 60 from sample 94T 45-2 recovered from the degradation matrix of an electric clock.

patch of what was probably a copper chloride hydroxide. A detailed view of this matrix can be seen in the photomicrograph in Figure 6 and the SEM data is summarised in Table V where it is seen that the presence of copper, zinc has changed the structure of the aluminium hydroxy sulphate sufficiently to bring about a corrosion matrix which does not have any corresponding well defined chemical or mineralogical phase. The presence of both sodium and chloride in the blue "glass" sample is evidence of direct entrapment of sea salts in the matrix.

Given the high degree of solubility of zinc corrosion products on shipwreck sites [5] and their propensity to be associated with hydroxy sulphates, the presence of zinc and sulphur as minor phases in the opal blue corrosion product is not unexpected. The blue colour is readily explained by the incorporation of trace amounts of copper in the aluminium corrosion product matrix. Since the matrix is associated with an electrical light fitting,

Table V: SEM analysis on the corrosion products from an electrical clock.

Sample Description	Major	Minor	Trace
Blue "glass"	Al	S, Si	Cu, Zn, Ca, Cl, Na, Fe
Bulk blue	Al	S, Cu, Zn	Si, Ca, Cl, Na, Pb
Opal blue	Al	S, Zn	Cu, Na, Cl, Ca
White	Al	S, Cu, Zn	Na
Green	Cu, Cl	Fe, Cu	Si, Na, Zn, S, Pb

the presence of copper and zinc, from the brass connecting pins and brass ferrules of the fixture, and the lead from the alloy contact at the base of the light globes are all consistent with the divalent metal ions being trapped in the hydrolysis matrix from the corroding aluminium shades which totally disintegrated, owing to the galvanic coupling with the "noble" metal copper-alloy bracket.

Newspapers were amongst the organic materials routinely recovered from the debris field (93/0079 A, B) and the corrosion products analysed as 45-5, 6 & 10, were seen as brown stains on the newspaper. The stains were mainly composed of elemental sulphur and amorphous iron oxides, along with adventitious clay-like minerals. The SEM analysis of the brown phases showed iron and sulphur as the major elements with minor amounts of calcium and trace amounts of silicon and aluminium. The black phase had the same major and minor phases as the brown but some potassium was also incorporated at the trace level. It is likely that the potassium is present as a small amount of jarosite, $KFe_3(SO_4)_2(OH)_6$ and that elemental sulphur is a result of the interaction of anaerobic bacteria producing sulphide ions, which have subsequently been oxidized to elemental sulphur by oxidation from iron(III) species emanating from the wreck.

Brass spittoon

The corrosion products from a brass spittoon (93/0090) was analysed and found to consist primarily of paratacamite [³-$Cu_2(OH)_3Cl$] mixed in with

Figure 7. Details of corrosion damage on the brass spittoon and the White Star logo.

quartz from adventitious sand grains. The brass spittoon was 22.8 cm in length, 18.2 cm in height and 18.3 cm in width and as such was a major identifiable artefact that reflected aspects of contemporary social life and customs of collecting spit in a semi-public space. There was a section of the spittoon that had been lost to anaerobic corrosion processes where all the sulphide minerals, which had formed in the area where the object had been partly buried, had come away to leave a large lacuna – see Figure 7, but no samples of the mineralised brass were available for analysis. The SEM analysis showed up the presence of adventitious clay mineral elements such as Al, K, Ca, Fe, Ti and Mg that are consistent with the partial burial of the object. Trace amounts of nickel and zinc were also found in the corrosion matrix. There were some of the lines of atacamite but the amount of the mineral present was too small to be positively identified.

Discussion of results

Extensive studies on the chemical sedimentology of oceans has resulted in a series of clearly defined relationships that provide methods of correcting surface pH measurements for the effects of temperature and water depth, according to the formula $pH = pH_s - 4.0 \times 10^{-4} P$ where P is the water pressure of 380 atmospheres and pH_s is the pH measured at the surface. Thus for samples of water recovered from the *Titanic* site, a surface pH of 8.05 would be reflected in an *in-situ* pH of 7.90. Although this correction may appear to be small, it does have an impact on the zones of stability of the materials on the wreck site. At a depth of 3800 metres at 2°C, the carbonate equilibria have been changed from being supersaturated at surface temperatures and

pressures to being significantly under-saturated, with the ratio of the ionic activity product (IAP) to the solubility product of calcite ($K_{calcite}$) falling from $3.85_{surface}$ to 0.58_{3800m}. This explains why the bulk of the artefacts recovered from the *Titanic* site were free of encrusting marine growth [16]. Although corrosion processes normally increase surface pH on cathodic sites on the corroding metal surfaces, the overall corrosion rates and kinetics of oxygen reduction on the *Titanic* site will not be sufficient to bring about formation of a permanent calcareous covering.

In order to gauge what affect the cold water and high pressure has had on the corrosion of materials on the *Titanic* site, it is useful to review the E_h – pH or Pourbaix diagrams for the main metal components [13]. With the aid of the HSC Program for developing Pourbaix diagrams for a range of temperatures and site conditions [17] we have been able to generate stability plots for iron/sulphur/ copper/zinc/tin/aluminium under the high pressure and low temperature pertaining to the *Titanic* wreck site. In the case of the leather from the suitcase, the presence of elemental sulphur would imply a maximum pH of 2.7 and an E_h of 0.2 volts. Given that only Fe^{2+} ions can be present under these pH and E_h conditions this means that the sulphur in the leather samples was not in a thermodynamically stable state since it cannot be in equilibrium with either goethite or lepidocrocite. The sulphur is clearly in a kinetically stable state inside the leather matrix. Given that sulphate reducing bacteria are going to have a significant presence on the wreck site, it is most likely that the elemental sulphur in the leather is the result of oxidation of iron sulphides which themselves had been produced via anaerobic corrosion of iron. Exposure of the leather to an oxidising microenvironment could result in either direct chemical oxidation of the sulphide to sulphur or bacteria such as thiobacillusferroxidans could have facilitated the oxidation. Significant amounts of sulphur have been found in iron-impregnated waterlogged timbers from the *Batavia* (1629) wreck [18].

One important factor to note is that when the sea water temperature is lowered from 25° to 2°C, the dielectric constant increases from 79.7 to 87.1 and so this means that the *Titanic* site is able to dissolve or solvate ionic species with greater ease. The changed physical properties of the cold water are also reflected in the values of the partial molar volume V of the sulphate and chloride ions as the water temperature falls. The value for the sulphate ion falls by more than 20% from 13.98 cm³ at 25°C to only 11.1 cm³ at 0°C whereas the chloride ion falls by 7.7% from 17.83 to 16.45 cm³ at zero degrees Celsius [19]. Clearly the sulphate ion is better able to pack into the water structure on the *Titanic* site and so has become more effective in bringing about

mineralisation of species that contain the sulphate ion. Data on the effects of hydrostatic pressure on the corrosion of copper indicate that, under conditions of constant dissolved oxygen levels, the corrosion rate of copper increases up to a pressure of 150 atmospheres owing to improved efficiency of the cathodic reduction process whilst the anodic process is unaffected [20]. The nature of the copper corrosion products formed on the pure metal was essentially the same as under normal conditions in shallow waters which supports our observations that the basic nature of the corrosion products on the *Titanic* site are generally similar to those observed on other wreck sites.

Acknowledgements

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