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THE PRESERVATION OF IRON CANNON AFTER
200 YEARS UNDER THE SEA

C. Pearson

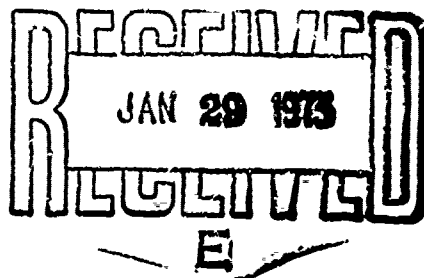
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THE PRESERVATION OF IRON CANNON AFTER 200 YEARS UNDER THE SEA

C. PEARSON

Abstract— In 1770 Lieutenant James Cook who discovered the east coast of Australia had to jettison iron cannon and carriages along with iron and stone ballast when the *Endeavour* struck a coral reef. These relics were recovered in 1969 and their condition and properties after almost 200 years under the sea are discussed. The treatments used to stabilise the iron cannon and carriage remains are then detailed. These include electrolytic reduction; followed by washing in inhibited distilled water before a final wax impregnation, also treatment in an activated molten caustic soda bath followed by heat treatment before wax impregnation. The historical aspects of the relics with regard to their authentication are also mentioned.

I. INTRODUCTION

The year 1970, being the bicentenary of the discovery of the east coast of Australia by Lieutenant James Cook, was also significant from the fact that six cannon which were jettisoned by Cook off the Australian coast were first seen by the public after almost 200 years under the sea.

Just before 11 o'clock on the evening of 11 June 1770, in between the taking of depth soundings, James Cook's vessel *Endeavour* hit and struck fast on a submerged coral reef. Cook had sighted Australia nearly two months previously, with his famous landing at Botany Bay ten days later. He then sailed north through the Great Barrier Reef, when this disaster occurred.

Once again James Cook's expert seamanship was shown as the holed *Endeavour* was fothered and she lifted off the reef at high tide. However, this was not before six cannon and their carriages, along with a large quantity of iron and stone ballast, had been jettisoned to help lighten the vessel [1].

Numerous attempts were made to locate the jetsam but none were successful until January 1969 when an American expedition from the Philadelphia Academy of Natural Sciences, under the leadership of Dr Virgil Kauffman, found the cannon and ballast with the aid of a sophisticated magnetometer detection device. The coral-encrusted relics were recovered and handed over to the Australian Government Department of Shipping and Transport who arranged for the preservation of these historic relics by the Department of Supply, Defence Standards Laboratories in Melbourne.

The transit of the six cannon, 7600 kg of iron ballast and 760 kg of stone ballast, to the mainland from the reef was carried out in large tanks filled with sea water. This was to ensure that the relics were not exposed to the atmosphere in which rapid drying out and subsequent oxidation and spalling of the metal surfaces would take place. The jetsam was

20

then transported to Melbourne packed in wet sawdust impregnated with a 10% solution of formalin (to destroy harmful bacteria during transit) contained in large fibreglass-lined wooden tanks.

2. PRESERVATION OF THE CANNON

2.1 Removal of coral

Fig. 1 shows the author examining a coral-encrusted cannon in the condition in which it was recovered from the sea bed. The first stage of the preservation process was to remove the coral encrustations.

The coral was removed by striking firmly with a hammer at right angles to the coral surface. This caused the coral to crack in large pieces, exposing the cannon surface which was covered with a wet layer of black corrosion products, the aqueous component of which had a pH of 8, close to that for natural sea water of pH 8.2. The coral varied in thickness and composition from 150 mm thick hard coral down to less than 6 mm of a soft and/or shell-type coral. It was easy to remove the hard coral, but the soft or thin coral was difficult because in places it had grown into pits in the surface of the cannon. Experience indicated that it was best not to remove these difficult spots at this stage as it was easier to remove them later in the preservation process.

It was also found that coral removal was easier and less messy in the dry state, i.e. water was not directed on to the cannon during cleaning as this would also cause continued corrosion of the cannon due to the large amount of chloride present on the cannon surface. In this way, between 90 and 140 kg of coral were removed from each cannon, and a cleaned cannon is shown in Fig. 1. Any appendages, such as those attached to the coral-encrusted cannon in Fig. 1, were carefully removed for separate treatment.

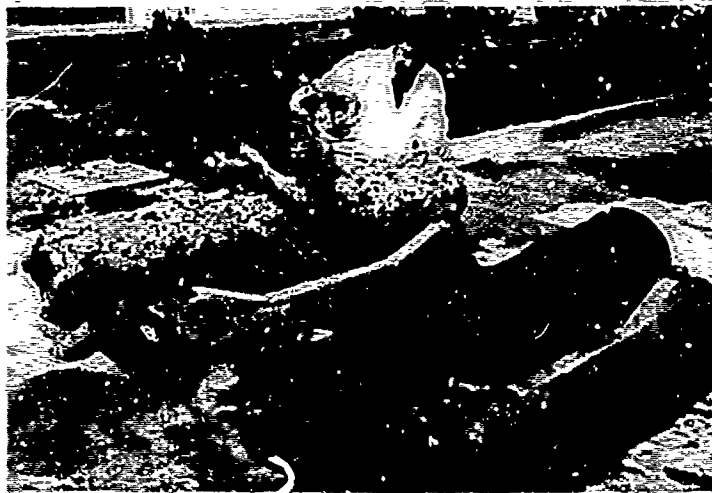


FIG. 1 The author is seen examining cannon before and after the removal of coral.

The bores of the six cannon which were completely choked with coral were cleaned out using special constructed tube drills. Great care was taken during this operation as the cannon might have been loaded. Cannon-balls were in fact found in two cannon and in front of one ball a large piece of wadding was encountered, and from behind the ball a lump of black material was removed, presumably the residue of a gunpowder charge. A second sample of gunpowder was obtained from behind the second ball. The wadding, ball and charge as recovered are shown in Fig. 2.



FIG. 2 From the left a piece of wadding, cannon-bail and gun-powder charge recovered from the bore of a cannon.

Both of the loaded cannon contained small fibrous plugs forced into the vent holes which were presumably to protect the charge on the exposed decks of the *Endeavour*. These plugs were carefully removed for separate preservation.

During the drilling of the coral from the bore of several of the cannon, the temperature of the barrel was observed to increase more than expected by friction from the cutting tool. Also, the piece of wadding, after removal from the cannon, began to smoulder and had to be placed under water.

This heat generation, when previously submerged or buried objects in anaerobic (lack of oxygen) conditions are exposed to the atmosphere, is well known, and is caused by partial oxidised corrosion products of iron being spontaneously converted to their final state, thus liberating heat. Therefore, cooling water was sprayed over the cannon during the cleaning of the bores to minimise any damage caused by this heat generation.

After removal of coral, the cannon were placed on wooden cradles in the fibreglass-lined wooden tanks (used throughout the preservation process) under a 2% solution of sodium hydroxide of pH 12.6 prior to the next stage of the preservation process. In this solution the cannon will not corrode due to passive film formation on the cannon surface [2].

Within minutes of the cannon being placed in the sodium hydroxide solution, gas bubbles were seen to evolve from the cannon surface at an initial rate of approximately 1 l/h which continued, slowly decreasing, for about 7 days. The analysis of the gas as determined by gas chromatography was 80% hydrogen, 10% nitrogen and a trace of methane, the remainder being unidentifiable.

The origin of the nitrogen is unknown, but it may be the remains of entrained air in the porous surface layers of the cannon, the oxygen having been used up in the corrosion processes.

From a study of the corrosion mechanisms of iron in anaerobic conditions and in sea water, it is considered that the hydrogen evolution was caused by two major processes; the first being a change in state of one or more of the corrosion products already there, and the second from entrained hydrogen resulting from earlier corrosion of the cannon while under the sea. The hydrogen evolution was not caused by fresh corrosion of the cannon in the sodium hydroxide solution [2]. This will be discussed in the following section.

2.2 Condition and properties of the cannon after removal of the coral

As this paper is basically concerned with conservation, the corrosion aspects of the cannon and also the processes involved when it was placed in the sodium hydroxide solution will not be discussed here in great detail. A full description of this work will be found in the main publication on the treatment of the *Endeavour* relics [3].

Removal of the coral revealed the detail of the cannon and showed that the coral had inhibited its corrosion to a remarkable degree, as all the surface markings on the cannon were still clearly visible.

A small piece of metal from a cannon was found attached to a piece of coral after removal. This enabled detailed metallographic examination of the metal and corroded surface layer and also provided material for analysis of the iron.

The analysis of the iron metal, detailed in Table 1, shows it to be a high-phosphorus grey cast iron of common composition.

TABLE 1

ANALYSIS OF CAST IRON CANNON

<i>Element</i>	<i>Cannon</i>	<i>Modern Commercial Grey Iron</i>
Total Carbon per cent	3.5	3.2-3.5
Silicon per cent	0.5	1.0-2.5
Manganese per cent	1.1	0.5-1.0
Sulphur per cent	0.03	0.15
Phosphorus per cent	0.6	0.15
Titanium per cent	0.04	NIL



FIG. 3 Microstructure of the cannon iron. Magnification $62\times$. Flakes of graphite (A) in a matrix of pearlite (B), with a few regions of ternary phosphide eutectic (C). The corrosion (dark areas, D) of the pearlite follows the lines of graphite flakes which are unaffected. Etched in 4% picral solution.

A photomicrograph of the metal/corroded layer interface in Fig. 3 shows that the cannon has corroded by what is colloquially called 'graphitisation' or 'graphite corrosion'. A small

galvanic corrosion cell is formed in the sea water between the pearlite in the metal as anode and the graphite flakes as cathodes. The pearlite corrodes leaving behind a continuous network of graphite flakes filled with iron corrosion products. This corroded layer was restricted to less than 6 mm in thickness by the coral growths around the cannon.

As the coral crust had provided such good protection, samples from the coral/cannon interface and a coral/wrought iron carriage fitting interface (discussed later) were analysed. This showed that the coral was heavily impregnated with iron corrosion products up to a depth of 40 mm in places. The main constituent of the crust was the very hard insoluble magnetite (Fe_3O_4), but the presence of calcium and a high chloride content was found at the coral crust/cannon interface. Chemical analysis also showed the presence of 1.75% sulphur or its products.

The presence of calcium at the interface indicates that coral commenced growing immediately the cannon arrived on the sea bed. The coral grew as the cannon corroded, slowly creating a hard dense coating over the cannon. These thick coral growths were the reason why it was impossible to detect the cannon by visual exploration as they blended perfectly into the background of the reef. A magnetometer, as used by the expedition, was therefore essential in locating the cannon.

The anaerobic conditions under the coral crust were the main reason why the cannon survived so well after such a long stay under the sea. Oxygen, which is essential for corrosion of iron, was prevented from reaching the cannon.

However, the anaerobic conditions were ideal for corrosion of the cannon by sulphate-reducing bacteria, the most common strain being *Sporovibrio desulphuricans* which are found in abundance in sea water. These microbes reduce dissolved sulphates to sulphides in a reaction [4] which depolarises the cathodic areas and accelerates corrosion. The formation of hydrogen sulphide during this process also accelerates corrosion.

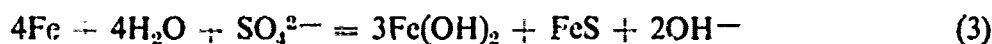
Although disagreement still exists as to the full mechanism of the corrosion of iron by sulphate-reducing bacteria the organisms require hydrogen for their life cycle by a reaction such as:



The hydrogen (probably atomic) originates from normal corrosion cathodic sites and its removal by reaction (1) causes depolarisation of the cathode areas allowing more iron to go into solution as Fe^{2+} . Ferrous sulphide is also formed, possibly by a reaction such as:



however, cathodic depolarisation predicts the formation of three moles of hydroxide to one of sulphide:

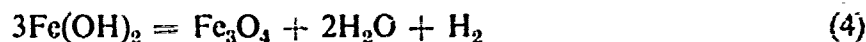


equation (3) being a simplification of the reactions proposed by von Woizogel, Kuhr and van der Vlugt [4].

Chemical analysis of the sulphur content at the coral/cannon interface showed 1.21%

sulphides, 0.40% sulphates and the remaining 0.14% as insoluble sulphates or possibly elemental sulphur. This is evidence of the role of sulphate-reducing bacteria in promoting corrosion as the sulphur content of the base metal was only 0.03%. Therefore, the main corrosion products resulting from anaerobic corrosion are essentially ferrous sulphide with some ferrous hydroxide.

Apart from hydrogen resulting from equation (2) there is also the possibility of its being evolved during the decomposition of ferrous hydroxide according to a Shikorr-type reaction [5].



This reaction only occurs in the absence of oxygen and could occur in the anaerobic conditions under the coral, and analysis of corrosion products mentioned earlier at the cannon/coral interface did show the presence of magnetite.

Reaction (4), however, is not as simple as it appears because, to function, it requires the presence of a 'catalytic agent' [6, 7]. These catalysts, which include platinum, copper and nickel powders and also the chlorides of these metals, are in fact cathodic to iron. Therefore, it is possible that the carbon flakes present in the grey iron of the cannon which are cathodic to iron could act as the catalyst for reaction (4) to occur.

This production of hydrogen from reactions (2) and (4) could both occur when the cannon was placed in the 2% sodium hydroxide solution as mentioned in the previous section. The entrapped hydrogen resulting from the action of the sulphate-reducing bacteria would be released along with that resulting from the decomposition of ferrous hydroxide. The latter reaction might also be a spontaneous result of the hydrolysis of, for example, ferrous chloride, or sulphide, formed deep in the porous surface layers of the cannon under normal corrosion processes. However, much more work is required to confirm this latter mechanism.

The numbers chiselled on the breech of each cannon, e.g. 11-2-15, indicate the original weight of the cannon in hundred-weights, quarters and pounds [3], i.e. 1303 lb (593 kg). Weight measurements after removal of coral showed that each cannon had lost between 60 and 130 lb (27 and 60 kg) by corrosion.

The thickness and type of coral growth which determined the degree of protection of the cannon was determined by the position of the cannon on the sea bed, the growth and subsequent protection being the least on the underside of the cannon where it lay. It is fortuitous that five of the cannon settled topside upwards where thick coral growths preserved a relatively pit-free surface. The sixth cannon unfortunately is heavily pitted on the top whereas the underside is well preserved.

2.3 Chloride removal and oxide reduction

The porous corroded surface layers of the cannon were heavily impregnated with salts from the sea water. The next stage of the preservation process was to remove these salts and also reduce the corrosion products already there, so that prolonged exposure to the atmosphere would not cause continued and rapid corrosion with subsequent spalling of the surface layers.

The salts (essentially chlorides) were removed by electrolysis making the cannon the cathode in a 900 l solution of 2% sodium hydroxide in the fibreglass-lined wooden tanks. The anode was a 1.83 by 0.91 m mild steel sheet on the opposite side of the tank, with an insulated

iron bar inserted in the bore of the cannon as an auxiliary electrode to provide good current distribution. Mild steel bands attached to the cannon and anodes acted as electrical contacts. The strength of the sodium hydroxide solution was chosen so that there would be no corrosion of the mild steel anodes during electrolysis [2].

The applied dc current caused the chloride ions to migrate from the cannon as cathode, into solution and towards the anode by an electro-osmosis effect. A current density of 10 A/m² was chosen for the optimum value, as higher current densities caused blistering of the surface layers by the hydrogen gas evolved there, and lower values merely prolonged the time required to remove chloride.

Along with chloride removal, reduction of the oxidised corrosion products in the graphitised matrix of the cannon also occurred. It was not possible to determine the degree of reduction, but brown patches of corrosion product ('rust') disappeared during electrolysis and the surface layers became much harder than their original state.

Chloride analysis of the bath solutions showed the extent and completion of chloride removal from the cannon. As the bath solution was changed weekly, electrolysis was continued until the chloride content of a solution remained constant for 1 week, indicating that no more chloride was coming from the cannon. The chloride content of the bath solution at this stage was about 5×10^{-4} M (20 ppm). The cannon was next washed with distilled water for a short time in the electrolysis tank, the current still being applied.

Electrolysis loosened the few hard pieces of coral still attached to the cannon and these were easy to remove at this stage.

2.4 Washing procedure

After electrolysis, the cannon were subjected to a prolonged washing procedure to remove the sodium hydroxide, final traces of chloride and any soluble products of reduction from the electrolysis stage of the preservation process.

Chromate-inhibited distilled water was chosen as the wash solution with a chromate ion concentration of 8.7×10^{-3} M (1000 ppm) and a pH of not less than 8.5 to ensure inhibition. The presence of a plentiful supply of oxygen promotes the inhibitor film formation by the chromate ion, so the solution was stirred by bubbling air through it. This also improved its washing efficiency.

It should be noted that chromate solutions may cause skin irritation with certain individuals and that disposal regulations should be observed.

A side advantage with the use of chromate is that it acts as a deterrent to fungal growth on the wax which is used for the final surface coating (discussed later).

The initial chloride level of the wash solution was approximately 5×10^{-4} M (20 ppm). Washing was continued for up to five months with fortnightly changing of the distilled water until no increase in chloride content of a fresh solution, initially between 3.6×10^{-5} and 1.1×10^{-4} M (1 to 3 ppm), was observed over a two-week washing period. Also, the pH of the solution was reduced from an initial value at the commencement of washing of 10.5 down to pH 8.5. Washing was then considered finished.

2.5 Drying procedure

After washing, the wet cannon were dried by placing infrared heaters around them. A simple and convenient technique for heating the cannon from inside was to pass compressed air through a copper tube inserted in the bore. This tube was heated outside the cannon by gas burners, and the air flow rate determined the air temperature which was adjusted to

150°C. An aluminium reflector canopy was placed over the cannon and heating elements. The cannon were held at a temperature of 120°C for 48 h to dry the surface layers.

2.6 Coating procedure

It is acknowledged that one of the first rules in conservation is that, if possible, no technique should be used which is irreversible. Therefore, it was decided to use a final protective coating on the cannon which could be removed relatively easily if this ever became necessary. Extensive work in overseas museums [8-10] has shown that a microcrystalline wax is probably the best form of protective coating for 'graphitised' cast iron, especially when it is proposed to exhibit the item inside a museum. This wax imparts a moisture-impervious and relatively hard surface to the cannon, ideal for indoor exhibition.

However, the type and grade of microcrystalline wax recommended [8-10] is not available in Australia. Therefore, a series of seven waxes was obtained to compare with a small sample of the recommended wax. The waxes covered a range of melting points from 74 to 93°C, a penetration (hardness) from 3 to 27 and colour from amber to white.

The tests (published elsewhere [3]) showed that the three hard waxes with a penetration lower than 8 and the soft wax with a value of 27 were unsuitable for impregnating the cannon. The remaining three waxes, including the recommended one, were all considered suitable. The different colours of the waxes made no difference to the final colour of the impregnated cannon surface. The properties of the three suitable waxes are listed in Table 2.

TABLE 2

PROPERTIES OF MICROCRYSTALLINE WAXES

Wax	Colour	Melting Point °C ($\pm 1^\circ$)	Penetration at 25°C (mm)
A (recommended)	white	80	18
B	white/yellow	80	10
C	yellow/cream	80	22

Waxes B and C were tested for the support of fungal growth in simulated tropical conditions [3], as there was the possibility of one or more of the cannon being permanently displayed in such an environment. Both waxes were found to support fungal growth, but, as stated earlier, the free chromate ion present in the cannon surface after drying should be an effective fungicide.

The wax chosen to impregnate the cannon was B in preference to C (Wax A being unobtainable), but only because it gave a harder surface finish.

In connection with the choice of wax, the manufacturers state that any specification of wax can be met as required simply by blending different grades. Only the colour, penetration and melting point need be specified.

Following the choice of wax the cannon were dried as described earlier and placed in a bath of molten wax at 120°C. The temperature of the bath was raised to 135°C at which the cannon remained until air bubbles ceased to evolve from the surface, which took up to five days.

The wax impregnation tank was fabricated entirely from mild steel, no metal such as copper being used which might tend to oxidise the wax. As a precaution against any oxidation, especially from the chromate present in the cannon surface, an anti-oxidant was added (2, 6 ditertiary-butyl-4-methylphenol) to give a concentration of 0.005 wt% in the wax. After all the air bubbles had ceased to evolve from the cannon, the temperature of the bath was allowed to drop to just above the melting point of the wax (80°C). Then, just before the wax had completely solidified, the cannon was raised and allowed to drain over the bath. This cooling of the cannon in the wax is the most important stage of the impregnation process as it is during this period that the majority of wax is absorbed into the graphitised matrix of the cannon. A fully preserved cannon is shown in Fig. 4.

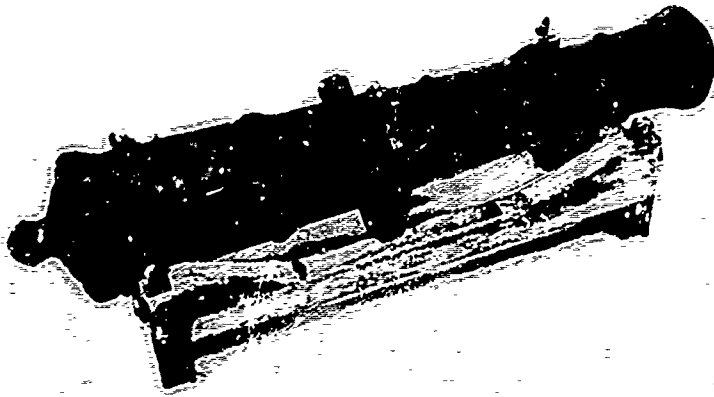


FIG. 4 Fully preserved cannon shown to be in an excellent state of preservation after 199 years under the sea.

The efficiency of wax impregnation was tested by comparing accurate weight measurements ($\pm 0.02\%$) of a wet cannon with those of a dry and also a wax-impregnated one. Due to the difficulties involved in weighing, readings could only be obtained for one cannon. The results showed that 94 volume % of the water present in the porous matrix of the cannon was replaced by wax.

This hot/cold immersion technique was compared with a vacuum impregnation technique using three pieces of cast iron ballast. Although results showed an approximate 10% increase in the volume of wax absorbed by vacuum impregnation, the corroded surface layers of the ballast differ from those of the cannon (discussed later) and the results may not be applicable. Finally, it was decided that the effort and cost involved in wax impregnating under vacuum was not warranted by the relatively small increase in wax absorbed.

The cannon are in a state suitable for exhibition after wax impregnation provided they are displayed indoors and away from children who might climb on the cannon and damage the wax-impregnated graphitised surface.

3. PRESERVATION OF OTHER ITEMS FOUND WITH THE CANNON

As mentioned earlier, a number of other items were recovered with the cannon, and their condition and preservation will now be described where these differ from that of the cannon.

3.1 Wadding, cannon-ball and charge

Two of the cannon were found loaded ready for firing. One contained a piece of wadding, ball and charge (Fig. 2) and the other just a ball and charge.

3.1.1 Wadding

Coral which had grown into one end of the wadding mass (Fig. 2) was not removed for fear the wadding might disintegrate. The wadding fibres were heavily impregnated with iron oxide which was removed before stabilisation of the wadding.

These oxide stains were removed by suspending the wadding in a stirred 1% solution of oxalic acid at 80°C for several days, changing the solution periodically. It was then washed in distilled water prior to the application of the stabilising treatment.

A few loose fibres were treated further to remove all non-fibrous matter. They were first teased apart and then treated for 15 min in 2% acetic acid solution at 40°C, 15 min in 1% oxalic acid solution at 80°C, 60 min boil in 1% sodium hydroxide solution and finally a 10 min boil in distilled water followed by drying at 100°C. In between each stage of the treatment the fibres were washed with distilled water.

This treatment allowed microscopical examination of the fibres, which were identified as hemp [11], and their appearance before and after cleaning is shown in Figs. 5 and 6 respectively. It was observed that most of the fibres were in a comparatively good condition after 199 years under the sea.



FIG. 5 Wadding fibre before cleaning.
Magnification 680×

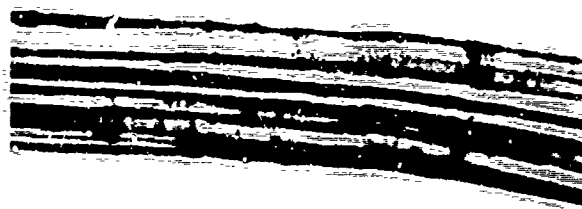


FIG. 6 Wadding fibre after cleaning.
Magnification 680×

After cleaning, the wadding was stabilised to prevent any further deterioration. Recent reports [10, 12, 13] indicated that replacement of the water in the hemp mass with polyethylene glycol or the use of soluble nylon were the best methods for treatment. The former application was chosen because a fungicide, sodium pentachlorophenate, could readily be incorporated and the fibres did not require drying prior to impregnation. The stabilising solution is detailed in Table 3.

TABLE 3

STABILISING SOLUTION FOR HEMP WADDING

<i>Component</i>	<i>Parts by weight</i>
P.E.G. 4000	10.0
Ethanol	69.5
Sodium pentachlorophenate	0.5
Distilled water	20.0

The hemp wadding was soaked in a number of solutions of ethanol in distilled water, successively increasing the ethanol content. Finally a soak in the P.E.G. solution, Table 3, was followed by drying in air.

The two vent-hole plugs were likewise cleaned and impregnated, as also was a twist of hemp rope found looped through a wrought iron eye-bolt from one of the gun carriages.

3.1.2 Cannon-balls

The two cannon-balls, both of 2.97 in (75.4 mm) diameter weighing 3.41 and 3.38 lb (1.55 and 1.54 kg) respectively, were treated in the same way as the cannon. Just prior to and during treatment, the surface layers of the second ball started to spall, finally reducing its weight to 3.10 lb (1.41 kg) and its diameter to 2.58 in (65.5 mm) in places.

As it was not possible to analyse the cannon-ball non-destructively, the reasons for the spalling of the surface layers could not be determined accurately. However, this spalling of cannon-balls has been reported on a number of occasions and is probably due to a weakening by corrosion of the surface layers which are lifted off by the unavoidable oxidation when the ball is exposed to the atmosphere. This did not occur for the first ball which was well sealed in the cannon bore by the mass of hemp wadding.

3.1.3 Gunpowder charge

A quantity of black sludge was recovered from behind the ball from the cannon containing the corroded cannonball. This sludge was filtered and dried. The sample was chemically analysed for the main constituents of gunpowder and showed 65% carbon, 2.7% sulphur, the remainder being the various corrosion products of iron. There was no trace of potassium nitrate which, due to its high solubility, would be expected to have been leached out.

The sample from behind the other ball (Fig. 2) was in one piece weighing 219 g and its chemical analysis was 42% carbon, 3.6% sulphur (the remainder being iron corrosion products) with again no potassium nitrate. The value of carbon in this sample is considered to be an approximate figure of the amount of carbon in the original charge. Investigations [3] have therefore shown that the probable weight of the charge used on board the *Endeavour* was approximately 1.5 lb (680 g).

The powdered sample was left untreated, but the solid lump was impregnated with micro-crystalline wax to strengthen it.

3.2 Gun carriage remains

As shown in Fig. 1, some of the cannon had appendages attached to them, and other coral-encrusted items were found lying near the cannon. From historical records [1], the carriages were jettisoned with the cannon and therefore these appendages were considered to be the metal remains of the carriages.

There was very little evidence of the wooden parts of the carriages due to the destructive action of the shipworm *Teredo navalis*; however, a few fragments were found and preserved.

3.2.1 Metal components

Prior to preservation, a total of 31 items were radiographed to establish what lay under the coral. Heavily filtered 250 kV x-rays were used. For two large aggregates the thickness was so great that gamma radiation from Co⁶⁰ was necessary to obtain suitable penetration. Of the items, 20 were rejected as either they contained no metal, or the metal that had been there had completely corroded, thereby being unidentifiable.

The remaining 11 items were positively identified [14, 15] as being the remains of the wrought iron fittings from a gun carriage, and a coral-encrusted aggregate of fittings is shown with its radiograph in Figs. 7 and 8 respectively.

From the radiographs, detailed drawings were made to assist in the design and construction of carriages for displaying the cannon.

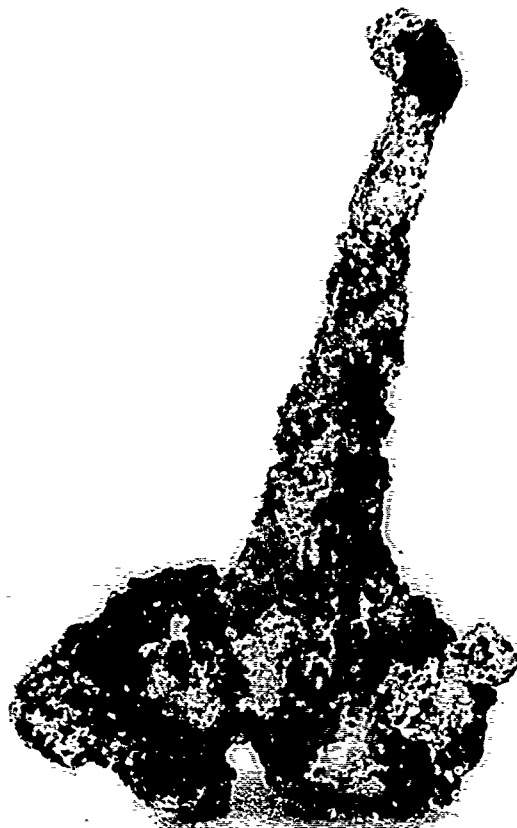


FIG. 7 A coral-encrusted aggregate of wrought iron carriage fittings. Magnification 0.12x.



FIG. 8 A radiograph of the aggregate in Fig. 7. Magnification 0.12x. From the lower left a Hoop (A), Eyebolt (viewed end on) (B), Side loop with square riveted plate and ring (C), a Bed Bolt (D) with the lower end of a Joint Bolt and washer touching it (E) and a Breast Loop and its riveted plate (F). The items were identified from references 14 to 15.

The next stage in preserving these iron relics was removal of the coral encrustations. Because of their fragile nature, mechanical removal was very difficult without damaging the underlying metal. Chemical dissolution tests were tried without success due to the insoluble nature of the crust at the metal interface which was shown earlier to be essentially magnetite. This was very difficult to remove except with hot 10% hydrochloric acid which, even if inhibited would tend to remove oxide surrounding any solid metal which is undesirable. However, treatment in an activated molten caustic soda bath at 550°C for 30 min [3] was successful.

After cleaning, four of the iron fittings were stabilised in the same way as the cannon, and one of these, a side loop through which was found wrapped one turn of hemp rope, is

shown before and after preservation in Figs. 9 and 10 respectively. The bottom plate shown in Fig. 9 was completely lost as only loose oxide remained.

The remaining fittings were preserved by heat treatment in vacuum at 1060°C (detailed later) followed by wax impregnation. This technique revealed examples, although badly corroded, of the majority of metal fittings used in constructing the carriages.

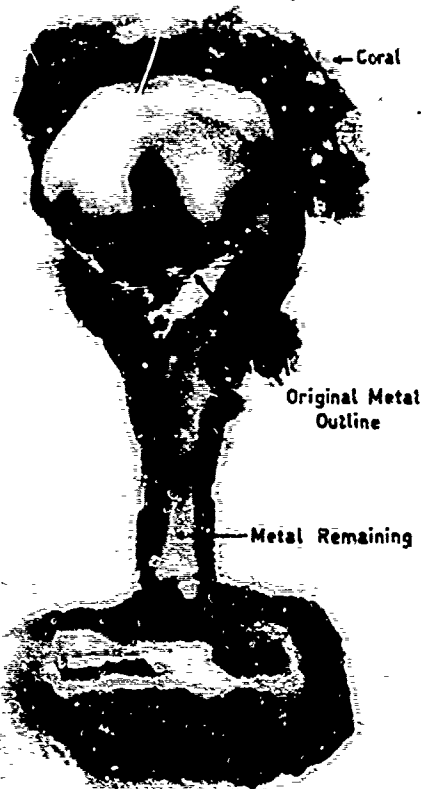


FIG. 9 Radiograph showing the outline of a Side Loop and riveted plate. The replica of the plate is completely devoid of metal. Magnification 0.42x



FIG. 10 The relic from Fig. 9 after preservation. Magnification 0.48x. All evidence of the original outer surface of the Side Loop and all of the riveted plate has been lost but a piece of rope was found. This is probably visible in Fig. 9 as two rounded outlines at the top right but was not originally distinguished from coral growths.

3.2.2 Wood remains

The few wood remains, totalling 83 g, were found attached to the wrought iron fittings. There was sufficient present to enable its identification as elm which was a common material of construction for carriages in the 18th century.

The wood fragments, which were heavily stained with rust, were cleaned and preserved by the same technique used for the hemp wadding.

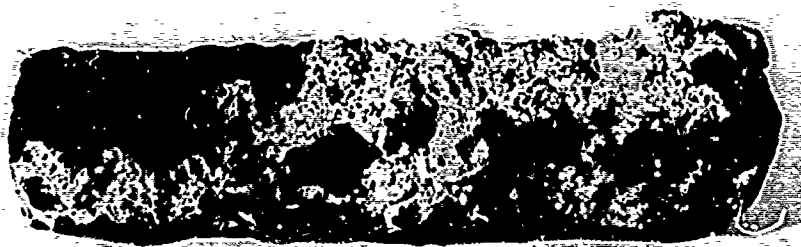


FIG. 11



FIG. 12

FIG. 11 Coral-encrusted ballast pig 0.15 m square and 0.92 m long, as recovered from the sea bed. FIG. 12 Cross-section through a piece of ballast showing the extent of corrosion. Magnification 6.15 \times . Unetched. The coral (dark) is still attached to the corroded region (grey) surrounding the sound metal of the ballast (white).

3.3 Iron and stone ballast

3.3.1 Iron ballast

The iron ballast pigs were located piled in a coral-covered pyramid on Endeavour reef, and underwater explosives were required to break up this pyramid. The 7600 kg of pigs (Fig. 11) were recovered in pieces 0.15 m square and between 0.23 m and 0.92 m long weighing between 40 and 150 kg respectively.

Mechanical removal of the coral from the ballast was again found very difficult as the corroded layers were very hard and were also firmly bonded to the coral, unlike the cannon which had soft graphitised corroded layers and a separated interface with the coral. Therefore, mechanical means tended to remove the ballast oxide along with the coral.

The activated molten caustic soda treatment so successful for removing coral from the wrought iron fittings was therefore tried, again with success.

Sampling a piece of ballast for examination necessitated the use of a diamond saw. The analysis of the metal [3] showed it to be a high-phosphorus white cast iron.

Corrosion occurred by the galvanic action between the regions of pearlite in the iron acting as anodes to the cathodic bulk of iron carbide and the ternary eutectic of ferrite, iron carbide and iron phosphide.

In contrast to the corrosion by graphitisation of the grey iron cannon leaving a soft porous graphite matrix filled with corrosion products, the pearlite in the white iron ballast corroded leaving a coherent matrix consisting of the very hard carbide and ternary eutectic filled with corrosion products.

From a cross-section of a piece of ballast (Fig. 12), it can be seen that corrosion has occurred on the average to a depth of 6.4 mm increasing up to 19 mm in a few places such as corners. Again, it is these porous surface layers from which chloride must be extracted and oxides reduced to achieve prolonged stabilisation.

The electrolysis technique used for the cannon would be too long and expensive for the large amount of ballast, and therefore investigations were carried out into alternative methods.

Work in Europe [16, 18] has shown that heat treatment can be used for stabilising corroded iron objects recovered from the sea. These techniques have the advantage over electrolysis techniques in that they require only about 2 weeks compared with the 9 months taken with the *Endeavour* cannon.

Eriksen and Thegel [16] heated cannon to a temperature of 850°C in air, which was claimed to prevent further corrosion. However, this tended to remove the surface features of the cannon, which is highly undesirable.

More recent work in Sweden [17, 18] used heat treatment in a reducing atmosphere at 1060°C. This technique is theoretically the best of all the preservation techniques, as under these conditions all chloride would be removed and oxides reduced back to the original metal. However, the technique was not used for the *Endeavour* cannon for fear of damaging the surface features, and also no suitable furnace has yet been found in Australia. There are also the problems of altering the metallurgical structure of the metal by the heat treatment process, which to many conservators is undesirable.

This technique [17, 18] has been confirmed by our own experiments, which showed that the chloride content of the corroded surface layers of a piece of ballast was reduced from 1.40% to 0.002% at 1060°C in hydrogen. However, much more experimental work is required on this technique, especially with large furnaces and with the use of graphitised cannon as 'guinea pigs'.

Although no furnace was available with a reducing atmosphere, a furnace large enough to accommodate the ballast up to 1060°C in vacuum or nitrogen was found [3]. By this process, using vacuum during heating and nitrogen for cooling, chloride concentrations lower than 0.002% were obtained for treated ballast samples. A preserved ballast block after wax impregnation is shown in Fig. 13.

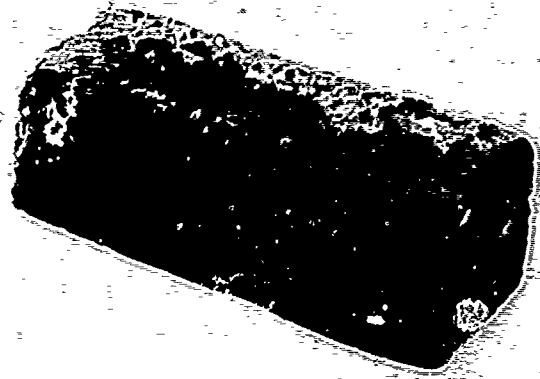


FIG. 13 Ballast block after preservation. Note the holes used for handling purposes at the end of the block.

3.3.2 Stone ballast

The stone ballast, which consisted of 54 pieces of stone of two major types, was cleaned by continued washing in fresh and then distilled water to remove sea water contamination.

The first type of stone was yellow and of a metamorphic nature whereas the second was grey and of basalt origin. Investigations [3] into the regions where James Cook took stone ballast on board the *Endeavour* reveal that the yellow stone, characteristic of Queen Charlotte's Sound, New Zealand, and the basalt rock which is characteristic of the volcanic Society Islands, were presumably taken on-board at these places.

3.4 Lead sheet

A piece of 2.5 mm-thick lead sheet approximately 0.6 m long, 0.2 m at the widest part and containing 18 circular holes was found near one of the cannon.

The lead had a thin yellow coating which was analysed by X-ray diffraction techniques to consist essentially of calcium carbonate with lead chloride and traces of silver chloride. This coating was removed by placing the lead in a 50% sulphuric acid solution at 25°C (lead being resistant to attack by this solution) followed by washing in distilled water. No further treatment was then required.

The spectrographic analysis [3] of the lead sheet showed it to be the same as a lead hull patch from H.M.S. *Loe* which sank in the Florida Keys in 1744 (sample provided by the Smithsonian Institution). This indicates that the sheet was possibly some form of weather-proofing or indeed a hull patch from the *Endeavour*.

4. DETAILS OF THE CANNON

A fully preserved four-pounder cannon (Fig. 4) is 6 ft (1.8 m) in length and weighs approximately 1200 lb (550 kg). The embossed monogram, letters on the trunnions and chiselled markings on the barrel are easily distinguished and are detailed in Table 4.

TABLE 4

INDIVIDUAL MARKINGS ON EACH CANNON

Cannon (Fig. 4)	Embossed monogram (Fig. 14)	Nos. chiselled on breech	Nos. chiselled at right angles and to the side of the monogram (Fig. 14)	Letter embossed on the trunnions	
				Right	Left
a	Crowned 'GR2'	11-3-0	6 Right of monogram	D	IC
b	Crowned 'GR2'	11-2-15	2 Left of monogram	D	IC
c	Crowned 'GR2'	11-2-2	3 Left of monogram	D	IC
d	Crowned 'GR2'	11-2-5	15 Right of monogram	G	Blank
e	Crowned 'GR2'	11-2-7	14 Right of monogram	G	Blank
f	Crowned 'GR2'	11-2-2	12 Right of monogram	G	Blank

All the cannon have the British Crown property 'Broad Arrow' chiselled on the barrel. The numbers chiselled on the breech give the weight of each cannon in hundredweights, quarters and pounds [3], Fig. 4.

A close-up of the embossed monogram 'GR. 2' (Fig. 14) on the cannon shows the detailed



FIG. 14 Close-up of the embossed crowned monogram 'GR2' found on the cannon, also the number 2 chiselled to the side of the monogram.

work of the gunfounder, and the cypher indicates that the cannon were made before 1760 during the reign of King George III.

The numbers chiselled to the side of the monogram (Fig. 14) are presumably manufacturer's serial numbers and appropriate to a batch from a particular foundry.

The letter G is embossed on the right trunnion of three cannon, the left trunnion being blank. Ordnance records in the Public Records Office in England show that this might stand for the gunfounders Graham and Sons who cast iron pieces during this period. The letters D and IC (or possibly JC) embossed on the right and left trunnions respectively of the remaining three cannon indicate that they were apparently made by Joseph Christopher, a British gunfounder whose family was active from 1760 to 1820.

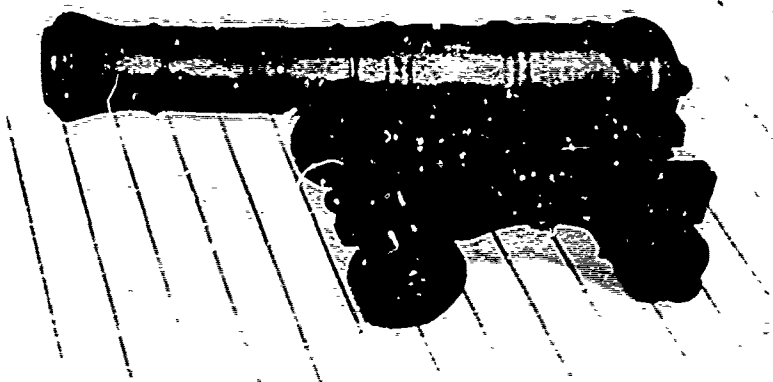


FIG. 15 Preserved cannon displayed on a carriage.

5. MOUNTING AND DISTRIBUTION OF THE CANNON

The six cannon, after preservation, were mounted on wooden carriages for display (Fig. 15). These carriages were designed and constructed by Mr W. G. Douglas of the Department of Shipping and Transport's Brisbane Office, and details are shortly to be released.

The carriages were based on information published in 1780 [15] which gives details of the design of gun carriages used during the 18th century. This information was supplemented by the tracings of the radiographs of the outline of the wrought iron carriage fittings while still encapsulated in coral [3]. There was excellent agreement between the shape and dimensions obtained from these radiographs and those calculated from the published data.

The other items recovered include cannon-balls, wadding, gunpowder samples, wrought iron carriage fittings and stone and iron ballast which are to be presented to various museums.

It is fortunate that the jetsam was located and recovered early in 1969 by Virgil Kauffman and his expedition, as this allowed sufficient time to preserve the cannon ready for display during the bicentenary celebrations of the discovery of the east coast of Australia by James Cook on 20 April 1770.

It is fitting that one cannon was allocated by the Commonwealth Government to the Philadelphia Academy of Natural Sciences which backed the expedition that located the cannon. This was presented to the Academy by the Prime Minister of Australia in Canberra on 17 March 1970. The remaining five cannon were presented to Queensland, New South Wales, Canberra, New Zealand and the Greenwich National Maritime Museum in James Cook's home country.

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REFERENCES

- 1 *Historical Records of New South Wales*, 1, part 1, Government Printers, Sydney 1893, pp. 133.
- 2 POURBAIX, M. J. N., *Thermodynamics of Dilute Aqueous Solutions*, Edward Arnold & Co, London 1949.
- 3 PEARSON, C., *The Preservation of the Iron Cannon from James Cook's 'Endeavour' after 200 years under the sea*. To be published.
- 4 VON WOLZOGEN KUHR, C. A. H., and VAN DER VLUGT, L. S., 'De grafiteering van gietijzer als electrobiochemisch proces in anaerobe gronden' ('The Graphitisation of Cast Iron as an Electrochemical Process in Anaerobic Soils'), *Water*, 18 (1934), 147-165.
- 5 SCHIKORR, G., 'The Decomposition of Ferrous Hydroxide at Room Temperature', *Z. anorg. allgem. Chem.*, 212 (1933), 33-39.
- 6 EVANS, U. R., and WANKLYN, J. N., 'Evolution of Hydrogen from Ferrous Hydroxide', *Nature*, 162 (1948), 27-28.

- 7 SHIPKO, F. J., and DOUGLAS, D. L., 'Stability of Ferrous Hydroxide Precipitates', *J. Phys. Chem.*, 60 (1956), 1519-1523.
- 8 WERNER, A. E. A., 'Synthetic Waxes', *Museums Journal*, 57 (1957), 3-5.
- 9 ORGAN, R. M., and SHORER, P., 'An Improved Method of Consolidating Fragile Iron Objects', *Museums Journal*, 62 (1962), 109-113.
- 10 WERNER, A. E. A., 'New Materials in the Conservation of Antiquities', *Museums Journal*, 64 (1964), 5-16.
- 11 MATTHEWS, J. M., *Textile Fibres*, Sixth Edition, Wiley, New York 1954.
- 12 ORGAN, R. M., 'Carbowax and other Materials in the Treatment of Waterlogged Palcolithic Wood', *Studies in Conservation*, 4 (1959), 96-105.
- 13 SHELL CHEMICAL CO., 'Stabilisation of Wood with Polyethylene Glycols', *Technical Bulletin I.O.C.*, 62'2, 1962.
- 14 BUGLER, A., *H.M.S. Victory, Building, Restoration and Repair*, Drawing XIII. H.M.S.O., London 1966, p. 57.
- 15 MULLER, J., *A Treatise of Artillery*, 3rd edition, London 1780.
- 16 ERIKSEN, E., and THEGEL, S., *Conservation of Iron Recovered from the Sea*, Tøjhusmuseets Skrifter. Royal Danish Arsenal Museum Publication No. 8, Nordlunde, Copenhagen 1967.
- 17 BARKMAN, L., *On Resurrecting a Wreck (Att Bota Vrak). Some Technical Observations about the Preservation*. Exhibition 1967, Wasaskrifter 6, Statens Sjöhistoriska Museum, Stockholm 1968.
- 18 BARKMAN, L., Private Communication, National Maritime Museum, Stockholm 1969.
- 19 VLASOFF, V., *In Search of a Cannon*, G. K. Bolton, Cairns 1969.

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Abstrait—En 1770, le Lieutenant James Cook, qui a découvert la côte orientale de l'Australie, a dû jeter à la mer canons et attalages, accompagnés de lest de fer et de pierres, quand la *Endeavour* touchait sur un récif de corail. Ces restes ont été découverts en 1969 et leur état et leurs qualités propres après quelque 200 ans sous la mer sont discutés. Sont expliqués ensuite les traitements appliqués dans le but de stabiliser le canon en fer et l'attelage. Ils comprennent la réduction électrolytique, suivie par un lavage dans l'eau distillée inhibée avant d'appliquer une imprégnation finale de cire; également un traitement dans un bain de soude caustique activée, suivi par un traitement à la chaleur, avant l'imprégnation de cire. Les aspects historiques des restes concernant leur validation sont mentionnés aussi.

Kurzfassung—Im Juli 1770 musste Leutnant James Cook, der Entdecker der Ostküste von Australien, eiserne Kanone und Wagen mit Eisen- und Steinballast überbordwerfen, als die *Endeavour* auf ein Korallenriff stieß. Diese Relikte wurden 1969 wiedergefunden und deren Zustand und Eigenschaften nach einem nahezu 200jährigen Aufenthalt am Meeresboden werden besprochen. Ausführlich werden dann die Behandlungen dargelegt, welche zur Erhaltung der eisernen Kanone und der Wagenreste angewandt wurden. Diese umfassen elektrolytische Reduktion, wonach sie in gehemmtem destillierten Wasser gewaschen werden, bevor eine endgültige Wachsimprägnation stattfindet. Auch wird die Behandlung in einem aktivierten flüssigen kaustischen Sodabad angewandt, gefolgt von einer Wärmebehandlung vor der Wachsimprägnation. Die historischen Aspekte der Relikte mit Bezug auf ihre Authentizität werden auch erwähnt.

Riassunto—Nel 1770 il Tenente James Cook, che scopre la costa orientale dell'Australia, dovette gettare in mare cannoni e carrelli di ferro insieme alla zavorra di ferro e pietra quando l'*Endeavour* s'incagliò su una scogliera di coralli. Questi relitti furono recuperati nel 1969, e si discutono la loro condizione e caratteristiche dopo quasi 200 anni sotto mare. Si precisano i trattamenti applicati per stabilizzare i resti del cannone e carrello di ferro. Essi comprendono la riduzione elettrolitica, seguita da lavaggio in acqua distillata inibita, prima di una impregnazione finale con cera, nonché trattamento in un bagno di soda caustica fusa attivata, seguita da trattamento termico prima di impregnazione con cera. Si parla anche degli aspetti storici dei relitti in quanto alla loro autenticazione.

Extracto—En el año 1770 el Teniente James Cook, que descubrió la costa este de Australia, tuvo que arrojar al mar cañones y cureñas de hierro así como lastre de hierro y de piedra al chocar su barco el *Endeavour* con un arrecife coralino. Estas reliquias se recuperaron en el año 1969 y se discuten su condición y sus propiedades después de casi 200 años debajo del mar. Se dan detalles sobre los tratamientos empleados para estabilizar los restos del cañon y cureña. Los mismos incluyen la reducción electrolítica seguida por lavado en agua destilada antes de una impregnación final con cera, también tratamiento en un baño de soda caustica fundida activada seguida por un tratamiento de calor antes de la impregnación con cera. Asimismo se mencionan los aspectos históricos de las reliquias respecto a su autenticación.

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