

CASTING TECHNIQUES OF CANNONBALLS FROM THE AKKO 1 SHIPWRECK: ARCHAEOMETALLURGICAL INVESTIGATION

D. Cvikel ^a, E. D. Mentovich ^b, D. Ashkenazi ^{c,*}, Y. Kahanov^a

^a Leon Recanati Institute for Maritime Studies, University of Haifa, Haifa, Israel

^b School of Chemistry, Tel Aviv University, Ramat Aviv, Israel

^c Faculty of Engineering, Tel Aviv University, Ramat Aviv, Israel

(Received 16 February 2012; accepted 27 January 2013)

Abstract

Eleven cannonballs were found in the Akko 1 shipwreck; two of them, a 9-pdr and a 24-pdr, were retrieved and studied using archaeometallurgical methods. Findings are reported in the present work. The aim of this research was to study the manufacturing technologies of the two cannonballs, and if possible to determine their date and manufacturing location according to the detailed technological analysis. The examination used optical microscopy, scanning electron microscopy, including energy dispersive spectroscopy, and hardness tests. The results show that the two cannonballs were casted by sand moulds, in two dissimilar processes and were made of different types of cast-iron. The non-uniformity of the 24-pdr cannonball could be the outcome of using a feeder of gray cast-iron in order to complete the casting process and compensating for the shrinkage of the metal. Based on their manufacturing process, it is suggested that the cannonballs were manufactured about the end of the first half of the nineteenth century. Combined with the archaeological and historical background, this supports the possibility that Akko 1 was a naval auxiliary vessel, which was in Akko harbour circa 1840.

Keywords: Akko 1 shipwreck; Archaeometallurgy; Cannonballs; Cast-iron; Casting; Metallography

1. Introduction

1.1. Historical background

The city of Akko (St. Jean d’Acre, Acre, Akka) is located at the north end of Haifa Bay, in northern Israel. It is one of the most ancient cities in Israel, with evidence of habitation since the Early Bronze Age (3300). The present harbour of Akko has a history of more than 2,500 years [1–4]. The town and harbour were conquered by the Ottomans in 1516 [5].

Between the end of the eighteenth and the first half of the nineteenth centuries, Akko was involved in three naval campaigns. Napoleon Bonaparte laid siege to the Ottoman town on 19 March 1799. The Ottomans, aided by a British squadron commanded by W. Sidney Smith, fought back, and after 61 days of indecisive siege, the French retreated toward Egypt [6–8]. In 1831, Ibrahim Pasha, the son of Muhammad Ali—the ruler of Egypt, laid siege to Akko, aided by an Egyptian fleet. On 9 December 1831, the Egyptian ships bombarded Akko heavily, but the engagement was not decisive. Gunfire from the town sank one gunboat and damaged the other ships. The Egyptian ships retreated to Haifa and later sailed back to Alexandria for repairs. However, the town was taken

by the Egyptian army on 27 May 1832, after a six month land siege [6, 9, 10]. Several years later, on 3 November 1840, a British-Austrian-Ottoman fleet bombarded Akko. A shell hitting the main Egyptian powder magazine of Akko resulted in an explosion which destroyed a significant section of the town. Akko was taken by the allied fleet the following day [6, 7, 10].

In these three naval operations, western European or eastern Mediterranean ships of various types, rates and classes, took part. From analyses of the archaeological data combined with the historical background, it is believed that the Akko 1 shipwreck is apparently a result of the 1840 campaign.

1.2. The Akko 1 shipwreck

The Akko 1 shipwreck was excavated for three seasons between 2006 and 2008 by an expedition of the Leon Recanati Institute for Maritime Studies at the University of Haifa. The shipwreck site is inside Akko harbour, 70 m north of ‘The Tower of Flies’, at a maximum depth of 4 m (Fig. 1). The shipwreck remains were 23 m long from bow to aft extremity, and 4.66 m wide from the line of the false keel to the

* Corresponding author: dana@eng.tau.ac.il

uppermost remains of the port side, lying in a northwest to southeast direction. The shipwreck comprised sections of the keel and false keel, bow timbers, hull planks, framing timbers, and ceiling planking. The shipwreck components were mainly (86%) made of eastern Mediterranean hardwood, and the remainder was made of softwood [11].

The original ship was apparently built at the end of the first quarter of the nineteenth century and shipwrecked about 1840. A reconstruction of the original ship suggests a 26-m-long two-masted brig carrying 16 guns. The cannonballs, lead shots, and muskets discovered, as well as traces of fire on the hull timbers, provide abundant evidence for the ship being involved in warfare. Considering the aspect of seamanship inside Akko harbour, and the navigational hazards, the chances of a vessel of this type entering the harbour to attack are unlikely if not impossible; thus, it would have been a friendly, rather than an enemy, ship [11]. Therefore, Akko 1 could have been an auxiliary vessel shipping ammunition and armaments to Akko, which sank inside the town's harbour.

Eleven cannonballs were found, of which ten were inside the shipwreck and one was found near the false keel under the bottom [11]. Three of the cannonballs were retrieved and identified as 9-, 12-, and 24-pdrs. The 9- and 24-pdr cannonballs underwent a series of metallurgical investigations. In a previous study to the present one, it was found that both cannonballs were manufactured after 1839. The 9-pdr cannonball may have been casted in Egypt [12]. This study, as part of a systematic series of investigations concerning the Akko 1 shipwreck [11–13], has determined the

microstructure, composition and properties of these two cannonballs. It aims to explain the reason for two types of cast-iron in the same cannonball, as well as to ascertain whether they were manufactured at the same foundry and with the same technology, and to obtain additional indications for the dating. Such a multi-disciplinary approach explores the relations between the manufacture of the objects and their production centres, local workshops, and general trends, as well as technological changes during prehistory and history [14, 15]. The section following the research background describes the metallurgical tests performed in order to determine the differences and similarities between the two cannonballs.

2. Research background

2.1. The solid round shot

The early round shots were often made of stone. They were lighter, faster, and put less strain on the cannon than iron ones. However, stone proved to be too brittle to withstand the explosive force of gunpowder, and not sufficiently dense to produce the proper effect when striking. This, in addition to the high cost of cutting a round ball out of stone and the improvement in the quality of gunpowder and cast-iron technology, resulted in the fact that, by the end of the sixteenth century, a cast-iron round shot had replaced the stone shot, and was the most common and simple projectile fired from smoothbore ordnance [16–18]. Cast-iron cannonballs initially appeared in Europe in the first half of the fifteenth century (in the county of Namur, Belgium, in 1414) [19]. Other substances were also tried; lead was appropriately

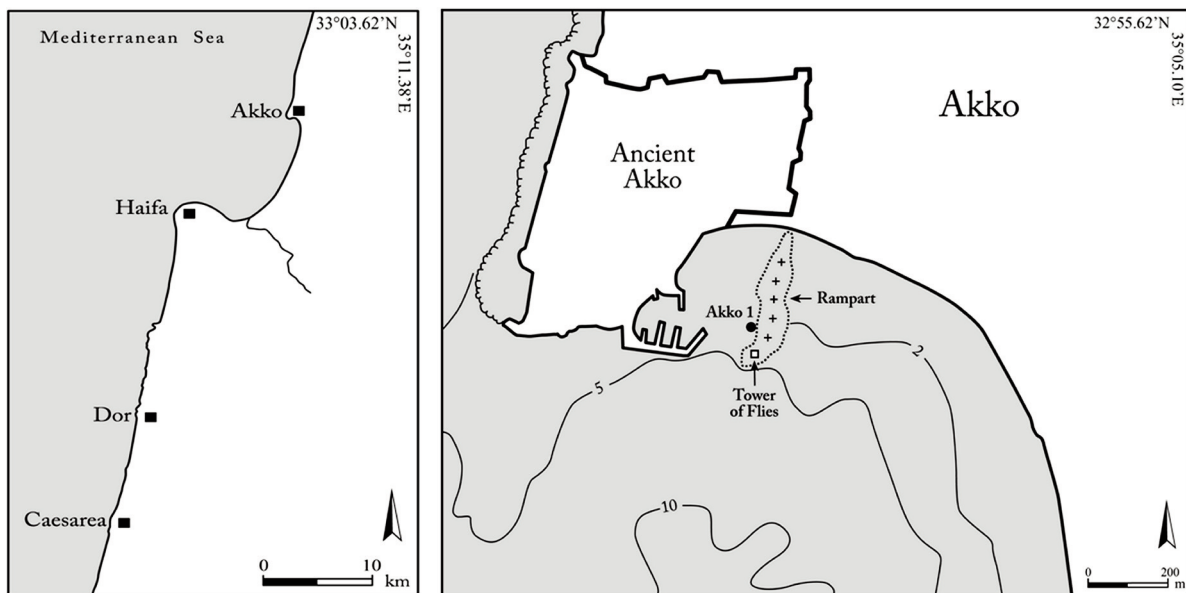


Figure 1. Location of Akko and the Akko 1 wreck site (Drawing: S. Haad).

dense and less brittle than stone, but too soft; wrought-iron was very strong but difficult to work and expensive; and cast-iron united the necessary qualities of hardness, strength, density, and cheapness [17, 18].

Iron or brass moulds, divided into two halves fitting each other exactly, were used for the production of cast-iron round shots. These moulds (termed *Coquilles à boulet* in French), were moulded in sand, and were made in a frame with a wooden pattern [20–22]. Later in the nineteenth century, it was found that iron moulds make an inferior, brittle article, liable to be easily broken, principally during the more rapid cooling of the metal. Therefore, moulds were made of sand, similar to sand used in casting guns, although less refractory sand was needed, as the mass of the metal was less, and consequently, possessed less heat. The sand was mixed with clay-water, to give it form and consistency [17, 23].

The liquid metal was brought from the furnace in a bucket or in a ladle made of iron and coated with clay, having wrought-iron or wooden handles. It was poured into the moulds in a small stream using a feeder, which entered the mould from the side, at the juncture between the two halves, in order to prevent injury to the form. As the metal was raised, the air escaped through a different vent, which also served as a dead-head to collect the scoria. This vent was vertically above the plane of the mould seam [17, 23]. To produce a sound casting, additional material had to be furnished in order to compensate for the shrinkage caused by the cooling and solidifying metal [17, 24].

External or internal flaws could have resulted from the ebullitions and the interception of air. The air would not have time to escape if the vent was filled up with the metallic liquid. This sort of problem was greater in casting small calibre cannonballs since they cooled down much sooner compared with large calibres [22].

Once taken out of the moulds, the cannonballs were imperfect, and their surface was seldom smooth. As closely joined as the moulds were, the cannonballs almost always had a circular seam formed by the metal running out through the juncture between the two halves, and tearing at the fracture of the vent. This irregularity could have scratched the bore of the cannon. Therefore, one method to smooth the cannonball was to remove the excess metal using a hammer and a chisel. Another method was to re-heat the shot until it became red-hot, and hammer it with mechanical hammers until it became as perfectly smooth as possible. In some navies, several cannonballs were later placed together in a large revolving iron cylinder, which, by friction, polished and made their surfaces more uniform [17, 21–23, 25]. Since it was technologically impossible to cast a perfect spherical ball without any irregularities, and exactly to the diameter required, the manufacturer was allowed a certain element of error [18, 24].

As a result of the casting process, three distinct identification marks were left on the shot: the mould seam; the filler hole sprue; and a circular mark, vertically above the plane of the mould seam, which was created as the metal began to fill the vent at the top of the mould. Identification marks such as the mould seam and a circular mark of 38 mm in diameter were found on the 24-pdr cannonball retrieved from the Akko 1 shipwreck (Fig. 2). No casting marks were seen on the 9-pdr cannonball, perhaps because of its inferior state of preservation.

2.2. Moulds and cast-iron

Moulding may be considered in two subdivisions: one is moulding proper, and the other is the formation of the pattern. Moulding proper was almost the same in principle and in practice for each of the various kinds of metals or alloys. Slight variations in the

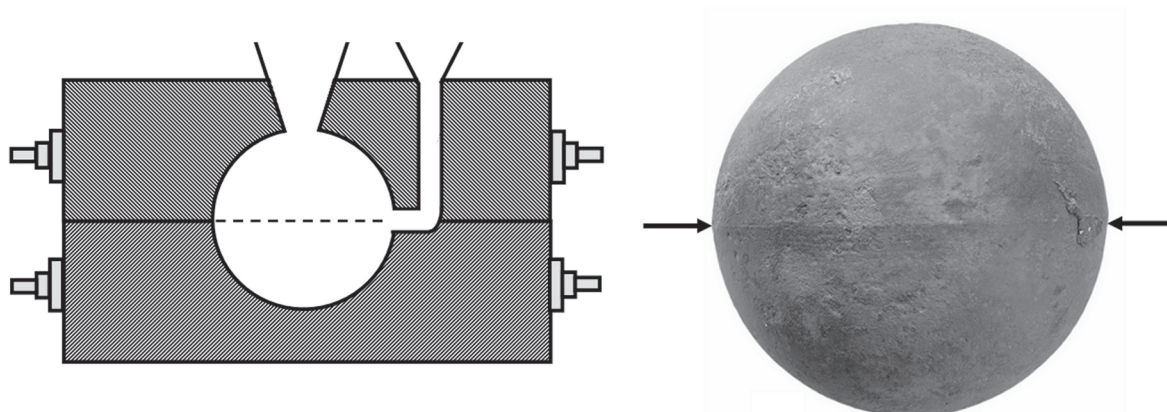


Figure 2. Images of a typical sand mould (left [24]) and a typical mould seam mark on the surface of the 24-pdr cannonball (right).

materials for moulding and in their treatment were the only differences in moulds which were designed to be used for metals. The principal materials used in moulding were sand of various kinds, loam, plaster of Paris, blackening, and metal [26].

Sand was the most common, and certainly the most convenient and available material, and was considered superior to all other materials for moulding [26]. As early as the Chalcolithic period, open moulds made of sand or sand and clay mixture were used for casting copper objects [27, 28]. Sand is more or less porous, and very refractory, so that the hot metals do not melt or bake it, two qualities of great importance in the successful operation of the process. The various kinds of good moulding sand employed in foundries for casting iron or brass have been found to be of an almost uniform chemical composition, varying in grain or aggregate form only [26, 29].

Clay was frequently used for improving the adhesiveness of sand. It was selected from the white luminous kind, argillaceous earth, or fine clay. The clay was either dissolved in a large quantity of water, and kept in the foundry for occasional use, or was dried, pounded, run through a fine sieve, and then mixed with the sand [17, 23, 26]. Moulds consisting partly of loam or sand and partly of metal were in frequent use in iron foundries of the nineteenth century [26].

Cast-iron smelting was already been used in China since 500 BCE (mostly gray cast-iron), but it was first introduced in Europe in the fifteenth century, and was used as a raw material for blacksmiths [30–33]. The Chinese produced their low carbon iron plates indirectly from treating cast-iron by various decarburization processes [33]. The mass production and use of cast-iron in Europe as an important structural material began in the eighteenth century in England when A. Darby developed a method of smelting iron with coked coal [30, 34, 35].

In 1810, a Swedish chemist, J. J. Berzelius, attempted to isolate silicon for the first time from its oxide at a temperature of 1500°C by melting Si, C, and Fe in a sealed crucible [36]. Four years later, the German scientist K. Karsten concluded that the different types of cast-iron result from different forms of carbon content [37]. During the nineteenth century many technical innovations were developed, including continuous melting; furnace improvements (such as better blowers and pouring devices); microscopic analysis of metals including the metallography process, developed by H. C. Sorby in 1863; moulding equipment; and many other tools that are commonly used in modern workshops and factories [38, 39]. In 1837, a dependable moulding machine was introduced into the market, and commercial mechanical blower devices entered the market after the middle of the nineteenth century. The

nineteenth century also brought many improvements in materials, equipment and processes, and as a result, the use of iron for castings increased significantly [40].

Cast-iron is characterized and classified according to its graphite percentage, shape, size and microstructure distribution, including ferritic, pearlitic and ferit-pearlitic matrix, and is divided into lamellar graphite cast-iron, modular, vernicular, etc. [41]. Cast-iron contains mainly 2–4 wt% carbon (C) and mostly 0.5–3 wt% silicon (Si). Other elements which can be found are sulphur, phosphorus, and manganese. Increment of carbon concentration results in a lower melting point of the cast [30]. Both modern gray cast-iron and the metallurgical control of metals were inaugurated at the beginning of the nineteenth century (between 1810 and 1815) [30, 42]. The main difference between gray and white cast-iron is the amount of silicon present in the alloy: gray cast-iron contains more than 1 wt% Si, whereas white cast-iron contains less than 1 wt% Si [43]. Since Si is a graphite stabilizing element, the addition of more than 1 wt% Si causes the C to precipitate as dark graphite flakes, surrounded by a bright pearlite matrix, and alternating thin layers of α -ferrite and a dark cementite (Fe_3C) phase [44]. The graphite formation results from a slower cooling rate solidification or according to the higher presence of silicon in the cast-iron [37]. However, a structural transition from white to gray cast-iron may occur in accord with heat released and inappropriate heat treatment [41]. Cast-iron is a gradient material, which means that different microstructures may occur for the same composition and the physicochemical state of molten metal as a result of different cooling rates [45]. Parameters such as shape and dimension of the mould and the casted objects, the pouring temperature, and the presence of small amount of different elements such as Mg, S and O, can influence the cooling rate and may cause changes in the microstructure [46]. The graphite flakes cause low strength and ductility, but have good machinability and wear resistance. Less than 1 wt% Si causes a precipitation of Fe_3C particles rather than graphite. The massive amount of cementite results in good hardness, good abrasion resistance and brittleness [40]. By 1860 metallurgists already knew that gray cast-iron has good castability, a low melting point (~1200°C), good fluidity, and that it is weak in tension but has high strength in compression [17, 23, 47]. Thermal heat treatment may improve the impact strength of the cast-iron compared to the as-cast material [48]. Different manufacturing processes of cast-iron, which varied from one foundry to another, resulted in variations in material properties [49].

Two dissimilar types of pores are formed during casting: the first is formed during the early stage of solidification, and the second is formed during the

last stage of the solidification process. The pore concentration depends on factors such as the cooling rate and the carbon content [50]. Gas porosity is a significant problem, which occurs in cast-iron products, and is usually caused by the development of gases during the casting process. Hydrogen and nitrogen are the common gases that cause porosity in cast-iron. Their presence during the casting process may result from the reaction between the metallic iron and the sand mould, or from the development of gas bubbles, which dissolve in the liquid metal through solidification. The solubility of hydrogen and nitrogen gasses in the liquid metal decreases as the amount of carbon and silicon in the cast-iron increases [51].

3. Experimental methods and testing

The two cannonballs retrieved from the Akko 1 shipwreck (9-pdr and 24-pdr, shown in Fig. 3) were studied using metallographic optical microscopy (OM), scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS), and hardness testing. The present results were compared with previous scanning SEM-EDS and X-Ray Fluorescence (XRF) spectrometry measurements [12].

Metallographic examination was performed for both cannonballs, including cutting samples with a diamond wheel dicing saw and creating strips that were cut into smaller pieces. First, a rough polish was performed on the samples using 80 grit silicon carbide (SiC) paper. Then the samples were mounted in Bakelite at a temperature of 180°C and a pressure of 20 bars. Surface preparation of the specimens began by grinding with 240–600 grit SiC papers, followed by polishing using 5–0.05 µm alumina pastes and finally polishing using 0.05 µm colloidal silica

polishing suspension paste. After that, the samples were first cleaned in an ultrasonic bath to remove any contamination, and then cleaned with ethanol and dried. Later the samples were etched with Nital acid (97 mL ethyl alcohol and 3 mL nitric acid). After preparation, the samples were examined in a metallographic OM (ZEISS, AXIO Scope A.1).

SEM-EDS analysis was performed for both cannonballs, characterized by a FEI Quanta 200FEG ESEM in high vacuum mode, using the Everhart-Thonley Secondary Electron (SE) detector. Chemical analysis was performed using SEM-EDS with Si(Li) liquid cooled Oxford X-ray detector. Following the metallurgical examination, Rockwell C hardness measurements were performed along the diameter of both cannonballs, with 15 N load using Future-Tech hardness tester.

4. Results

Visual observation of both cannonballs revealed a uniform corrosion layer at the external surface of the object. Graphite flakes are known as sites for iron-oxide formation, so the corruptions initiate along the graphite flake boundaries [52]. The corrosion products on the surface of archaeological objects depend on different factors, among them the composition and the environment in which the object was held, including the pH, temperature and time [53]. The metallographic OM and SEM-EDS analysis of both cannonballs, the presence of cavities containing sand [12], and the seam marks on the 24-pdr shot, reveal that the 9-pdr and 24-pdr cannonballs were manufactured by sand mould casting of cast-iron. A comparison with previous SEM-EDS and X-Ray Fluorescence (XRF) spectrometry measurements is shown in Tables 1 (SEM-EDS) and 2 (XRF).

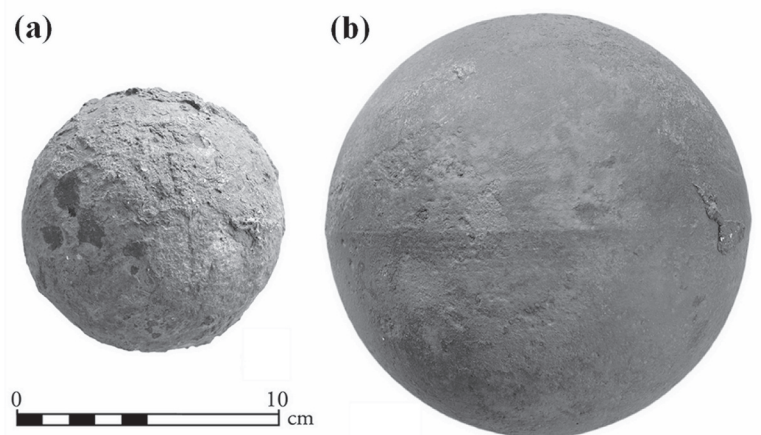
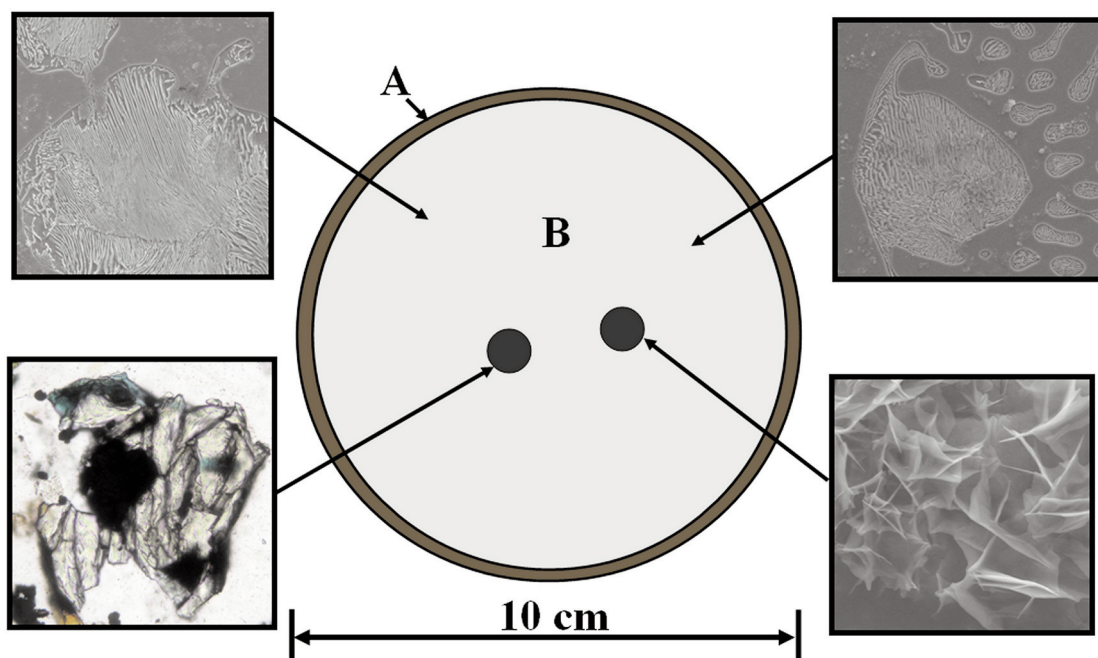


Figure 3. Images of the cannonballs after cleaning the marine encrustation: (a) 9-pdr and (b) 24-pdr (Photo: J. J. Gottlieb).

Table 1. SEM-EDS results of the cannonballs cast-iron (values in wt%), using Quanta 200 ESEM FEG from FEI.

Specimen description	Compositions weight				
	Fe	C	Si	Mn	P
The 9-pdr cannonball, white cast-iron (Fig. 4, internal part of the cannonball, area B')	96.5	2.7	–	0.8	–
The 9-pdr cannonball, white cast-iron (Fig. 4, internal part of the cannonball, area A') [ref. 13]	95.4	3.8	–	0.8	–
The 24-pdr cannonball, gray cast-iron containing graphite flakes (Fig. 10, near external surface of the cannonball, area A)	96.7	2.3	0.5	–	0.5
The 24-pdr cannonball, gray cast-iron containing graphite flakes (Fig. 10, near external surface of the cannonball, area B)	95.3	4.7	–	–	–
The 24-pdr cannonball, gray cast-iron containing graphite flakes (Fig. 10, near external surface of the cannonball, area A) [ref. 13]	97.4	1.3	1.3	–	–
The 24-pdr cannonball, gray cast-iron, graphite flakes (Fig. 10, near external surface of the cannonball, area B) [ref.13]	10.2	89.8	–	–	–
The 24-pdr cannonball, white cast-iron (Fig. 10, internal part of the cannonball, area C, measurement 1)	95.4	3.9	–	0.7	–
The 24-pdr cannonball, white cast-iron (Fig. 10, internal part of the cannonball, area C, measurement 2)	94.6	–	–	0.6	4.8
The 24-pdr cannonball, white cast-iron (Fig. 10, internal part of the cannonball, area C, measurement 3)	98.3	–	0.9	0.8	–
The 24-pdr cannonball, white cast-iron (Fig. 10, internal part of the cannonball, area C, measurement 4)	98.4	–	1.1	–	0.5
The 24-pdr cannonball, white cast-iron (Fig. 10, internal part of the cannonball, area C, measurement 5) [ref.13]	93.7	4.8	–	0.8	0.7

**Figure 4.** Different materials, phases and morphologies observed in the 9-pdr cannonball: Area A is a general corrosion layer; and area B is white cast-iron, including corrosion and sand casting cavities containing Riebeckite granite at the centre of the cannonball (schematic drawing).

4.1. The 9-pdr cannonball

The OM and SEM examination of the 9-pdr cannonball revealed two different areas (Figs. 4 and 5). A corrosion layer (Area A) was observed at the external surface of the cannonball; and beneath it, white cast-iron (Area B). The structural modification in the 9-pdr is uniform dendritic microstructure of white cast-iron, including cementite plates (bright) in ledeburite matrix, but with no evidence of gray cast-iron occurrence.

The two EDS measurements of the 9-pdr cannonball micrographs shown in Table 1 revealed

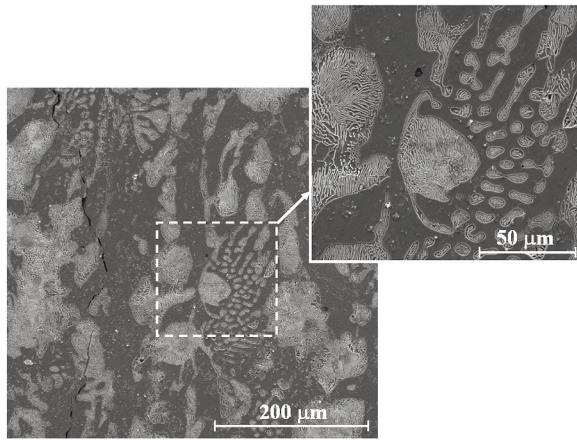


Figure 5. SEM micrograph of the internal part of the 9-pdr cannonball shows a white cast-iron.

the presence of Fe with C, and Mn (both at 0.8 wt%). The SEM and SEM-EDS analysis of the white cast-iron near the external part of the 9-pdr cannonball exposed a lamellar structure made of Fe and C (Fig. 6). The XRF results of the 9-pdr cannonball [12] revealed the presence of Fe, Si, P and Mn (0.6 wt%), as shown in Table 2. However, elements such as C and O were not detected due to the XRF machine limitations. The SEM including SEM-EDS analysis of the iron-oxide near an internal cavity showed a crystalline structure (akaganeite-FeOOH(Cl_x) [54] with the presence of Fe, C and P as well as Cl, O and Al (Fig. 7). A similar structure was also observed, but with the absence of Cl (Fig. 8). The elements Cl, O and Al are common corrosion elements. However, according to the Israeli coastline sea water quality monitoring plan which was conducted in 2002 [55], the main sources of Fe and Al were soils and desert dust particles carried by the wind along the coast. Nevertheless, the Al could have been the result of contamination from the polishing process with alumina paste, although the specimens were cleaned

Table 2. XRF results of the 9-pdr and 24-pdr cannonballs cast-iron [13].

Specimen description	Compositions weight			
	Fe	Si	Mn	P
The 9-pdr cannonball	97.7	1	0.6	0.7
The 24-pdr cannonball	97.7	1	0.6	0.7

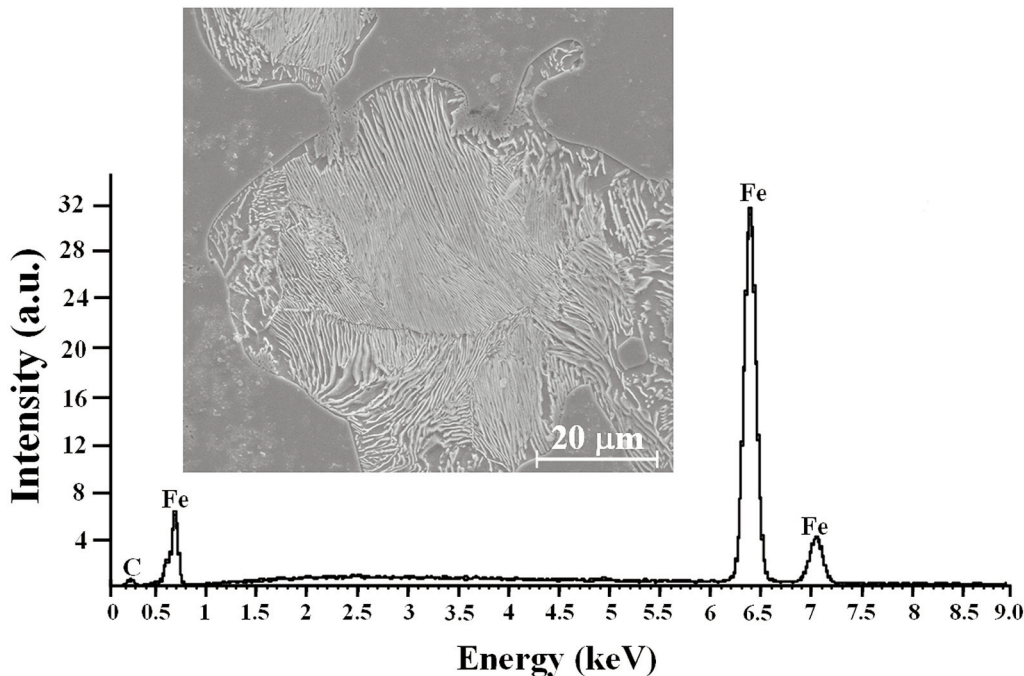


Figure 6. SEM-EDS analysis of a lamellar area of white cast-iron near the external part of the 9-pdr cannonball shows presence of Fe and C elements.

with an ultrasonic bath before their examination.

The Rockwell hardness test results along the diameter of the 9-pdr cannonball showed that the hardness near the external surface of the cannonball was moderately higher than the hardness in its inner part, as shown in Fig. 9.

4.2. The 24-pdr cannonball

The OM and SEM examination of the 24-pdr cannonball revealed three different areas (Fig. 10). A corrosion layer (Area A) was observed at the external

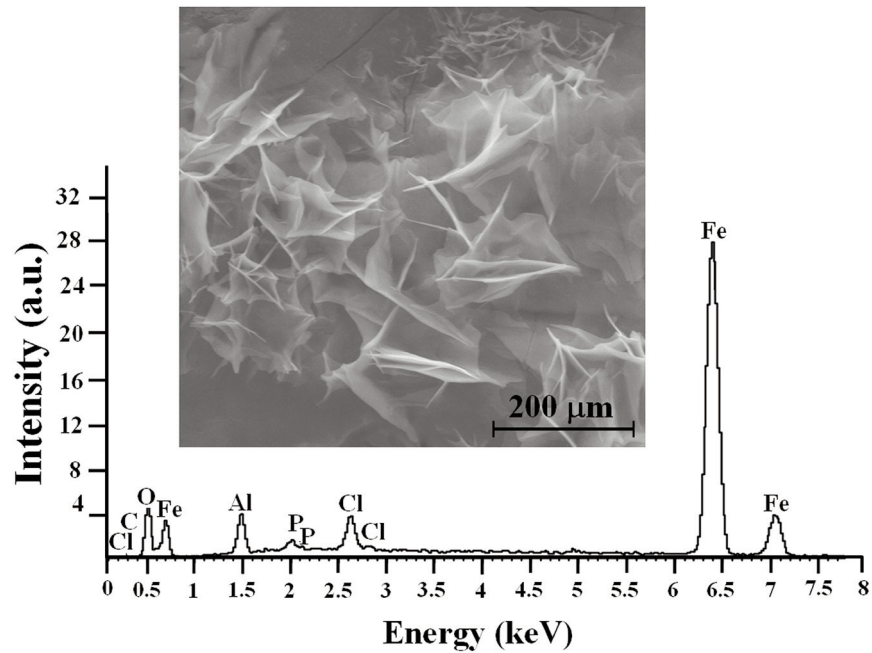


Figure 7. SEM photography showing akaganeite-FeOOH(Cl_x) iron-oxide including SEM-EDS analysis near the internal cavity in the 9-pdr cannonball revealed the presence of Fe, C and P, which are typical elements of cast-iron, as well as Cl, O and Al, which are corrosion and soil elements.

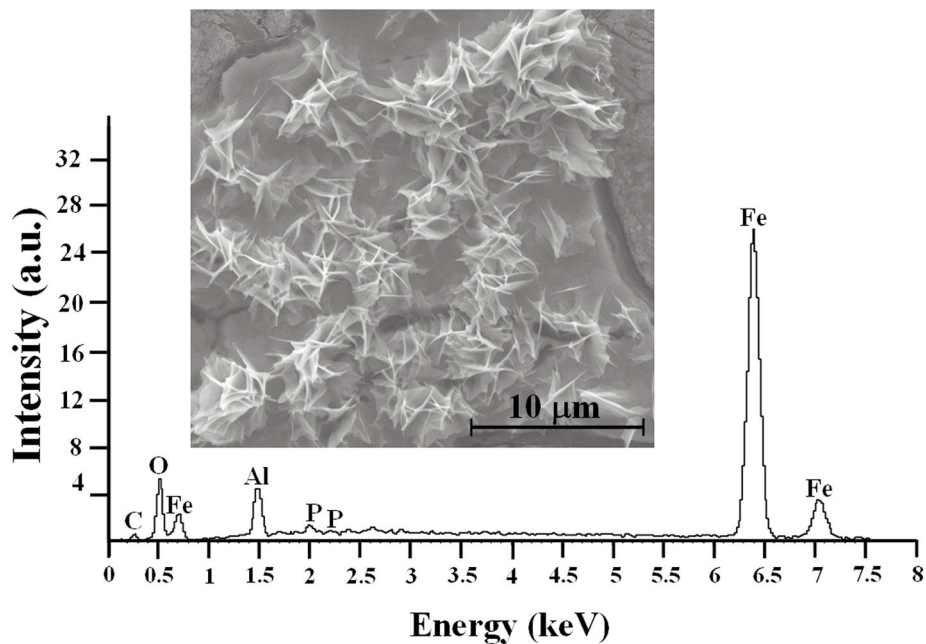


Figure 8. SEM photography showing akaganeite-FeOOH(Cl_x) iron-oxide including SEM-EDS analysis at the internal cavity in the 9-pdr cannonball revealed the presence of Fe, C and P, which are typical elements of cast-iron, as well as O and Al, which are corrosion and soil elements.

surface of the cannonball; and beneath it a dendritic cast-iron microstructure, containing two different structures including gray (Area B) and white (Area C) cast-iron. The 24-pdr cannonball microstructure near the external surface was made of gray cast-iron including pearlite phase and graphite flakes (as shown by SEM in Fig. 11), and white cast-iron at the centre of the cannonball (Fig. 12).

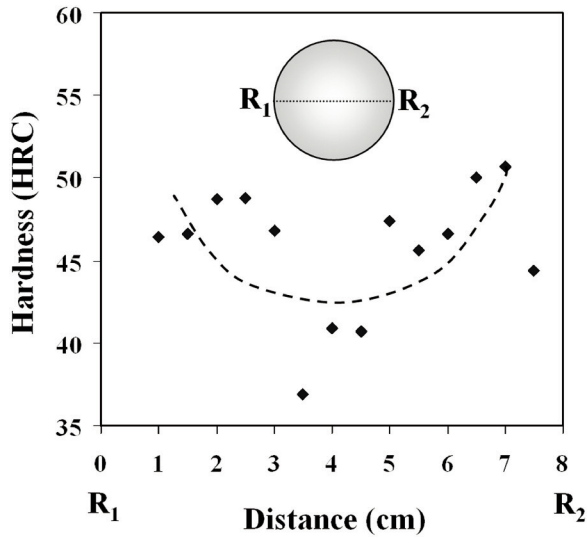


Figure 9. Rockwell C hardness test results along the diameter of the 9-pdr cannonball.

The EDS analysis of the 24-pdr cannonball micrographs (Table 1) showed the presence of Fe, C, Si, Mn and P, which are typical materials in white cast-iron [36]. The EDS analysis of the gray cast-iron revealed the presence of Fe, C, Si and P, but no Mn was observed. The EDS analysis of the white cast-iron revealed the presence of Fe, C, P and Mn (0.8 wt% on average). At the places where P was observed, the surface of the metal was brighter. At the centre of the cannonball, sand remains were found, probably resulting from the sand casting process. The XRF examination of the 24-pdr

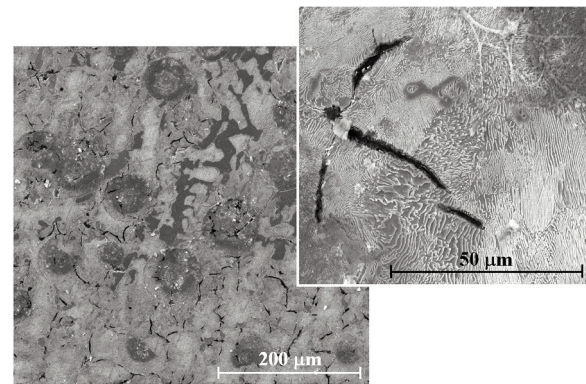


Figure 11. SEM micrograph near the surface of the 24-pdr cannonball shows gray cast-iron containing a graphite flake (black area).

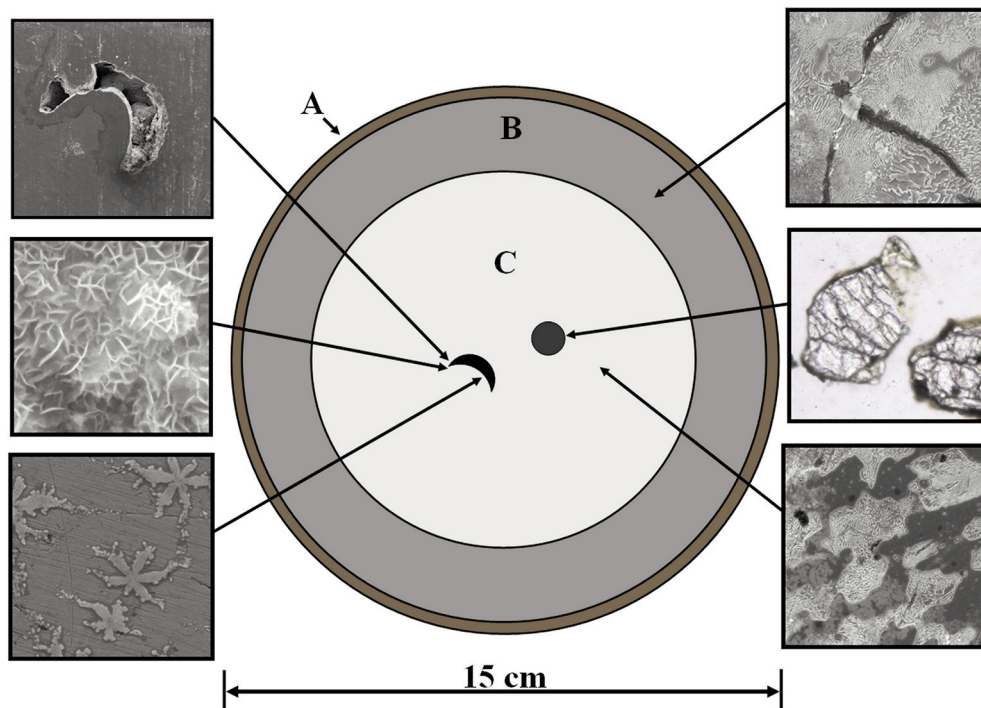


Figure 10. Different materials, phases and morphologies observed in the 24-pdr cannonball: Area A is a general corrosion layer; area B is gray cast-iron with graphite flakes; area C is white cast-iron, including corrosion and sand casting cavities containing quartz sand at the centre of the cannonball (schematic drawing).

cannonball [12] showed the presence of Fe, Si, Mn (0.6 wt%), and P (Table 2).

A SEM micrograph at the external surface of the cannonball, including EDS analysis, disclosed uniform corrosion (near the gray cast-iron area). Corrosion products such as Na, Cl, O, K, Zn, Ca and Al were observed in different areas of the 24-pdr cannonball, as shown in Table 3. The SEM including SEM-EDS analysis of the cavity (Figs. 10 and 13) observed in the bulk of the 24-pdr cannonball (a white cast-iron area) before grinding, polishing and etching, exposed crystalline structure of akaganeite- $\text{FeOOH}(\text{Cl}_x)$ iron-oxide morphology (Fig. 14), which is the most common corrosion product of iron in a marine environment [54]. The chloride ions are necessary materials for akaganeite formation and stabilization. Flower-like or star-like carbide morphology [40, 54], which is characterised by the presence of isolated variable multi-arm carbide solidification microstructures, was also observed in the 24-pdr cannonball (Fig. 15).

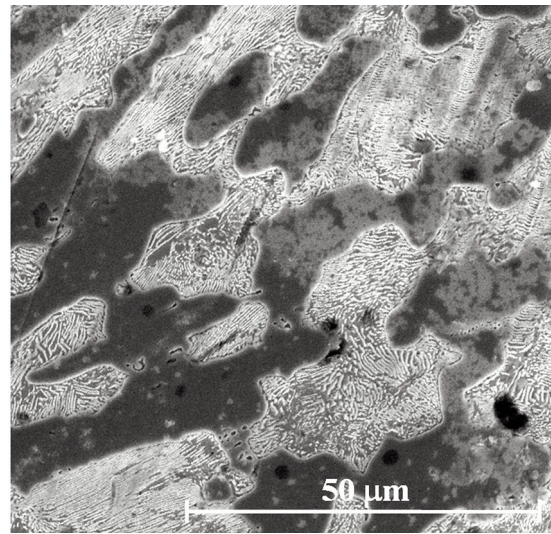


Figure 13. SEM micrograph of the 24-pdr cannonball shows a cavity near the centre of the cannonball, which results from the sand casting

Table 3. SEM-EDS results of the 24-pdr cannonball at the corrosion areas (values in wt%), using Quanta 200 ESEM FEG from FEI.

Specimen description	Compositions weight percentage (wt%)											
	Fe	C	O	Si	Mn	Na	Cl	K	Zn	Ca	Al	P
Gray cast-iron containing graphite flakes	77.6	8	2.1	1.4	–	4.2	4.2	0.6	1.4	–	–	0.5
White-iron, akaganeite $\text{FeOOH}(\text{Cl}_x)$	86.6	4	2.8	0.9	0.4	1.8	0.7	0.4	2	–	–	0.4
White-iron, corrosion with flowers morphology	75.7	–	–	1.3	–	13.2	9.2	0.6	–	–	–	–
Gray cast-iron, general corrosion near the external surface of the cannonball	55.8	23.9	13.8	2.8	0.7	–	0.3	0.4	0.9	0.4	–	1
Gray cast-iron, general corrosion near the external surface of the cannonball (at a cavity)	59.8	23	4.8	1.8	–	–	0.5	–	7.8	0.3	1.6	0.4

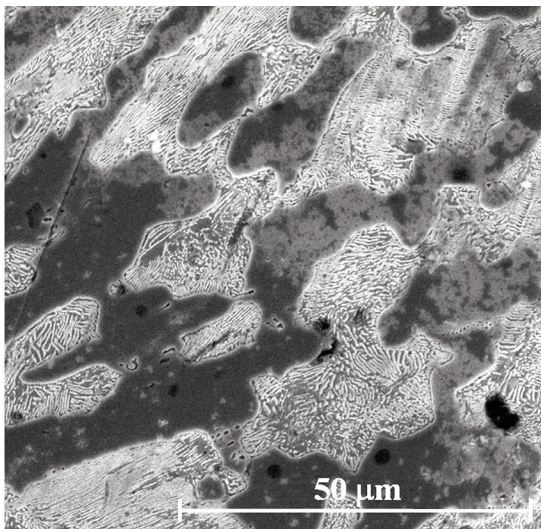


Figure 12. SEM micrograph of the internal part of the 24-pdr cannonball shows a white cast-iron.

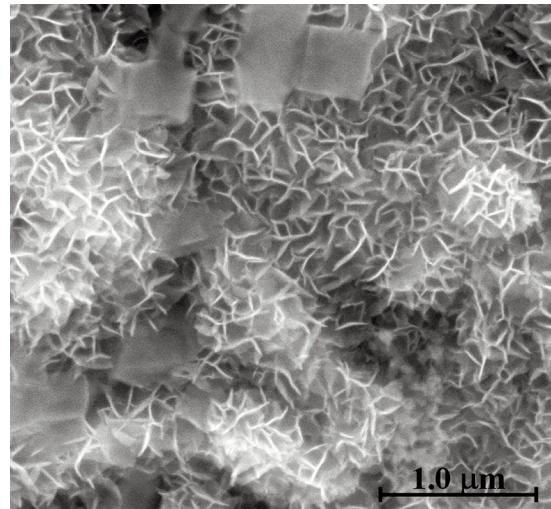


Figure 14. SEM micrograph of a cavity near the centre of the 24-pdr cannonball reveals akaganeite- $\text{FeOOH}(\text{Cl}_x)$ iron-oxide morphology.

The Rockwell hardness test results along the diameter of the 24-pdr cannonball showed that the hardness near the external surface of the cannonball was significantly higher than the hardness in its inner part (Fig. 16).

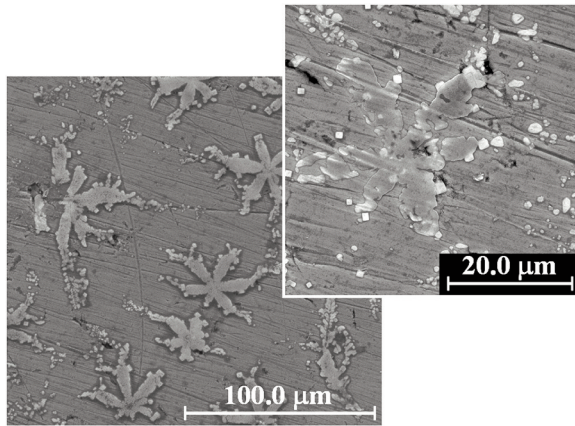


Figure 15. SEM micrograph of a cavity near the centre of the 24-pdr cannonball shows flower-like or star-like morphology.

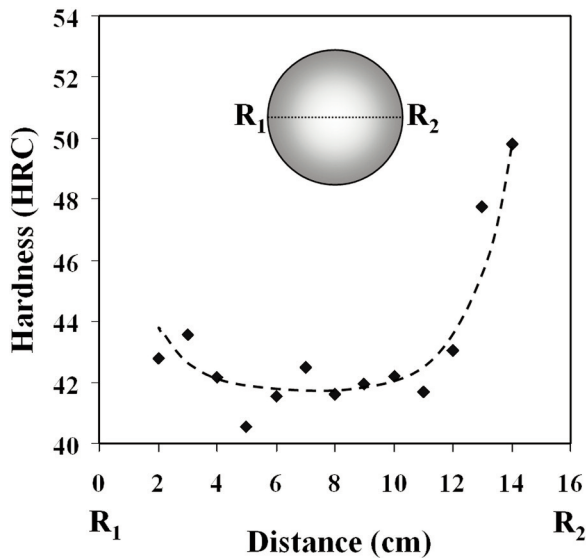


Figure 16. Rockwell C hardness test results along the diameter of the 24-pdr cannonball.

5. Discussion

A thorough study of the manufacturing technologies of the two cannonballs may provide information about the cannonballs' date and manufacturing location. The various tests performed on the two cannonballs were designed to determine their microstructure, composition and properties in

order to understand their detailed manufacturing process. For example, the use of a feeder in the 24-pdr cannonball in order to compensate for metal shrinkage suggests that it was manufactured during the first half of the nineteenth century. The technological analysis may provide us with additional information regarding manufacturing techniques of different workshops during the first half of the nineteenth century.

The sand found in the pores inside the 9-pdr and 24-pdr cannonballs could not have come from the seabed environment of the shipwreck site, since the cavities were located near the centre of the cannonballs, in places where no presence of corrosion products was observed [12]. Therefore, it is suggested that this sand is the remains of the sand casting.

The Rockwell hardness test, as well as the OM and SEM-EDS microscopy results along the diameter of the two cannonballs, demonstrated that they were made of different cast-iron (see Tables 1 and 3). While the 9-pdr cannonball hardness is uniform (according to its uniform structure), as shown in Fig. 9, the 24-pdr cannonball is non-homogeneous according to its non-uniform gray and white cast-iron structure, as shown in Fig. 16, with higher hardness near the external surface of the cannonball.

The fact that the two cannonballs are different in terms of their microstructure and their hardness distribution could result from two dissimilar processes:

(a) The casting of the 9-pdr cannonball was made in one step, without the use of a feeder and without any feeding of additional molten material. Therefore, the white cast-iron is present in all parts of the cannonball including the external part, where the heat removal rate is higher [37].

(b) In the 24-pdr cannonball gray cast-iron is present only in the external part of the cannonball, while white cast-iron is present in the internal part. Therefore, it may be assumed that in the 24-pdr cannonball the liquid material of the white cast-iron was poured into the casting mould first, and only then was the liquid material of the gray cast-iron poured in using a feeder.

The addition of liquid material (gray cast-iron) into the sand mould during the solidification, apparently results from the need to close spaces inside the bulk of the cannonball and thereby reduce porosity to the minimum. It is also possible that the use of gray cast-iron was intended to ameliorate the hardness and wear resistance of the external surface of the 24-pdr cannonball. This may indicate that during the period of the cannonballs' manufacture, it was already known that the presence of porosity in a cannonball could result in a reduction of their target firing capability. Adding manganese to both

cannonballs during solidification results in reducing gas holes and porosity [12, 56, 57], which probably improved firing capabilities. The importance of using a feeder in the 24-pdr cannonball results from the fact that the bigger the mould is, the larger the shrinkage problem caused during solidification [24].

Shell guns were introduced in 1837 [58]. The fact that only cannonballs were found in the shipwreck, might indicate a pre-1837 dating. However, cannonballs were still in use during the Crimean War (1854–1856) [58]. Considering that the introduction of modern gray cast-iron occurred at the beginning of the nineteenth century (between 1810 and 1815) [30, 42], combined with the presence of gray cast-iron in the 24-pdr cannonball, suggest that the two cannonballs were casted during the first half of the nineteenth century. It seems that they were not manufactured post-1860, since at that time the qualities of gray cast-iron were already known [17, 23, 47], and the use of white cast-iron was less likely. Thus, the casting of the cannonballs could have taken place between about 1810 and not later than 1860. This is supported by the relatively high concentration of manganese in both cannonballs, since the presence of more than 0.1 wt% Mn means that the manganese was added deliberately into the alloy and designates a post-1839 manufacture date [12, 56]. Therefore, the manufacturing technologies presented in this study, reinforce the possible dating of the two cannonballs.

Considering the metallurgical and chemical composition analysis, the naval context of Akko 1 shipwreck, and the fact that no naval campaign took place in the Akko vicinity after 1840, it is suggested that the Akko 1 shipwreck could have taken part in the battle of 1840 and sank. However, its being an auxiliary vessel that entered Akko harbour with ammunition and supply a short while earlier or even later than 1840 is no less logical. The approximate 1840 or earlier dating reinforces the assumption that it was a ship friendly to the Egyptian forces controlling Akko at that time [11].

6. Conclusions

The two cannonballs retrieved from the Akko 1 shipwreck were made of cast-iron and manufactured by sand casting moulds. The fact that the cast-iron in the 24-pdr cannonball is non-uniform might indicate the use of a feeder in order to compensate for metal shrinkage during the cooling process, and was perhaps also done in order to improve the hardness and wear resistance of the external surface of the 24-pdr cannonball. The different manufacturing process observed on the two cannonballs, suggest that they were manufactured by two different technologies at the same foundry, or in different foundries and with different technologies. The latter may support the

possibility that they belonged to different navies. The cannonballs were apparently manufactured about the end of the first half of the nineteenth century, and considering the archaeological and historical background, this may reinforce the suggestion that Akko 1 was a naval auxiliary brig which was in Akko harbour about 1840.

Acknowledgements

The underwater excavations and research of the Akko 1 shipwreck have been supported by Ron Marlar, the Yaacov Salomon Foundation, Reuven Sadnai—Coral Maritime Services Ltd., the Halpern Foundation, the Sir Maurice Hatter Fellowship, Hecht Trust, the Jewish National Fund Fellowship, the President, Rector, Dean and Faculty of Humanities, University of Haifa, and anonymous donors, to whom the authors are most grateful.

The authors would also like to thank Rudi Roth, artillery historian, for his valuable insights and advice; and Barbara Doron for the English editing. Further thanks are due to Mario Levinstein and David Schreiber from the School of Mechanical Engineering at Tel Aviv University for their assistance.

References

- [1] M. Dothan. Tell Acco, in: E. Stern (Editor), *The new encyclopedia of archaeological excavations in the Holy Land*, Vol. 1, Israel Exploration Society, Carta, Jerusalem (1993) 17–24.
- [2] N. Makhoul, C. N. Johns. *Guide to Acre*, Government of Palestine. Department of Antiquities, Jerusalem (1946).
- [3] A. Negev, S. Gibson (Eds.). *Archaeological Encyclopedia of the Holy Land*. Continuum, New York/London (2005).
- [4] A. Raban. The Harbours of Akko, in M. Yedaya (Editor), *The western Galilee antiquities*, Ministry of Defence Publishing, Tel Aviv (1986) 180–189 (in Hebrew).
- [5] B. Masters. Acre, in G. Ágoston, B. Masters (Editors), *Encyclopedia of the Ottoman Empire*, Facts on File, New York (2009) 9–10.
- [6] R. C. Anderson. Notes on Acre and some of the coast defences in Syria (papers on subjects connected with the duties of the Corps of Royal Engineers, VI), John Weale, London (1843).
- [7] R. C. Anderson. *Naval wars in the Levant 1559–1853*. University Press of Liverpool, Liverpool (1952).
- [8] C. La Jonquière. *L'Expédition d'Égypte, 1798–1801*, H. Charles-Lavauzelle, Paris (1900).
- [9] A. J. Rustum, Notes on Akka and its defences under Ibrahim Pasha. American University of Beirut, Beirut (1926).
- [10] G. E. Durand-Viel. *Les campagnes navales de Mohammed Aly et d'Ibrahim*, Vol. II, Imprimerie National, Paris (1935).

- [11] D. Cvikel, Y. Kahanov., *Int J Naut Archaeol*, 38.1 (2009) 38–57.
- [12] E. D. Mentovich, D. S. Schreiber, Y. Goren, Y. Kahanov, H. Goren, D. Cvikel, D. Ashkenazi., *J Archaeol Sci*, 37(10) (2010) 2520–2528.
- [13] D. Ashkenazi, D. Cvikel, N. Iddan, E. Mentovich, Y. Kahanov, M. Levinstain., *J of Archaeological Sci* 38(9) (2011) 2410–2419.
- [14] M. L. Mascelloni, G. Cerichelli, S. Ridolfi., *J Min Metall Sect B-Metall* 45(2) B (2009) 175–185.
- [15] A. Giumlia-Mair., *J Min Metall Sect B-Metall* 45(2) B (2009) 149–163.
- [16] B. Lavery. *The arming and fitting of English ships of war 1600–1815*, Naval Institute Press, Annapolis; 1987, Reprint (2006).
- [17] J. Gibbon. *The artillerist's manual compiled from various sources and adapted to the service of the United States*, D. van Nostrand, New York / Trubner and Co., London (1860).
- [18] D. McConnell. *British smooth-bore artillery: A technological study to support identification, acquisition, restoration, reproduction, and interpretation of artillery at National Historic Parks in Canada*, National Historic Parks and Sites Branch, Parks Canada, Environment Canada, Ottawa (1988).
- [19] B. G. Awty., *Technol and Cult* 48 (2007) 783–803.
- [20] G. Crabb. *Universal technological dictionary, or familiar explanation of the terms used in all arts and sciences*, Vol. I, Baldwin, Cradock and Joy, London (1823).
- [21] D. Diderot. *le Rond D'Alembert J. Encyclopédie ou dictionnaire raisonné de Sciences, des Arts et des Métiers*, Tome 4, Briasson, David, Le Breton, Durand, Paris (1754).
- [22] L. De Tousard. *American artillerist's companion, or elements of artillery*, Vol. I, C. and A. Conrad and Co., Philadelphia (1809).
- [23] E. Simpson. *A treatise on ordnance and naval gunnery*, D. van Nostrand, New York (1862).
- [24] D. J. Williams, W. Johnson., *Int J Impact Eng* 24 (2000) 429–433.
- [25] J. Boudriot. *Le vaisseau de 74 canons. Traité pratique d'art naval. Tome II; Construction du vaisseau*, Jean Boudriot, Paris (1977).
- [26] F. Overman. *The moulder's and founder's pocket guide*, Hart A, Philadelphia (1851).
- [27] Y. Goren., *Geoarchaeology* 23(3) (2008) 374–397.
- [28] S. Shalev, J. P. Northover., *Archaeometry* 35 (1993) 35–47.
- [29] T. S. Piwonka. *Aggregate molding materials*, in H. J. Frissell (Editor), *ASM Metals Handbook Vol. 15: Casting*, ASM International, Ohio (1996) 450–451.
- [30] M. Goodway. *History of casting*, in H. J. Frissell (Editor), *ASM Metals Handbook Vol. 15: Casting*, ASM International, Ohio (1996) 12–54.
- [31] J. L. Coze., *Mater. Trans., JIM* 41(1) (2000) 219–232.
- [32] W. Zise, X. Chunchun, D. Xiqing., *Chinese J of Chem. Eng.* 16(2) (2008) 299–305.
- [33] J. S. Park., *J Archaeol Sci* 39 (7) (2012) 1925–1932.
- [34] M. W. Flinn., *Economica* 26(101) (1959) 54–59.
- [35] N. Clark. *Abraham Darby and Brosely*, *Brosely Local History Society* 31 (2009) 2–6.
- [36] M. G. Voronkov, *Glass Phys Chem* 35(3) (2009) 231–236.
- [37] R. Menon, T. McKay. *Welding of cast irons and steels*, in H. J. Frissell (Editor), *ASM Metals Handbook Vol. 15: Casting*, ASM International, Ohio (1996) 1136–1140.
- [38] R. H. Nuttal. *Technol Cult* 22(2) (1981) 275–280.
- [39] L. E. Murr, *Mater Charact* 60 (2009) 397–414.
- [40] J. R. Davis (Editor). *Cast Irons*, *AMS Specialty Handbook*, ASM International, Ohio (1996).
- [41] D. Dobrotă, C. Iancu, *Metalurgija* 52(2) (2013) 247–250.
- [42] M. Kusy, L. Caplovic, P. Grgac, A. Vyrostkova, J. Mater Tech 157–158 (2004) 729–734.
- [43] D. M. Stefanescu. *Classification and basic metallurgy of cast iron*, in K.M. Zwilsky (Editor), *ASM Metals Handbook Vol. 1: Properties and selection: irons, steels, and high performance alloys*, ASM International, Ohio (1996).
- [44] J. S. Park, M. E. Hall, *IAMS* 25 (2005) 9–13.
- [45] E. Fras, M. Górny, H. F. López, *Metall Mater Trans A* 43A (2012) 4204–4218.
- [46] M. Hosadyna, M. Dobosz, J. Kusiński, *Archives of Foundry Engineering* 12(1) (2012) 43–46.
- [47] A. L. Caporaso, C. G. Carlson-Drexler, J. Masters. *Metallurgical analysis of shell and case shot artillery from the civil war battles of Pea Ridge and Wilson's Creek*, *Technical Briefs in Historical Archaeology* 3 (2008) 15–24.
- [48] T. Szykowny, K. Ciechacki, A. Skibicki, J. Sadowski, *Archives of Foundry Engineering* 10 (1) (2010) 75–80.
- [49] B. Rajani, *J Eng Mater Tech* 134 (2012) 041005-1–041005-7.
- [50] H. Fredriksson, J. Stjern Dahl, J. Tinoco, *Mater Sci Eng A* 413–414 (2005) 363–372.
- [51] R. J. Fruehan. *Gases in metals*, in H. J. Frissell (Editor), *ASM Metals Handbook Vol. 15: Casting*, ASM International, Ohio (1996) 175–183.
- [52] C. Thomas, R. Hunter, R. Gordon. *J. Archaeol Sci* 39 (2012) 2714–2721.
- [53] J. C. Coelho, C. M. Oliveira, M. D. Carvalho, I. T. E. Fonseca, *Mater Corros* (2012) doi: 10.1002/maco.201206584
- [54] M. L. A. Gil, A. Santos, M. Bethencourt, T. García, S. Fernández-Bastero, A. Velo, L. Gago-Duport, *Anal Chim Acta* 494 (2003) 245–254.
- [55] B. Herut, E. Shefer, Y. Cohen. *Environmental Quality of Israel's Mediterranean Coastal Waters in 2002*, IOLR Report H39/2003, Israel Oceanographic and Limnological Research Report, Haifa (2003).
- [56] M. L. Wayman, *Mater Charact* 45 (2000) 259–267.
- [57] T. S. Wiltzen, M. L. Wayman, *Archaeometry* 41 (1999) 117–135.
- [58] J. Boudriot. *L'Artillerie de Mer. Marine Française 1650–1850*. Ancre, Paris (1992) 116–119