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Craft production of large quantities of metal artifacts at the beginnings of industrialization: Application of SEM–EDS and multivariate analysis on sheathing tacks from a British transport sunk in 1813

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ABSTRACT

In June 1813, several ships from a combined fleet that unsuccessfully tried to liberate Tarragona from Napoleonic forces ran aground in the Ebro Delta (Catalonia coast, Spain). One, a British transport is currently the subject of research by the Catalan Centre for Underwater Archeology (Centre d'Arqueologia Subaquàtica de Catalunya). During the excavations at the stern area of the ship, hundreds of unused sheathing tacks were recovered, among other items of the cargo. A sample of these artifacts was subjected to characterization by means of energy dispersive X-ray spectroscopy, light microscopy and scanning electron microscopy. Based on the multivariate statistical analysis of the data obtained, an evaluation of the production of large quantities of artifacts was performed. The emphasis was on the control of chemical composition, thus providing novel information about the persistence of craft practices within the context of the remarkable growth at the beginnings of industrialization.

1. Introduction

In June 1813, a combined fleet of three ships of the line, three frigates, a brig, a schooner, six gunboats, and a hundred and thirty-two transports, led by Lieutenant General John Murray,[1] besieged Tarragona, key location for the strategic operations east of the Iberian Peninsula. But after the fruitless attempt to free the city from Napoleonic troops, several vessels ran aground in a storm at the mouth of the Ebro river (to South of Tarragona). Some of the ships finally sunk; sources are inconsistent regarding their number (Blanch, 1861:382; Suchet, 1829:22). A little over two-hundred years later, a local fisherman found the remains of a shipwreck at the area where the tragedy occurred. Archeological investigations at the site, named Deltebre I thereafter, began in 2008 and developed annually by the team of the Centre d'Arqueologia Subaquàtica de Catalunya (CASC), Museu d'Arqueologia de Catalunya (MAC).

The study of naval architecture and the objects found at the stern area indicated that this ship — of about thirty meters of length — is indeed among those that ran aground in 1813. The excavated areas revealed part of the cargo, consisting mainly of ammunition (e.g. musket balls; round shot and bombs; gunpowder and gunflint barrels) and artifacts related to navigation, personal hygiene, cooking, clothing and religious worship (Vivar et al., in press). Within the objects associated to the cargo, a discrete array of hundreds of sheathing tacks was located at the ship's hold, to the port and aft of the mizzen-mast step. No evidence of their original container was preserved in this area. Sheathing tacks are small nails, usually made of copper or copper alloy, used to fasten protective metal sheets to a ship's hull (McCarthy, 1996:185,186) (see Section 2). The vast majority of pieces from the Deltebre I site show no signs of use, as it is likely that they were destined for minor repairs both on the ship itself or other vessels of the convoy.

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[1] Murray commanded a fleet sailed by men of many different nationalities. A detailed account of their provenances was reported in an article from the newspaper *El Redactor General*, Cadiz, Spain, July 12th 1813, No. 758.

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In this study, the results of the physicochemical analyses performed on a sample of twenty five tacks are presented, paying particular attention to chemical composition variations and the manufacturing methods applied. Taking into consideration the high temporal and spatial definition of the pieces, the data obtained shed light on several aspects regarding the quality of serial production of such artifacts in early 19th century England. The significance of this work lies in the assessment of the dynamics of the transition from a craftsman production modality to an industrialized one, distinctive of the modern world, and in a case for which scant historical documentation is available.[2]

2. Metallic sheathing in navy ships

Anthropic material in seawater is affected by the action of wood-boring bivalve molluscs (Teredinidae and Pholadidae families, known as shipworms and piddocks) and isopod crustaceans (Limnoriidae and Sphareomatidae families, known as gribble and pill bug), as well as by biofouling (benthic micro and macro-organisms added to artificial substrata) (see Robinson, 1981; Grosso, 2014). For centuries, these organisms represented a serious problem for the operation of wooden ships, for example affecting speed, maneuverability and durability. Aiming to mitigate the difficulties caused by them, diverse protection methods began to be implemented, such as metal sheets or sacrificial wooden planks, and mixtures of pitch and tallow, among other compounds. However, it was not until the second half of the 18th century, after a process of experimentation, that copper sheathing was finally introduced (see Bingeman et al., 2000; Staniforth, 1985; US Naval Institute, 1952).

The first vessel thoroughly sheathed in copper (its hull, below the waterline) was the 32-gun frigate HMS *Alarm*, in 1761. The success of the trial led to the practices broader implementation in other Navy ships first, and in commercial vessels some time after that (see Harris, 1966; Harland, 1976; Wilkinson, 1842). In subsequent years, numerous innovations regarding materials and manufacturing methods appeared, for many of which patent registers were granted (e.g. Muntz metal, Cu 60% and Zn 40%, in 1832) (see Jones, 2004). This practice had great economic importance for the copper industry in Great Britain, and for Royal Navy contractors (e.g. Raby, Forbes, Collins, Westwood & Williams, and Roe & Co.), that also supplied other European powers (McCarthy, 2005:106,108; Staniforth, 1985:25–26).

The dimensions of the sheets had to meet certain specifications of size and shape. In places outside the Navy's scope, however, the pieces were less regular. Furthermore, their dimensions also depended on the sector of the hull they covered. On the other side, each sheet was manually bored using a special punch and fixed to the structure with copper or copper-alloy tacks, following a stipulated sequence (Bingeman et al., 2000:220–221; Boudriot and Berti, 2004:14–15; Staniforth, 1985:28). The rudder from the Deltebre I site is illustrated in Fig. 1. This, as the hull's bottom, was sheathed in copper, with the exception of its back, at the height of the pintles, which was protected with lead. The sheathing, that originally reached 12 in. (ca. 30.5 cm) below the waterline, was extended up to 16 in. (ca. 40.5 cm) above the latter since 1783, by a warrant of the Navy Board (McKay and Coleman, 1992:8).

Since the last quarter of the 18th century, the need to protect the hulls of an increasing number of Navy ships demanded vast quantities of copper sheets and their fastenings, including the bolts and nails used to secure the plating to the structure. These needed be of the same composition to avoid the effects of galvanic corrosion. The data reported by Winfield (2005:76) on the 50-gun vessel *Hannibal* are supportive: 2010 copper sheets (total weight: 6 t and 12 cwt, equivalent to about 6700 kg) and 40.5 cwt of sheathing tacks (about 2050 kg). If an amount of approximately 90 tacks per pound is considered (see Section 4.1), it follows that a fourth rate British warship of the late 18th century required about 400,000 sheathing tacks. To illustrate the amount of sheets and tacks that a first rate ship required, around 17 t of sheathing were removed during the reparation tasks of the HMS *Victory* (1765–present) in the 1960s (Bingeman et al., 2000:226). For comparison, at the beginning of the 19th century a 130-gun Spanish vessel required 2.128 sheets (total weight, ca. 340 cwt) and ca. 50 cwt of nails (i.e. tacks) (Artiñano y de Galdácano, 1920:380). These are significant numbers if it is taken into account that the British fleet, considering first to fourth rate vessels and frigates, consisted in more than 250 units in service during the 1800 decade (see Gardiner, 2011).

Several contributions have been made within the fields of history and maritime archeology to improve the knowledge of this technology. Regarding the period that is dealt with in this work, it is worth mentioning the characterization studies of the sheathing elements (sheets and tacks) and the structural fastenings from various shipwrecks (e.g. Bethencourt, 2008/9; Ciarlo et al., 2013; De Rosa et al., 2008; Jones, 2004; Samuels, 1983, 1992; Viduka and Ness, 2004). Taking into account that a ship's sheathing used to be periodically repaired (Winfield, 2005:76), the remains from shipwrecks can include materials from different provenances (see Section 5). The materials used for the initial equipment could also come from different factories, if the common practice of supplied the Navy by contractors is taken into account (Stanbury, 1994:37). For instance, the chemical composition analyses of sheathing samples found in the HMS *Sirius* (1790) allowed the identification of two distinct batches, providing evidence about the initial fitting out of the vessel in 1781, and the later refurbishment in 1786 (see MacLeod, 1994:274,275). The Deltebre I site constitutes an exceptional case to this respect, as it provides an opportunity to analyze aspects of this technology in a specific time and place.

3. Materials and methods

From the hundreds of sheathing tacks recovered at the site, twenty-five were selected to be analyzed. Given that all tacks came from the same location in the site, the array considered for this study was sampled randomly. Nonetheless, as general criteria, complete and well preserved tacks were selected. The main morphological features of the tacks were registered by macroscopic observation with the naked eye and optical stereomicroscope (20×).

After that, the pieces were axially sectioned for the energy dispersive X-ray spectrometry analysis (EDS). The surface was ground with emery papers reaching a particle size of 1000. In the case of the attached sheathing tacks (see Section 4.1), only the shank was ground, from the tip to a sector close to the head. Aiming to obtain a surface free of dirt, the pieces were ultrasonic cleaned, immersed in acetone. Measurements were performed on a layer that, as was observed in the metallographic analysis, presented a non-corroded structure.

Artifacts made of a copper-zinc alloy (brass) are susceptible to deterioration in seawater by a selective dissolution of zinc, process known as dezincification. This implies a drawback, especially when surface chemical analyses of samples from this environment are performed, as it is likely that results do not represent the original composition. MacLeod and Pitrun demonstrated that both different site conditions (e.g. chloride ion activity, temperature, water velocity and oxygen), and variances in chemical composition and microstructure of artifacts from shipwrecks, play a key role in the long-term materials' behavior, and

[2] During the 18th century, the industrial production of some metal artifacts gradually became a centralized and standardized task. Regulations concerning the processes, materials and products were also established in many places. And an increased level of specialization of the craftsmen was encouraged (see Coriat, 2008). This was framed in a process of technological change that affected labor organization and materials used in many areas of industry in Britain and other places (see Musson, 1972; Harris, 1992; among others). In the case of a maritime power such as Britain, which had a long established program of ship construction and had faced continuous conflicts with other European countries, manufacture centers owned or directly supervised by the government were not uncommon (see Rodger, 2004). This centralization made it possible to achieve a better control of production and obtain more uniform qualities than that expected from craft production in domestic workshops.

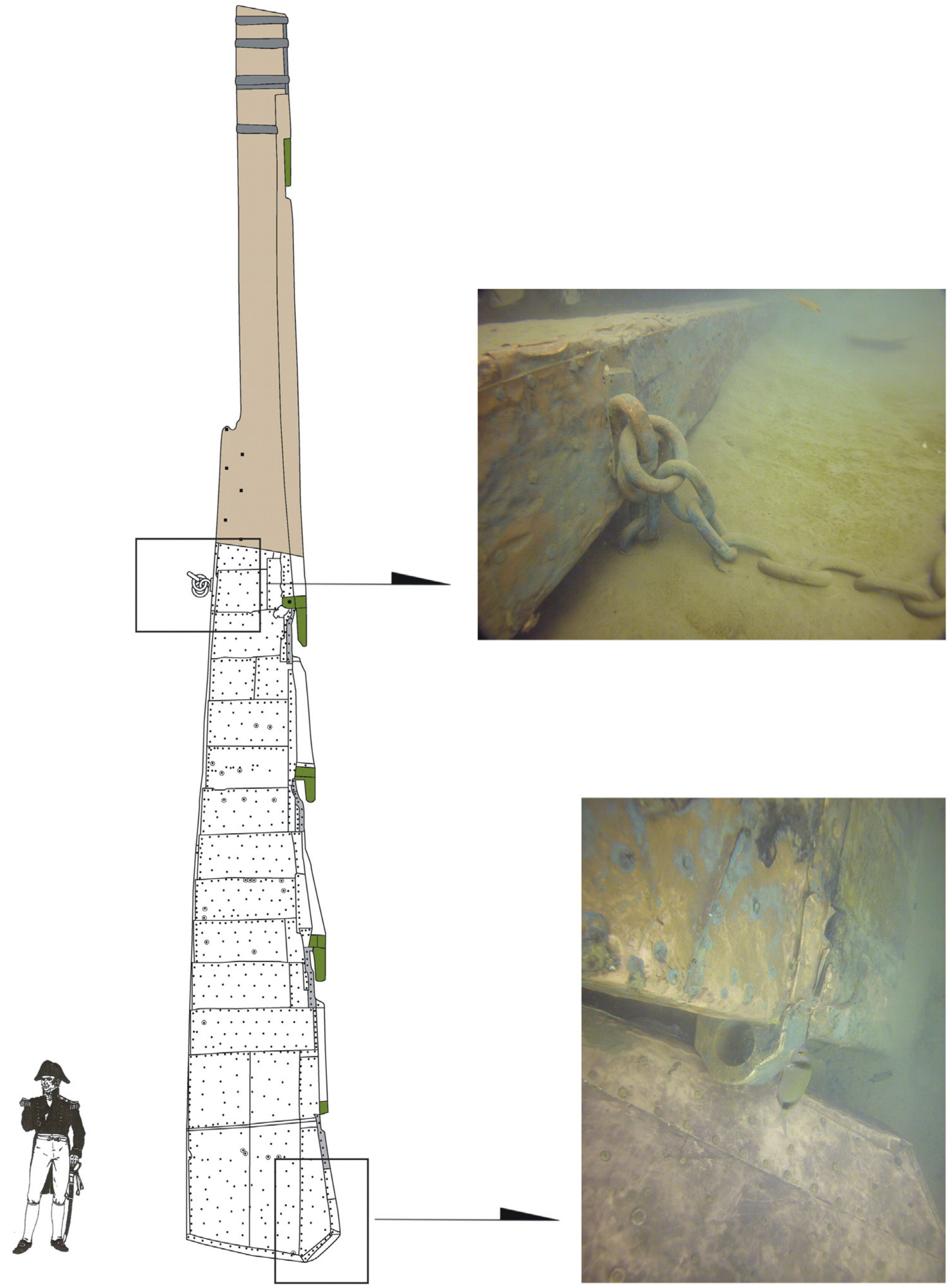

Fig. 1. The rudder from the Deltebre I site. Elevation drawing (height: 9.5 m). Left: drawing of the piece in which the metallic sheathing and the copper alloy pintles (the superior, that stood above the waterline, is iron-made) can be appreciated. Right: underwater pictures of the chains that secured the piece to the hull (to both sides of the helm port) and the foot of the rudder, together with one of the gudgeons that was held to the rudder. Graph: R. Geli Mauri 2009. Photos: CASC-MAC.

can promote different corrosion mechanisms (see MacLeod and Pitrun, 1986). For instance, EDS analyses of bronze sheathing tacks recovered from the HMS *Sirius* (1790) showed remarkable variations in composition between the corroded surface layers and the inner sections of some pieces (MacLeod, 1994:271). In short, for ships' fastenings in seabed McCarthy stated that one cannot assume the composition of artifacts from shipwrecks remain unaltered through time (see McCarthy, 2005:139–141). Thus, information from samples which were subject to this kind of corrosion should be treated with caution when making historical interpretations.

In the case of tacks from the Deltebre I site, the latter issue was not a biasing factor for the study. The copper–tin alloy pieces, with a zinc content up to 3.5%, were examined in areas that showed no evidence of corrosion. This was previously checked by means of light microscopy. An EDAX Inc. brand (Software Genesis, Version 6.32) energy dispersive microprobe was used at the Scanning Electron Microscopy Laboratory, Department of Mechanics of the National Institute of Industrial Technology (INTI-Mecánica). Samples were analyzed at a high vacuum mode, according to the following main parameters: accelerating voltage (25 kV), working distance (34 mm), magnification (65×), analyzed area (ca. 3.3 mm^2), and scanning time per each replica (300 s). To perform the measures, a standardless quantification was selected, with automatic background subtraction, matrix correction, and normalization to 100% for all the elements in the peak identification list.

To determine the existing variability regarding the composition of the tacks, a multivariate statistical analysis was performed on the data by means of the free-access program *PAST*, *PAleontological STatistics* 2.7 (Hammer et al., 2001). Both the main and minor elements — some of

Fig. 2. Sheathing tacks from the Deltebre I site. From left to right: types I, II and III. Photo: N. Ciarlo.

which could have been added intentionally — were taken into consideration, in order to asses the quality of the materials (e.g. impurities from the mineral itself or the manufacturing process) and of the serial production (e.g. heterogeneity of the alloys used).

On the basis of the former analysis, some were selected to identify possible differences between them at a microstructural level. In order to reveal the original structure, the probes, previously ground was polished with alumina powder (1 μm and 0.3 μm) and diamond paste (0.25 μm). The microstructure was revealed using the reactive NH_4OH, H_2O, H_2O_2, in accordance with the ASTM E407 standard, taking into consideration the need to preserve the copper oxide inclusions. The observations via light microscopy (LM) were performed with the following devices: *Reichert Me F* y *FOCUS MMI-5T*, from the Materials Laboratory, Department of Mechanical Engineering of the School of Engineering, University of Buenos Aires. A scanning electron microscope (SEM) was also used: Philips brand, SEM-505 model, at the mentioned laboratory of INTI-Mecánica, and under the same conditions reported above for EDS.

4. Characterization of the cargo tacks from Deltebre I site

4.1. Macroscopic features and typology of the pieces

From the differences registered in the macroscopic analysis, a preliminary distinction could be established between the pieces, that in this work were classified in types I, II and III (Fig. 2) to facilitate their study.

The state of general preservation of the analyzed samples is very good. At a macroscopic level, none of the type I tacks present signs of use (e.g. rounded tip, curved shank, damage of the latter close to the head), which are usually observed in archeological sites. The general dimensions of the samples considered are: total length (35.3 ± 1.2 mm), head's diameter (13.7 ± 1.3 mm), section of the shank at the head's height (4.3 × 4.3 ± 0.3 mm), and weight (5.3 ± 0.4 g). If the modality of the description per weight unit is considered — besides the quantity/weight references, fastenings could be described by their cost, shape and purpose, among others (see McCarthy, 2005:169–187) — the artifacts in question corresponded to 95 tacks per pound. This approximated ratio is close to that of the tacks used in HMS *Victory* (1765–present) (Bugler, 1966, in Staniforth, 1985:30).

Most of the studied pieces exhibit traces of the fabrication process of casting in molds, such as burr (remnants of metal on the edges or joints of pieces, in this case along the head's perimeter given to overfilling) and evidence of the runner (the channel through which the melted metal runs, in order to fill the cavities of the mold), which is generally appreciated in one or both sides of the latter (Fig. 3). On the finishing of the sheathing tacks, Steel mentioned that the superior surface of the heads was polished to prevent unwanted organisms, such as seaweeds, from adhering (Steel, 1805:119). In the tacks from the Deltebre I site, the location of the runner remains suggests that the casting was carried out using a multi-cavity mold, i.e. a mold with various holes, shaped as tack negatives and placed vertically. These were connected serially to each other by a longitudinal runner passing through the tacks' heads, which could have adopted different configurations (e.g. single or parallel lines). On the other hand, some paired tacks were found in the ship (Fig. 4), adding to the statement that the specimens found there had not yet been utilized.

Regarding type II tacks, these are different from the former group not only in their morphology and weight, but because they exhibit evidence of use (the shank of both specimens is bent). The average dimensions of the two pieces considered are the following: total length (33.3 ± 1.1 mm), head's diameter (11 ± 0.4 mm), section of the shank at the head's height (3.5 × 3.5 ± 0.7 mm), and weight (3.6 ± 0.1 g). In this case, ca. 125 tacks would weigh a pound.[3]

Type III tacks were identified as jagged (ragged, barbed) tacks, according to an advertisement for pure copper nails for sheathing, patented by Samuel Guppy in Bristol (1806), where pieces of similar characteristics are illustrated. The rags or jags of those tacks patented by Guppy were meant to prevent the tacks from detaching from the timbers because of prolonged use, conferring an advantage over smooth tacks (see Jones, 2004:111–112). Such artifacts are extremely scarce in the Deltebre I site, so it is estimated that they did not belong to the cargo. It is worth noting that the pieces present an engraved “P” at the top of the shank, which could be indicating the name of the producer

[3] The size of sheathing tacks used in British ships was not regular, and the discrepancies become more pronounced when different Navies are compared. In the case of French ships, these pieces were usually bigger. For instance, the *Dictionnaire technologique* indicates the use of copper alloy tacks with a size of about 66 to 70 per pound (Francœur et al., 1825:169).

Fig. 3. Evidence of the manufacture process. Type I tacks with traces of the runner. In the right image the head's burr can also be appreciated. There are some differences in the remains of the runner appreciated in other pieces of the site, which suggest that the separation between pieces from a same mold was irregular. Photo: N. Ciarlo.

or some of the Navy's facilities (e.g. the rolling mill of the Portsmouth naval shipyard [Admiralty's Portsmouth Dockyard Rolling Mill]). Applying fabrication marks (e.g. the name of the producer or patent year) in nails and bolts of considerable dimensions was common practice at that time, which may allow for these objects to be diagnostic elements of a site (Jones, 2004:116). The main contractors of the British Navy agreed to meet this condition, so that the quality of their products could be checked (McCarthy, 2005:106; Staniforth, 1985:25). A preliminary analysis by means of EDS indicated that sheathing tacks of this type were made of unalloyed copper.

4.2. Elemental chemical composition analysis and statistical assessment of data

The study was centered on type I, taking into consideration that most pieces corresponded to this group. For comparative purposes, a pair of those cataloged as type II was also considered. The composition

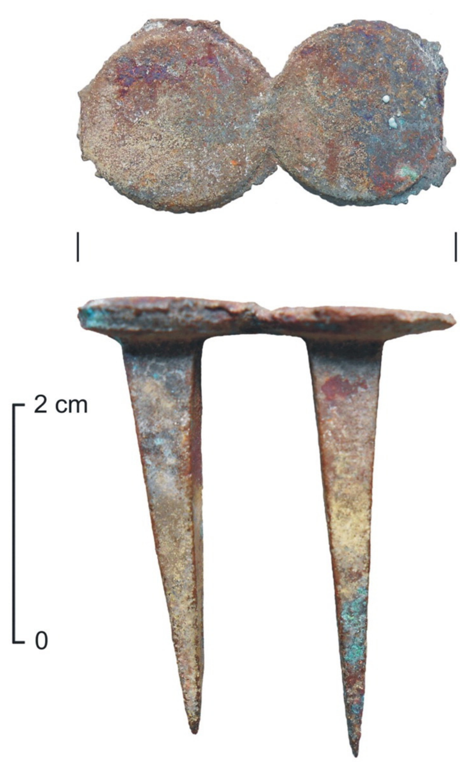

Fig. 4. Pair of tacks, joined together. Photo: N. Ciarlo.

data assessed in the pieces (average value of five measures for each sample) is shown in Table 1. On the basis of the obtained results, the dispersion of the different elements at various points of each of the tacks was initially assessed. For this purpose, the coefficient of variation (CV) of each element within the *n* replicas of a same piece was calculated. From that calculation it was observed that the variability of the main constituents of the alloy along the shank is very low, in average: Cu (0.3%) and Sn (2.4%). Likewise, in the case of other elements considered (Pb, Zn and Fe) the VC values are relatively low (ca. 10%). The latter indicates homogeneity within each tack, and, by extension, of the cast used for their manufacture. Values below 0.5% and elements not detected were considered as null.

To establish the possible correlation between the present elements (Cu, Sn, Zn, Pb and Fe) and facilitate the analysis using as few variables as possible, the principal components analysis (PCA) was applied. According to the calculated eigenvalues the first two components (CP1 and CP2) account for 87.3% of the variance of the system, a figure that rises to 96.8% if component CP3 is considered. The confidence ellipse (95%) of the bivariate distribution (CP1 and CP2) indicates that the latter is representative of almost the totality of the data. Only tack No. 20 and one replica of the No. 24 are left outside this ellipse. In Fig. 5, the five original variables are plotted according to the new axes (CP1 and CP2). Overall, tacks high in Cu exhibit negative CP2 values; pieces with high Pb and Sn contents are located in the 1st quadrant; while the 2nd quadrant represents those with the highest content of Sn and Fe.

In order to distinguish the degree of similarity between the tacks (the homogeneity of the composition among pieces), a hierarchical dendrogram (Fig. 6) was created. Distances were calculated using the Ward model. With this algorithm, the clustering of groups is carried out by minimizing the resulting variability, aspect of interest for analyzing the production of pieces in large quantities. Thus, tacks were concentrated into two groups (A and B) and each of these, into two subgroups (a_1, a_2, b_1 and b_2). Samples of branch A correspond to those located in quadrants 1 and 4 of the graph CP1 vs CP2, while of branch B, to those which are arranged in the 2nd and 3rd quadrants (see Fig. 5).

The interleaving that is present in the replicas of different tacks deserves special attention in some cases (e.g. Nos. 6, 7, 11 and 15; or 2 and 23). This indicates that there is no significant difference between their compositions, probably because they belonged to the same casting material or even the same mold. The latter, although harder to establish, is unequivocally represented by the case of specimens Nos. 9 and 10, which correspond to the tacks that remained attached.

Considering the main constituents analyzed together with the matching tacks-groups obtained from the hierarchical dendrogram, a new classification of four groups is identified (Table 2). The groups are distinctive in terms of their composition (Table 3).

Table 1
Results of the chemical composition analyses of the tacks.

Tack	Type	Provenance[a]	Elemental percentage in weight[b]				
			Cu	Sn	Pb	Zn	Fe
1	I	Q 1/2 B	87.5 (0.31)	10.8 (0.23)	0.6 (0.07)	0.6 (0.04)	0.5 (0.02)
2	I	Q 1/2 B	85.6 (0.40)	12.1 (0.20)	0.9 (0.11)	0.8 (0.11)	0.5 (0.03)
3	I	Q 1/2 B	86.0 (0.23)	11.2 (0.12)	0.9 (0.07)	0.9 (0.09)	1.0 (0.03)
4	I	Q 1/2 B	89.4 (0.15)	9.6 (0.16)	0.8 (0.05)	n.a.	<0.5 (0.03)
5	I	Q 2/3 B	86.8 (0.27)	10.8 (0.18)	0.8 (0.11)	1.1 (0.07)	0.5 (0.02)
6	I	Q 5/6 B	86.7 (0.34)	9.0 (0.13)	2.1 (0.14)	1.9 (0.09)	<0.5 (0.04)
7	I	Q 5/6 B	87.4 (0.17)	8.3 (0.16)	2.2 (0.14)	1.9 (0.09)	<0.5 (0.04)
8	I	Q 5/6 B	85.8 (0.30)	11.4 (0.24)	1.0 (0.10)	1.1 (0.04)	0.7 (0.03)
9[c]	I	Q 5/6 B	86.6 (0.17)	10.7 (0.13)	0.9 (0.07)	1.1 (0.04)	0.7 (0.04)
10[c]	I	Q 5/6 B	86.8 (0.27)	10.6 (0.22)	0.9 (0.08)	1.0 (0.05)	0.7 (0.03)
11	I	Q 8/9 B	86.6 (0.25)	8.6 (0.06)	2.3 (0.14)	2.2 (0.13)	<0.5 (0.03)
12	I	Q 8/9 B	85.9 (0.24)	8.1 (0.07)	2.6 (0.20)	3.2 (0.10)	<0.5 (0.03)
13	I	Q 8/9 B	85.2 (0.06)	12.0 (0.13)	1.4 (0.13)	0.6 (0.14)	0.8 (0.03)
14	I	Q 8/9 B	86.6 (0.22)	11.4 (0.13)	0.9 (0.06)	0.7 (0.08)	0.5 (0.04)
15	I	Q 8/9 B	87.1 (0.15)	8.2 (0.15)	2.6 (0.09)	1.9 (0.08)	<0.5 (0.03)
16	I	Q 8/9 B	86.2 (0.18)	7.9 (0.19)	2.3 (0.18)	3.4 (0.05)	<0.5 (0.02)
17	I	unk	87.4 (0.14)	9.3 (0.06)	1.0 (0.05)	1.1 (0.07)	1.2 (0.02)
18	I	unk	87.5 (0.49)	10.6 (0.37)	0.9 (0.14)	0.6 (0.05)	<0.5 (0.01)
19	I	unk	89.6 (0.38)	8.4 (0.32)	0.7 (0.09)	0.8 (0.03)	0.5 (0.03)
20	I	unk	92.0 (0.15)	7.8 (0.12)	n.a.	n.a.	<0.5 (0.03)
21	I	unk	88.1 (0.23)	9.6 (0.17)	1.0 (0.10)	0.5 (0.08)	0.8 (0.03)
22	I	unk	86.5 (0.18)	7.8 (0.10)	2.3 (0.19)	3.1 (0.08)	<0.5 (0.03)
23	I	unk	85.4 (0.27)	12.3 (0.22)	1.0 (0.10)	0.8 (0.05)	0.6 (0.02)
24	II	Q 8/9 B	91.7 (0.22)	5.3 (0.11)	2.1 (0.11)	0.7 (0.05)	<0.5 (0.10)
25	II	Q 8/9 B	90.3 (0.12)	6.1 (0.08)	1.8 (0.13)	1.7 (0.15)	<0.5 (0.01)

n.a.: indicates that no data are available, because the element was not detected by the equipment.
[a] The position of the tacks within the site is indicated according to their relation with the frames of the ship's hold (numbered from the stern knee onwards). For instance, Q1/2 B stands for frames Nos. 1 and 2, to the port. In those cases where the exact location is unknown, the abbreviation 'unk' is used.
[b] For each sample the average of five replicates (measurements) is reported. The standard deviation of values is in brackets.
[c] Paired tacks.

Tacks grouped into a_1 and b_1 present the highest values of Cu, while the higher concentrations of Sn (the main alloying of Cu) were identified in a_2 and b_2, primarily in the latter. Relative to Pb and Zn, which could have been added on purpose with diverse aims (e.g. lower the melting temperature, improving the castability of the alloy or increase the corrosion resistance of the product obtained), the highest tenors are found in a_1 and a_2 subgroups. It is worth noting the absence of these two elements in tack No. 20 (b_1). Iron, which can be regarded as

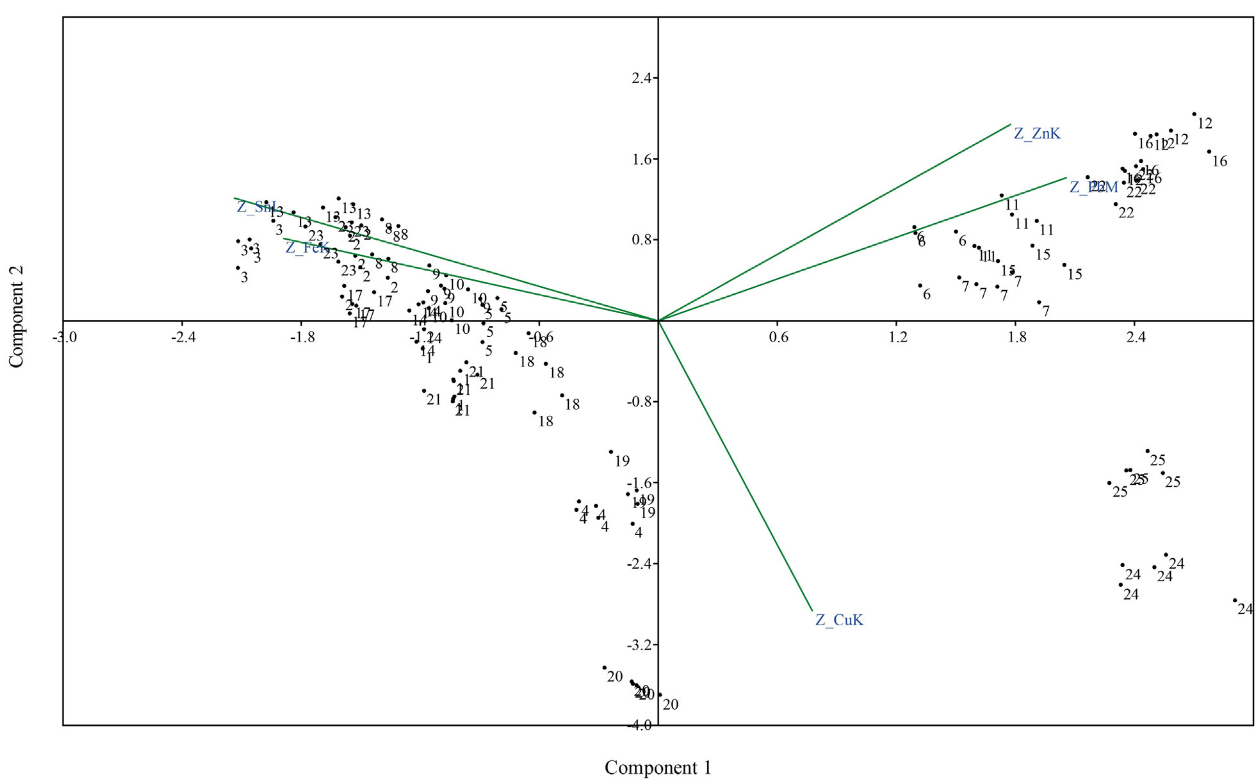

Fig. 5. Diagram of charges for the original variables in the system CP1 vs CP2. Graph: N. Schicchi.

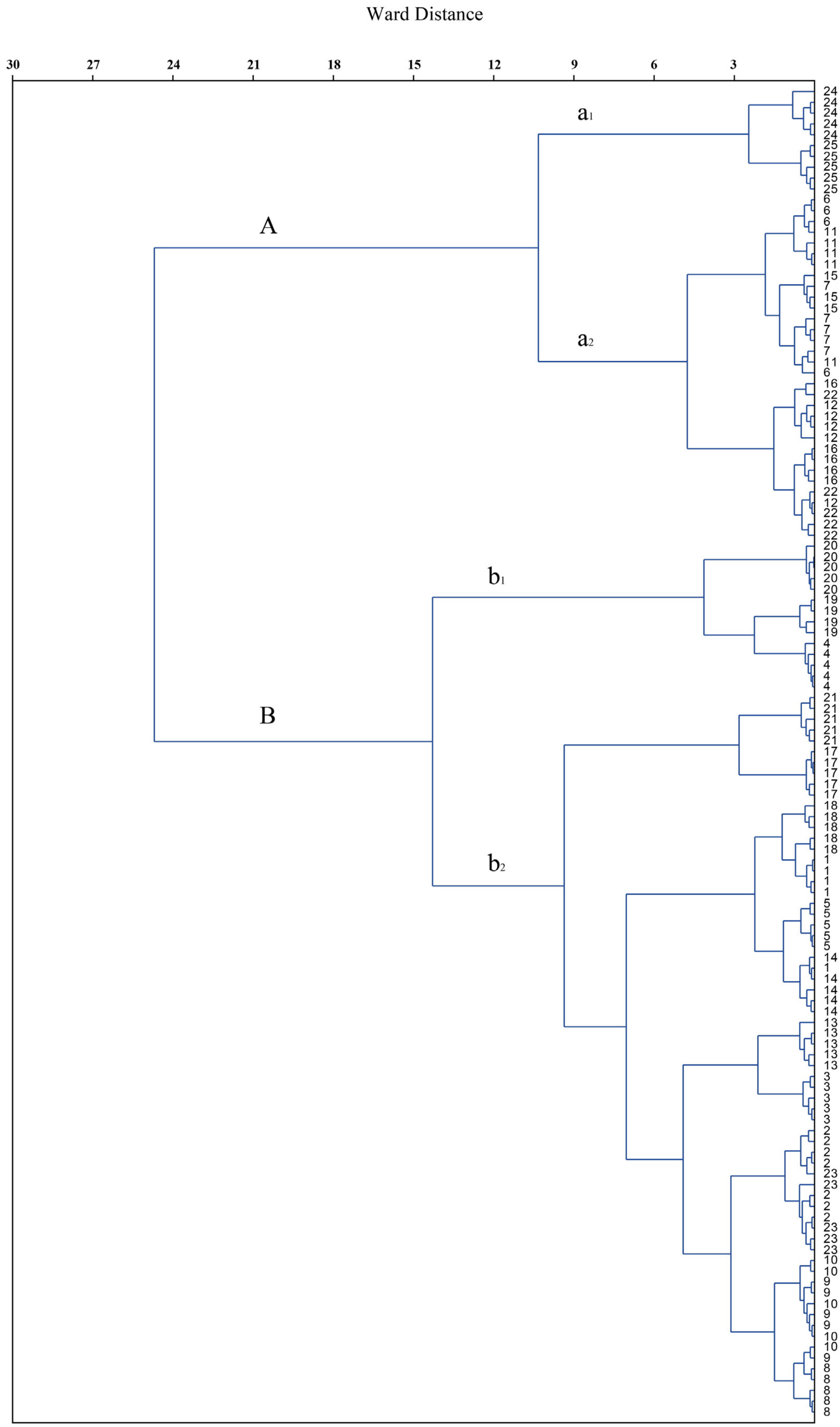

Fig. 6. Dendrogram (based on Ward's method). The groups that the twenty-five analyzed tacks conform, according to the composition data, can be appreciated. Graph: N. Schicchi.

Table 2
Tacks' grouping. Correspondence based on the joint analysis of principal component analysis and hierarchical dendrogram.

Group	Subgroup	Tack
A	a_1	24, 25
	a_2	6, 7, 11, 12, 15, 16, 22
B	b_1	20
	b_2	1, 2, 3, 4, 5, 8, 9, 10, 13, 14, 17, 18, 19, 21, 23

an impurity — associated with any of the other alloying elements or accidentally incorporated during manufacture — presents similar concentrations in the a_1, a_2 and b_1 sets, with higher tenors found in tacks classified as b_2. Low iron tenors in copper based alloys for the fabrication of fastenings had been previously tried in England. However, given the registered percentages, it seems unlikely that the iron present in the tacks from the Deltebre I site is the result of an intentional addition.

In Fig. 7, four subgroups based on the relationship of the main constituents of the alloy (Cu–Sn), can be distinguished. This differentiation is consistent if the relation Sn–Pb is also considered.

To assess the possible intentionality in the differential use of materials, the liquidus temperature of the alloy was calculated for each tack subgroup. To achieve this, the *Thermo-Calc 3.0* program was used, by employing two different thermodynamic data bases (*SGTE Solutions Database*, vol. 5, and *TCS Solder Alloy Solutions Database*, vol. 1, see http://www.thermocalc.com/TCDATA.htm). The greatest difference is seen in the alloys of subgroups a_1 and b_2; around 50 °C (ca. 1030 °C and ca. 980 °C, respectively). Recorded temperature differences suggest that the use of different copper alloys would not have had a significant impact in terms of reducing the melting point of the raw material used.

The corrosion behavior of the different subgroups of sheathing tacks was analyzed by measuring the open circuit potential (OCP) and by the examination of potentiodynamic polarization curves. A potentiostat equipment VoltaLab ZGP 210 and a three-electrode cell for electrochemical corrosion were employed. All the potentials were measured with a saturated calomel reference electrode, a platinum counter electrode and a work electrode prepared from polished samples (free from surface irregularities), with an exposed area of between 0.5 and 0.6 cm. A 1 M sodium chloride solution (prepared with analytical etchings/reagents and distilled water), pH = 6.76, and at room temperature (ca 25 °C), was used as electrochemical agent. The scan in this aqueous medium was run from 100 mV (before OCP) up to 800 mV_{ecs}, at a speed of 0.5 mV/s.

For all of the samples, the open circuit potential was measured for 90 min on a longitudinal section of the tacks, on which metallographic analyses had been previously performed. Before submerging them in solution, the samples were rinsed in distilled water, by ultrasonic cleaning. Then, aiming to remove native oxides formed in contact with air, they were held for 1 min at −800 mV_{ecs} (considering the OCP of copper-based alloys from the bibliography).

The samples' stabilization was reached 10 min after the beginning of the test (Fig. 8). The formation of the oxide layer in the samples Nos. 20 and 4 was fast and similar in both cases, while samples No. 11 and No. 24 (particularly), displayed the oxide formation in two stages (around 450 mV). The sample with less copper percentage presented the more cathodic potential. Tacks Nos. 20 and 24, having similar percentages of this element, exhibited similar potentials as well, but higher to those of sample No. 4. A certain tendency is noted between the open circuit potential and the tin content, except for the case of sample No. 11, due perhaps to its higher copper content.

The polarization curves indicate that the corrosion potential (dynamic conditions of potential) of tacks Nos. 20 and 4 has an anodic displacement of 30 mV respect to tacks Nos. 11 and 24 (Fig. 9). In every case, an initially uniform corrosion process is observed until 0 mV_{ecs}; however, the samples Nos. 11 and 24 present lower currents. Considering that potential, sample No. 24 is different from the others, given that it presents a zone of pseudo passivation at high currencies, with a pitting potential around 500 mV_{ecs}. This could be due to the presence of oxides, different from the other samples, which formed during the stabilization in stages observed in OCP curves.

Considering the latter, we can affirm the following: 1) the corrosion behavior of type 1 tacks presents slight differences; 2) the parameters of type 2 tack (No. 24), despite the particularities mentioned, are within the limits that the array shows. In short, it is likely that discrepancies within the composition of pieces did not have serious implications regarding their corrosion resistance in the aquatic medium.

For bronzes, Samuels reported that iron in amounts exceeding 0.3% appears as alpha iron particles (ferrite), which are anodic with respect to copper. Thus, they can be subjected to selective corrosion. This author stated that the values registered in cannons studied by him are most likely given that they were sometimes cast from recycled bronze artifacts, such as bells and redundant cannons. These could contain some ferrous components that were in this way incorporated to the new alloy (Samuels, 1992:99). In the case of Deltebre I site, low percentages of iron registered in the majority of the copper alloy tacks seem not to have had negative effects on corrosion resistance. The only tack with a content of iron above 0.5% belongs to the subgroup b_2 (with only two pieces with ca. 1% or iron). Nonetheless, analyses performed on tacks from different groups do not show noteworthy differences regarding corrosion potentials among them. It is worth mentioning that bronzes with a certain amount of lead show a good corrosion resistance, even though high iron contents tend to annul the normal passivation mechanism (MacLeod and Pitrun, 1986:4).

Regarding the castability of the alloys used for each subgroup of tacks, the different contents of lead could be related with a variable behavior. Fig. 10 illustrates the relation between the tin and lead content registered in the tacks. Nowadays, it is well known that lead has several technical benefits for this kind of casting, such as increasing the fluidity (Günter and Kundig, 1999:72). By other side, due to its low solubility in copper, lead tends to fill the small spaces between dendrites (interdendritic pores) related to the solidification process (Davis, 2001:85). Other beneficial properties of this element in copper-base alloys were reported in French historical accounts. Lead improves the machinability of the material (Hervé, 1839:400,401). The latter is suggestive, taking into account that a way of finishing the tacks was lathing their heads after the casting process (see Section 5). Besides, in some cases lead and other elements were added to bronzes with the aim to reduce costs (Courtin, 1829:120). All this data points to a purposeful addition of lead in the case of tacks from the Deltebre I site, especially in subgroups a_1 and a_2.

It is worth highlighting that both tacks corresponding to subgroup a_1 also belong to the initial type II, defined by morphological criteria. These specimens are clearly differentiated from the rest of the tacks. Based on the information presented, it is estimated that the division into subgroups established in pieces classified as type I, which are morphologically similar to each other, would be strongly related to the existence of different production batches. Although the previous results cannot be considered as an estimate of the number of tacks per batch, they do suggest that hundreds of pieces could be produced from a single batch. This is what was expected, considering that the output of a kilo of alloy was

Table 3
Chemical composition data, according to subgroups presented in Table 2.

Subgroup	Elemental percentage in weight[a]				
	Cu	Sn	Pb	Zn	Fe
a_1	92.0–90.1	6.2–5.1	2.2–1.7	1.9–0.7	<0.5
a_2	87.7–85.6	9.2–7.6	2.9–1.9	3.4–1.8	<0.5
b_1	92.2–91.8	8.0–7.6	n.a.	n.a.	<0.5
b_2	90.0–85.1	12.5–8.1	1.5–0.6	1.2 max.	1.3 max.

n.a.: indicates that no data are available.
[a] The percentage values for each element are expressed as maximum and minimum.

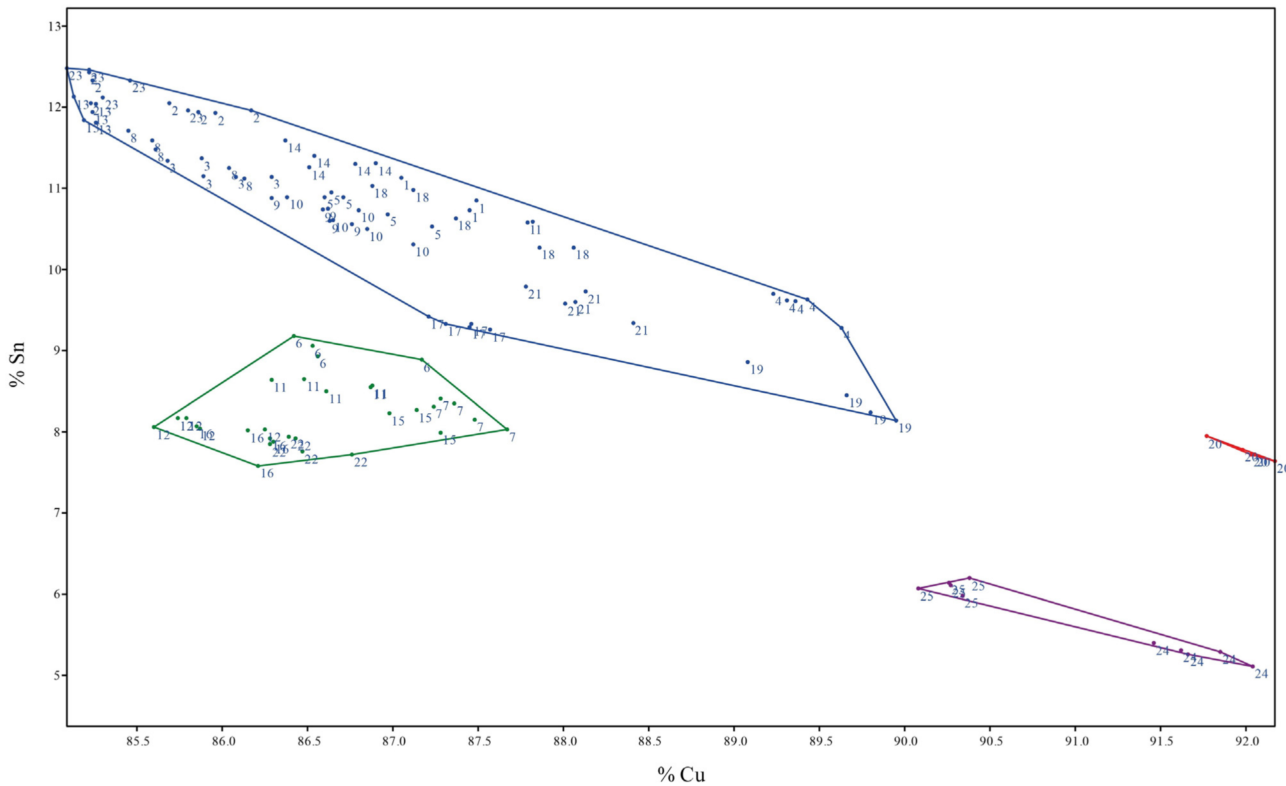

Fig. 7. Grouping of the tacks. The grouping was done according to the relation between the main elements (Cu vs Sn). Graph: N. Schicchi.

more than two hundred tacks. Using other criteria for grouping the tacks, more batches may emerge (e.g. subgroup b_2 can be also divided in two; see Fig. 6). But the minor differences of the tacks within the batches, as were defined here, are likely to be related with the usual variability that metals from this period present (see Charles, 1973; for a study of heterogeneity in composition of artifacts due to the solidification process during its manufacture).

4.3. Metallographic observation by LM and SEM

At a microstructural level, the various parts (tip, shaft and head) of type I tacks and the type II specimen present similar features. In all cases, a dendritic morphology was detected, and the presence of pores and microshrinkages in variable quantities and sizes (Fig. 11). This is evidence of a solidification process, which is typical of casting in molds manufacture.

Regarding microstructural evidences of use, Samuels' work on fastenings from the HMS *Sirius* (1790), in which one of the tacks of the vessel is analyzed, is worth mentioning. The structure of the piece' head shows signs of plastic deformation (strain marks), whose intensity decreases towards the tip. The hardness also decreases gradually in the same direction (from 150 to 85 HV). This shows that the tack was likely subjected to beating, i.e. that it was actually used (Samuels, 1983:77, Fig. 8). In the case of the Deltebre I site specimens, type I tacks have a solidification structure with no traces of posterior thermo-mechanical modification, whereas in those of type II signs of deformation were recorded in different sectors (Fig. 12). This is consistent with the macroscopic evidence described above (see Section 4.1).

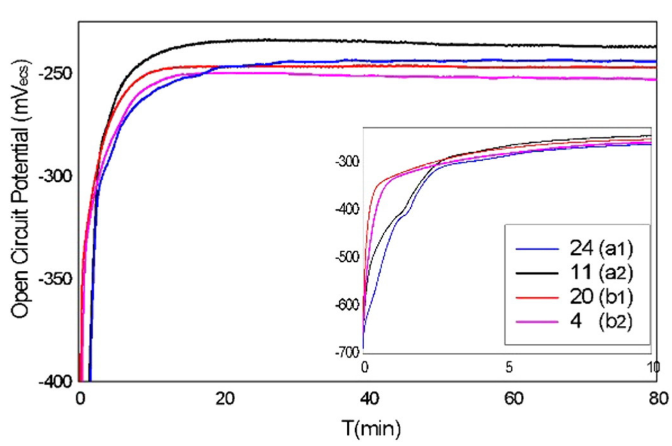

Fig. 8. Open circuit potential curves (OCP). Graph: M. Rañi.

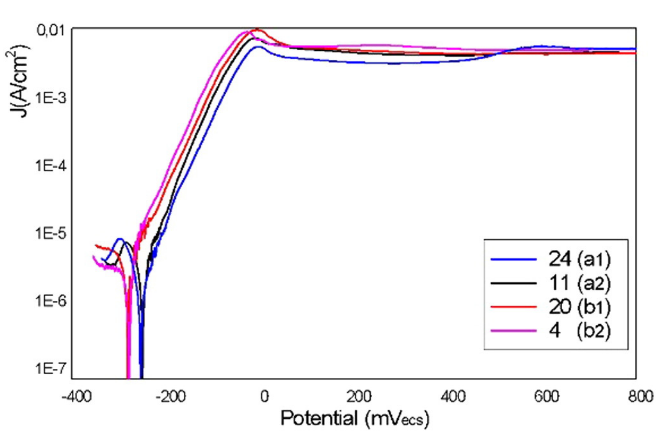

Fig. 9. Potentiodynamic polarization curves. Graph: M. Rañi.

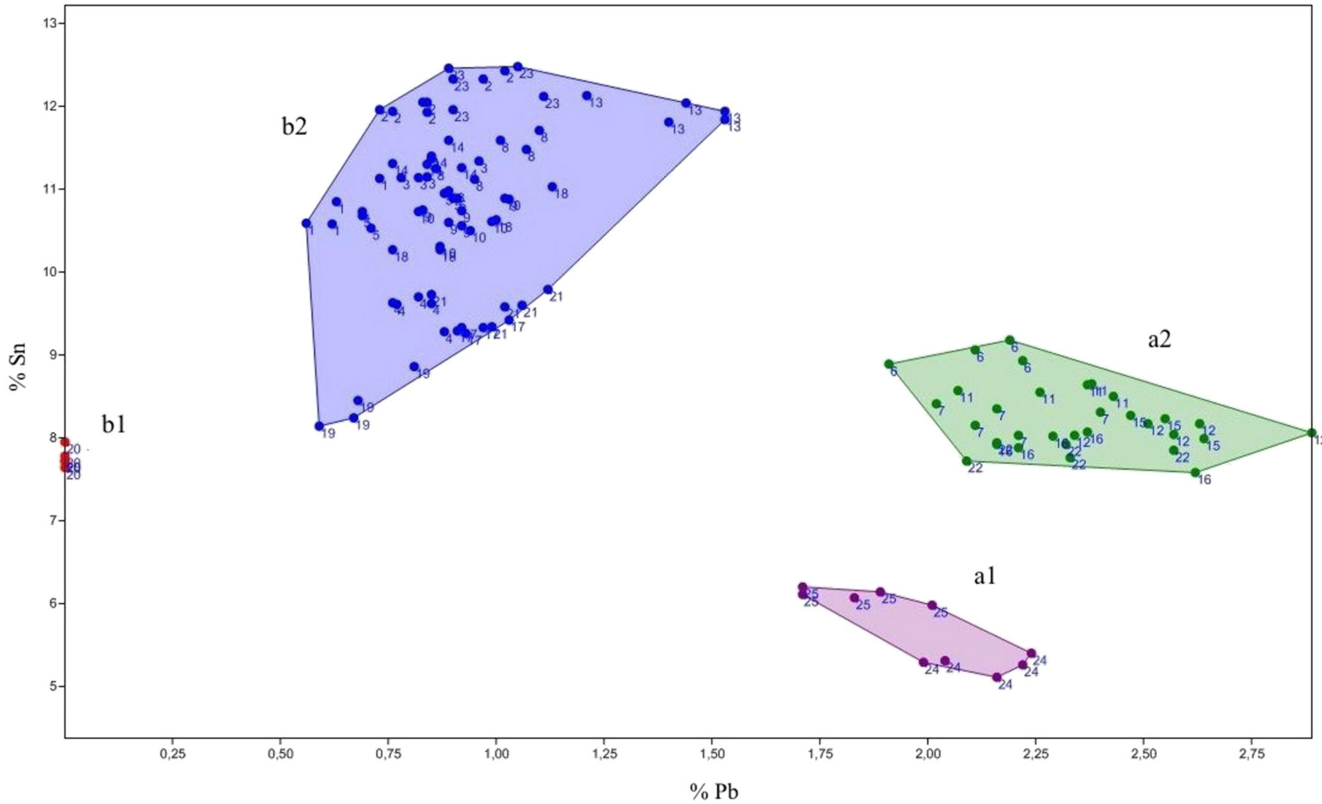

Fig. 10. Tack subgroups, according to the different values of Sn–Pb. Graph: N. Schicchi.

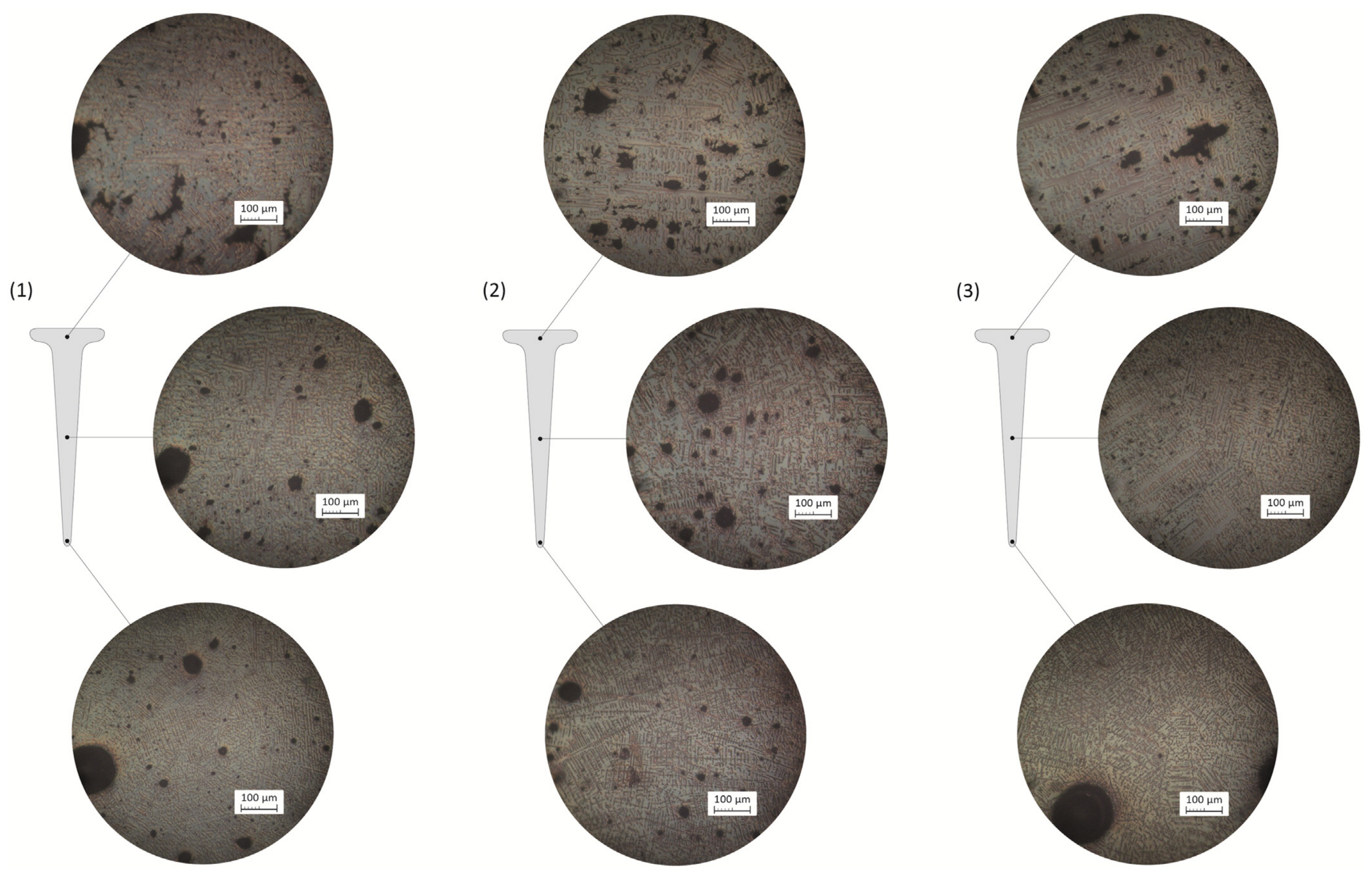

Fig. 11. Dendritic microstructure of the tacks. As cast structure of the type I tacks, belonging to the following subgroups: 1) a_2 (Table 1, No. 11); 2) b_1 (Table 1, No. 20); and 3) b_2 (Table 1, No. 4). Photos: N. Ciarlo.

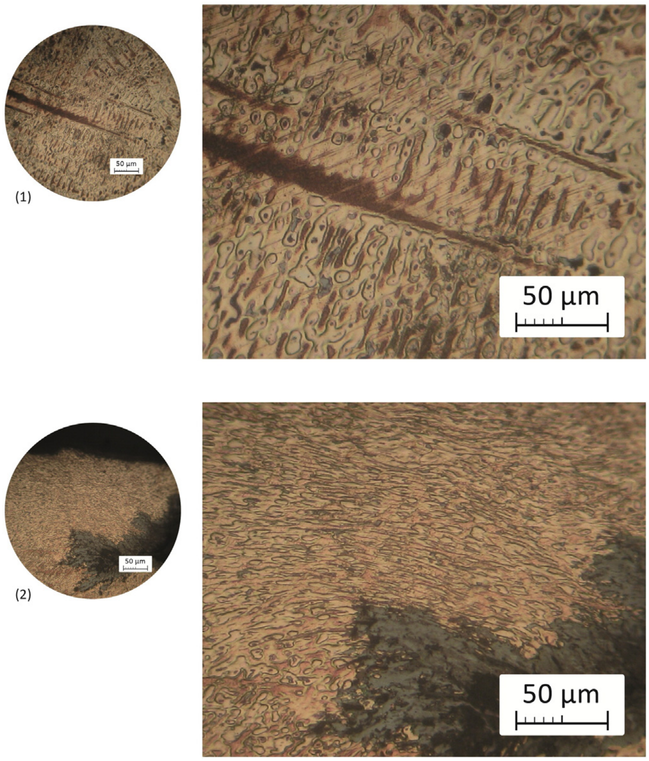

Fig. 12. Evidence of plastic deformation. One of the tacks from the subgroup a_1 (Table 1, No. 24) in which a distorted structure, product of plastic deformation, can be appreciated: 1) strain marks close to the head; and 2) curved dendrites, near the point. Photos: H. De Rosa.

Microhardness presents some variations within areas of each tack (i.e. head, shank and point), and between the pieces from different subgroups. Mean values for the tacks Nos. 4 (b_2), 11 (a_2), 20 (b_1), and 24 (a_1) were considered as a reference, viz.: 101 ± 11 HV, 90 ± 7 HV, 95 ± 10 HV, and 91 ± 15 HV. Porosity and minor elements could account for some of the reported discrepancies. In particular, the value of tack No. 24 is slightly overrated due to a measure of 124 HV near the point (if it is not considered, the resulting mean is 87 ± 7 HV). Compared with type 1 tacks (Nos. 4, 11, and 20), the lower microhardness of type 2 tacks is probably related to the lesser content of tin (see Table 1).

5. Final remarks about craft production of tacks in the early 19th century

Despite the substantial information available on the use of metallic sheathing in late 18th and early 19th century European ships, as well as on the production of forged and machine-cut nails (generally not exclusive to the naval industry), relatively few historical references that refer specifically and in detail to the tack's manufacturing process are available.

In his book on copper production in Anglesey, Augustin G. L. Lentin succinctly describes how the tacks for coating boats in Holywell (Flint, Wales) were made: a copper–zinc alloy with added tin was used, and it was poured in ash and clay molds; then, the pieces' heads were lathed one by one, an activity that demanded numerous operators (Lentin, 1800:125). On the other side, in the advertisement referred in Section 4.1, Guppy mentions the damage occasioned by the fragility of copper-alloy nails, most commonly used at the beginnings of 19th century, a quality given precisely to their elaboration in molds (Jones, 2004:113). It is likely that the tacks' shank breakage — at the height of the head — during its extraction was, to a great extent, due to the effects of corrosive deterioration by use. Likewise, Steel's work (1805:119) briefly describes the manufacturing method of casting in molds and the features of the pieces thus obtained. The use of molds for casting copper alloy tacks was also mentioned for the case of French sheathing from the early 19th century (e.g. Francœur et al., 1825:169). Regarding the chemical composition, McCarthy (2005:102–104) highlights that, at that time, the alloys used for the tacks (mainly Cu–Sn–Zn, under different names, e.g. mixed metal, compound metal, composition metal) were predominant over the use of pure copper.

From the above, it can be stated that at that time the sheathing tacks were mostly made manually, in copper or copper alloys and by casting in molds. In that respect, research conducted on the basis of shipwreck remains constitutes a relevant source to deepen the available knowledge about the production process of the time. For the Deltebre I case, an array of pieces associated to the ship's cargo, most of which must have been carried for repair tasks, was taken for analysis. They allowed for an assessment and research questions in a significant level of detail. Therefore, this work can be considered a contribution within maritime archeology studies to the understanding of large quantities of pieces manufactured by traditional craft methods — unlike what happened with the copper alloy bolt production — within an international context of remarkable industrial growth.[4]

Considering previous studies, in the light of the chemical composition analysis of tacks recovered from ships covering a time span from ca. 1780 to 1820, a considerable diversity in the copper alloys used by the maritime powers can be appreciated. Samuels reported the chemical composition of sheathing tacks from different shipwrecks from this period. Most of them were cast in tin bronzes, and present a wide variability in the percentage of the main alloying element, both between ships and within the same site (e.g. the case of the *Lively*' consignment, a French cutter captured by the British, which sunk in 1810). To account for this variability, the author suggests that the chemical composition control at the factories could be rough, or that the opinions of shipbuilders and nail makers differed regarding the optimum composition for the pieces (Samuels, 1992:92, Table 3). On the hand, MacLeod analyzed a collection of artifacts from the HMS *Sirius* (1790), the flagship of the First Fleet that brought the first European settlers to Australia in 1788, and wrecked at Kingston on Norfolk Island (South Pacific Ocean) (see Stanbury, 1994). The array of copper, brass, and bronze objects recovered includes nails, bolts, sheathing, and other fittings. In particular, bronze sheathing tacks analyzed by Atomic Absorption Spectrometry (AAS) show slight discrepancies in the concentration of the two main elements, i.e. copper and tin. It is worth mentioning that differences in trace elements such as antimony and iron can have a major effect on the corrosion performance of the objects (MacLeod, 1994: Table 1, Table 2, 273). The characteristics of microstructure and composition of one bronze sheathing tack from the *Sirius* were also reported by Samuels (1983): 75–77, Table 3). In the study of the site of HMAV *Bounty* (1790) and the associated materials from the mutineer settlement on Pitcairn Island (Southern Pacific Ocean), Viduka and Ness analyzed an array of diverse copper alloy artifacts by means of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Among them, sheathing tacks are the largest single artifact collection found in the shipwreck. These objects were made by casting in a copper-based alloy, tin being the only element added in a concentration above 1%. According to the authors, the variation in ratios of copper/tin and tin/arsenic in the samples could be related to the use of ores from different provenance, the level of technology of that time, and the production standards (Viduka and Ness, 2004:163, Table 2). Recently, some metal artifacts recovered from the 74-cannon Spanish ship *Triunfante* were analyzed. This ship carried out several military, scientific and diplomatic missions in the service of the Navy for almost 40 years, and sank in the Gulf of Roses (Catalonia, Spain) during the local defense against the

[4] There are some other recent archaeometric investigations that dealt with several aspects related to the mass-production of objects (e.g. Birch et al., 2014; Martinón-Torres et al., 2014).

French military forces early on 1795 (see Pujol i Hamelink et al., 2011). In this double sheathed ship, the study of copper alloy sheathing tacks and small nails for sacrificial wooden planks by means of LM, SEM–EDS, and AAS, showed that both types were made by casting but present significant differences in their chemical composition (see Ciarlo, in press: Table 3; Ciarlo et al., 2013). As was the case of the previously mentioned ships, the presence of nails of varying compositions could be due to the ship's refitting during years of service.

Based on the evidence quoted above, the registered variability within a single shipwreck could be associated to one or several of the following factors: 1) the presence of tacks from different sites, due to ship's refits during service; 2) the rough chemical composition control at the factories; 3) the opinions of shipbuilders and nail makers about the optimum composition for the pieces; and 4) in the case of trace elements, the use of different ore sources. Items 2 and 3 are mainly related to production standards. Taking into account that all but one of these studies was conducted with tacks coming from the hull structure of the ships (i.e. they were not cargo), the variability in composition does not necessarily account for the manufacture quality control.

The sheathing tacks recovered from the Deltebre I site, which showed no signs of use, allowed an analysis focused on the quality of production. The information obtained suggests that the majority of the pieces carried onboard the British transport were produced at the same establishment. The variability appreciated among the tacks can be associated, on the one hand, with the two different classes of samples analyzed; on the other, within pieces with similar morphologies (classified as type I), with different production batches (i.e. different castings). In general terms, the main constitutive elements of the studied samples — even those present in low proportion, leaving aside percentages below 1% — do not present profoundly dissimilar concentrations when compared to each other. Unlike what the analyses on tacks from other sites seem to suggest, the pieces found in Deltebre I site were manufactured at an establishment where certain standards regarding the alloy quality were accomplished.

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