



Archaeometric and Archaeometallurgical Studies on Historical Shipwrecks: Research Experiences in Argentina

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Abstract

Archaeometry could be defined as the interdisciplinary field where knowledge and analytical methods and techniques from natural and applied sciences have enhanced research carried out in archaeology. Many studies have been focused on answering questions related to dating, exploration, artefact function and use, materials sources, and manufacturing methods. In the last decades, materials considered, research topics, and scale of analysis have broadened, allowing to reach a more comprehensive and detailed understanding of social knowledge, behaviours, technologies and other aspects from ancient periods to recent times. Investigations within the field of maritime archaeology show an increasing interest in the application of archaeometric tools to a plethora of sites, including shipwrecks, harbours, dockyards, military batteries, and coastal cities. So far, noteworthy progress has been accomplished in the identification of materials and manufacturing methods, dating, provenance, in situ and laboratory conservation, exploration and survey. In Argentina, the application of archaeometric means of analysis has also gained an important place, especially since the new century. Interdisciplinary studies of wooden and metal artefacts—among other organic and inorganic remains—recovered from 17th to 20th century shipwrecks have not been left out of this trend. Based on a quantitative perspective, studies on metal artefacts show a special place in the country as well as in Latin America. This paper presents a review of the outcomes achieved on archaeometric research on shipwreck remains since the early 2000s, with an emphasis on archaeometallurgical studies, and explores ideas on how future research could be conducted in order to exploit the potential of these studies.

Keywords Maritime archaeology · Archaeometry · Archaeometallurgy · Materials characterization · Shipwrecks

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Opening Remarks

Archaeometry (or archaeological science) could be defined as the interdisciplinary field where knowledge and analytical methods and techniques from natural and applied sciences have enhanced research carried out in humanities and the social sciences, primarily, but non-exclusively, in the fields of archaeology and art history (see Wells 2014). This interaction has allowed for systematic means of collecting, analysing, and interpreting data to be applied. To thoroughly study a complex reality, i.e. to answer archaeological enquiries related to the life of past societies, a single point of view does not suffice. In this regard, an interdisciplinary approach is of crucial relevance for the entire research process. The key issue is to combine different sources of information to reach a more comprehensive and detailed picture of the topics under examination. This can be achieved by a continuous effort made towards surpassing disciplinary boundaries.

The studies undertaken in this research area have provided a great amount of physico-chemical information about different types of artefacts and other archaeological remains. Until two decades ago, they were focused on answering questions mainly related to dating, exploration, artefact function and use, raw materials sources, and manufacturing methods (see Ehrenreich 1995). Since then, the research topics and materials considered have expanded to include diet and health, movement of artefacts, authentication, site formation process, and paleoenvironmental reconstructions, among others. The scale of analysis was amplified, some analytical means became more complex, and additional ones were incorporated.

The interrelationship between the researchers has also become more fluid. Over time, it was possible to achieve an increasingly better understanding of social knowledge, behaviours, technologies and other non-technological aspects, as well as the environments—and interactions between those domains—from ancient periods to modern times. This has increasingly gone beyond the particularistic studies associated with analysis focused on events, such as shipwrecks.¹ As Jones pointed out: “if we assume that a focus on materiality places the material qualities of artefacts at the centre of a web that ties together questions relating to social relations, symbolization, physical interactions with the environment and subsistence, then we have an extremely powerful analytical tool” (Jones 2004: 336).

Given the broad range of means available for artefact analysis, and the increasing integration of these methods and techniques in research agendas, the horizons of archaeometry keep expanding further every day. Evidences of this are the international meetings, symposiums and publications continuously being held worldwide. The boundaries of archaeometry also overlap with those of other disciplines or specialties, which benefit from the characterization results of cultural heritage. The advantages of this interaction are clear, for example, in object conservation and restoration, especially if non-destructive analyses can be employed. Conversely, in some cases they could increase the available knowledge of material qualities and behaviour, under certain environmental conditions and during long periods, then being useful to materials science studies.

¹ Within the field of maritime archeology, research projects concerning shipwrecks (i.e., nautical archeology) have held a predominant place (Bass 2011:4). In this regard, it is worth mentioning that watercraft has been part of a socio-cultural and environmental interweave, an expression of a complex array of factors, both material and non-material, and therefore it might help to elucidate many aspects of past societies (Adams 2001). For a discussion on the relationship between large-scale socio-cultural factors and singular characteristics of ships or wrecks under study, see Gould (2011).

On the other side, maritime archaeology deals with the study of human activities associated with water scenarios (seas, rivers and lakes, maritime navigation and land operations related to them) through their surviving remains (see Muckelroy 1978, 1998; Jasinski 1999; among others, for a discussion about the scope of the field). In the case of historical sites, documentary sources have played an integral role in archaeological investigations (see below). The research in this field covers a broad spectrum of sites worldwide. As was stated in the introduction of *The Oxford Handbook of Maritime Archaeology*, maritime archaeology is now a “confident and maturing field that seeks to expand its horizons into areas for which methods and concepts are only just being addressed” (Catsambis et al. 2011: xiii). However, there still are some regions of the world where the situation is different, and maritime archaeology is at initial stages in terms of legislation, and professional and academic development. Enriching collaborations between international researchers have helped to improve this panorama.

A new horizon can be glimpsed in archaeometry and its many applications to the sites under study, mainly shipwrecks of different periods, but also harbours, dockyards, military batteries, and coastal cities. Some of the advances made so far in several areas include artefact recognition, identification of materials and manufacture methods, dating, provenance, in situ and laboratory conservation, exploration and survey. There are numerous scientific means of analyses for materials characterization and techniques available for field-related activities, post-excavation stabilization and conservation of artefacts. Most of them were not developed originally for this particular purpose (e.g. remote-sensing equipment, positioning and computer systems, and other analytical tools borrowed from natural and applied sciences, see the ‘Appendix: Scientific Analyses and Dating Techniques’, in Catsambis et al. 2011). The study and preservation of materials from underwater sites, in particular, has created special challenges. Methods and techniques used in conservation can be considered highly environment-specific, for instance the lyophilization method for the preservation of waterlogged organic objects (e.g. Aguer 2013), and the application of subcritical and supercritical fluids for the stabilization of some artefacts (e.g. González-Pereyra et al. 2010).

In the last decades, archaeometric research gained a progressive relevance within the field of maritime archaeology worldwide.² In this article, an overview of these studies, with focus in Argentinean historical shipwrecks and the study of modern metallurgy is provided.

Some Comments About Historical Archaeology and Archaeometric Research

Research on historical shipwrecks in Argentina has been closely related to historical archaeology. Several studies in this field cover the same period of time and try to explain similar social themes. This situation also extends to other countries of Latin America, broadly speaking, given the history and academic tradition they share (see Argüeso and Ciarlo 2017). Some thoughts on the potential of archaeometric analyses within this singular scenario will be addressed below.

² News about the application of archaeometric methods and techniques for the study and conservation of underwater cultural heritage are published periodically since 2014 in a special section (Maritime Archaeology) of the *Newsletter of the Society for Archaeological Sciences* (SAS Bulletin).

The definition of historical archaeology has implied intense international reflection and discussion during decades, but, currently, no single position prevails. Some scholars, from a methodological perspective, argued that this field of study comprises the archaeology of people with written documents (i.e. literate societies). Making emphasis on the temporal scale, others have defined it as the study of European colonial expansion and its consequences in overseas regions (in America, post-Columbian sites). Finally, others stressed on the processes under analysis, and have characterized the field as an archaeology of capitalism, or an archaeology of the modern world. The characteristics, strengths and weaknesses of these positions were debated *in extenso* in many opportunities (see Orser and Fagan 1995; Funari 1999; Hall and Silliman 2006; Hicks and Beaudry 2006; among others). Several theoretical and methodological matters (e.g. the uses of archaeological and historical documents, the singular characteristics of the modern world, the roles played by people and things, the relation between historical archaeology and other social disciplines, the different scales of analysis, and the link between central and peripheral contexts, among others) have been widely discussed from different perspectives.³

Leaving aside disagreements about theoretical and methodological issues, this conceptually heterogeneous label has been widely used in American academics, where a strict separation of history from prehistory—based on the date of European arrival—was kept. In Europe, the discipline's history differed greatly, and led to an archaeology compartmentalized according to periods or regions. These delimitations, of course, do not necessarily apply to other regions of the world. In practice, the distinctiveness of American and European traditions—with their particular conception about history, archaeology and anthropology—is still predominant. Fortunately, this situation has not prevented mutual understanding or the possibility of finding common ground.

In historical archaeology—and its closest relative in Europe, post-medieval archaeology—a temporal framework defined from around AD 1500 onwards now seems to be widely accepted. Studies on shipwrecks in Argentina were mainly conducted within these general boundaries. In this regard, they are mainly comprised in the field of historical maritime archaeology (see Flatman and Staniforth 2006). Opposed to definitions based exclusively on temporal or methodological criteria, and in the light of recent discussions, we consider that these fields are better characterized in terms of the diversity of new scenarios and social relationships (economic, political, and ideological, among others) developed worldwide during the last centuries.

Within this scenario, it is worth mentioning that the applicability of many archaeometric methods and techniques is certainly cross-cutting most of the arbitrary frontiers mentioned above, especially those related to time. Thus they can be potentially applied to studies covering multiple historical periods and subjects, which actually tend to overlap more than it is recognized. Bearing in mind this lack of exclusivity in the object of archaeometric research, results obtained from Argentinean sites could be of particular interest to researchers who are working in other historical contexts around the world. Undoubtedly, this could be considered as another meeting point between the different traditions mentioned above, and an additional point to highlight continuity rather than abrupt change, and disciplinary interweaving rather than isolation (by periods, subareas, etc.), as the most fruitful path.

³ An outline on these is presented in some works previously cited in this section. Also, for more details about each specific topic, see Johnson (1996), Orser (1996), Kepecs (1997), Little (1997), Pedrotta and Gómez Romero (1998), Paynter (2000), Cochran and Beaudry (2006), among others.

A Brief Overview of Archaeometric Studies on Historical Shipwrecks

In Argentina, archaeometric research has established itself as an increasingly important component of the archaeologists' agenda since the new century, partially due to a greater dialog between specialists from different fields. This is reflected by the increasing number of published studies and regular specific meetings, such as the *Congreso Argentino de Arqueometría* (Argentinean Congress of Archaeometry) and the *Jornadas Nacionales para el Estudio de Bienes Culturales* (National Meeting for the Study of Cultural Heritage). These and other scientific events are held regularly in pursuit of knowledge, conservation, management and enhancement of archaeological, historical and artistic heritage. The previous scenario resulted in a virtuous circle, allowing for a deeper approach and greater understanding of the issues discussed (e.g. Pifferetti and Bolmaro 2007; Palacios et al. 2009; Bertolino et al. 2010; among others). This picture is remarkable, if the overall development of archaeometry in Latin America is considered (see Vidal 2009, for a discussion about the main topics and analytical studies carried out during the last two decades), with which seems to have gone hand in hand. Interdisciplinary studies of remains recovered from historical ships in Argentina have played an important part in this development.

Maritime archaeology was established as a scientific specialty in Argentina during the second half of 1990, it being one of the few countries in South America that has extensively focused on research on historical shipwrecks (see Ciarlo 2008; Elkin 2011). Since then, archaeometric analyses on artefacts from 17th to 20th century shipwrecks were progressively introduced. They were mostly related to projects conducted by the Underwater Archaeology Program of the National Institute of Anthropology (PROAS-INAPL). Those dedicated to investigations based on metal and wooden remains played a significant role. The research was conducted in close collaboration with biologists, engineers, chemists and geophysics from different national research institutions such as University of Buenos Aires, National Scientific and Technical Research Council, National Atomic Energy Commission, and National Institute of Industrial Technology (e.g. Elkin 2007; Murray et al. 2007; Ciarlo 2013; among others). A particular site has attracted the greatest attention in regard to the archaeometric analysis of shipwrecks: HMS *Swift* (1770), a British sloop-of-war stationed in the Falkland [Malvinas] Islands, which sunk in Puerto Deseado, Province of Santa Cruz. The remains, underwent archaeological investigations by PROAS-INAPL staff since 1997 under the direction of Dr. D. Elkin, and were subjected to several different analyses (see below).

Analyses of wooden remains from historical shipwrecks have focused on the identification of species by anatomical and structural characterization, which in some cases has revealed the possible regional distribution of the wood used as raw material. This information, together with other sources of data, was mainly used to study the ship's architecture and construction, through the different structural components, and to identify the possible place of origin/shipbuilding (e.g. Marconetto et al. 2007; Murray et al. 2009; Elkin et al. 2015a, b), as well as the personal possessions and other items carried on board (e.g. Grosso 2013). These results also shed light on refitting activities during service and navigation routes (e.g. Castro and Aldazabal 2007). On the other side, possible links between the wooden remains of indigenous boats and specific populations were suggested (e.g. Aldazabal and Castro 2003). Dendrochronological analyses have also been incorporated as a valuable tool for dating wood from shipwrecks (Mundo 2012).

A pioneering work within Latin American maritime archaeology was the study of natural site formation processes. The focus has been on the identification and behaviour of

biofouling communities and wood-boring organisms, which have included in situ experimental analysis and the characterization of sediments. This research was conducted with the aim of assessing the physical and chemical effects of these natural agents upon the sites with regards to the differential conservation and spatial distribution of the remains. Extensive work was carried out for several years on the remains of HMS *Swift* (e.g. Bastida et al. 2004, 2008; Grosso 2008). Currently, other wooden and metal shipwrecks from the 19th to 20th centuries are also under examination (e.g. Elkin et al. 2015a, b). This type of assessment has also made it possible to clarify issues related to cultural processes of site formation. For the case of wooden and metallic shipwrecks located in the Peninsula Valdes and the city of Puerto Madryn, Province of Chubut, the studies that dealt with the scraping activities of the ships' hull over time (e.g. Gutiérrez 2014) are noteworthy. In short, through this type of study a better understanding of both post-depositional agents and the processes that shaped underwater and intertidal sites was achieved, allowing for a greater accuracy in archaeological interpretations (Grosso et al. 2013).

Other powerful analytical tools have been applied for research in maritime archaeology, such as μ -Raman Spectrometry and Energy Dispersive X-Ray Fluorescence (Stefaniak et al. 2008); Total Reflection X-Ray Fluorescence (Vázquez et al. 2010); Raman Spectroscopy and Fourier Transform Infrared Spectroscopy (Elkin et al. 2012). These studies identified different organic and inorganic remains and, in combination with other data, their possible function and use on board. Until now the application of the mentioned techniques has been restricted to a small number of samples, all from HMS *Swift*, but has proven to have a promising future in the field. As for the latter, the volume that compiles the results of archaeological research carried out in HMS *Swift* (Elkin et al. 2011) has a special section with the following studies: characterization of metal artefacts (De Rosa et al.), wooden objects (Castro and Murray) and glass pieces (Lavat and Ordóñez); bioarchaeological analysis of a human skeleton (Barrientos et al.);⁴ sedimentology and investigation of site formation process (Bastida et al.); taxonomical identification of botanical remains (Picca); and the analysis of other organic and inorganic materials (Edwards and Maier; Rodríguez; Vázquez et al.). To date, this publication is likely one of the most comprehensive works about the archaeological research of a shipwreck in Latin America.

In the following lines, a special place is dedicated to the research conducted on archaeometallurgy of historical shipwrecks, bearing in mind it constitutes one of the areas that most rapidly developed in Argentina in the last 15 years.

Nautical Technology and Archeometallurgy

Characterization of Metal Artefacts from Wooden Shipwrecks

Archeometallurgy was among the first specialties to be organized within archaeometry during the 1960s, and soon became a field of knowledge in its own right. It deals with the study of metallurgy in history, by means of analyses on archaeological remains related to the extraction, production, circulation and use of metallic objects. The investigations within this field draw on the application of specific knowledge, methods and analytical

⁴ A special publication compiles the results of the analysis of artefacts associated with these human remains (Maier et al. 2010).

instruments, as well as on other sources of information, such as written and oral records (see Bayley et al. 2001; among others).

With respect to historical shipwrecks, metal characterization analyses have been of great interest for the study of nautical technology (e.g. hull construction and equipment), ordnance, and other matters of greater scope (see below). Internationally, this kind of work has been carried out regularly since the beginning of the 1980s and continues to be applied nowadays (e.g. Samuels 1980, 1992; MacLeod 1985, 1994; MacLeod and Pitrun 1996; Viduka and Ness 2004; Bethencourt 2008/9; McAllister 2012; Mentovich et al. 2010; Ashkenazi et al. 2014; Birch et al. 2014). For instance, they have allowed defining temporal and spatial coordinates of archaeological materials, which have also contributed with the assessment of sites; identifying technical features of the objects such as manufacturing methods and alloys employed; and studying economic, political, and cultural aspects of a given society.

In the case of Argentina, since early in 2000 physicochemical characterization results were incorporated in the study of metal artefacts recovered from 17th to 20th century shipwrecks located there and other places.⁵ This research has been undertaken mainly by the Archaeometallurgy Group at the School of Engineering of the University of Buenos Aires, under the direction of chemical engineer H. De Rosa. The activities carried out by this Group since its beginnings have placed focus on three large areas: historical maritime archaeology, battlefield and frontier site archaeology (mostly on military settlements and sites of the contact-period), and urban archaeology. Among the topics studied, the following should be highlighted: (a) composition and quality of raw materials; (b) processes and techniques of artefact manufacture; (c) identification of use-wear traces; (d) dating (relative chronology) and provenance of artefacts; (e) analyses of deterioration processes and materials diagnosis; and (f) application of conservation treatments. These investigations were mainly conducted hand in hand with archaeologists and various specialists from other institutions.

Broadly speaking, studies on nautical technology have dealt with aspects such as the functionality of metal artefacts, the materials and production methods employed and the metallurgical knowledge of the time. In unidentified shipwrecks, typological and physicochemical characterization analyses on structural artefacts such as bolts, nails and sheathing, were especially useful to assess the temporal and spatial coordinates of the associated remains, thus contributing to an initial examination of the sites themselves (Fig. 1). Analyses on other nautical components and objects used on board the ships have also been carried out in sites located in Argentina. Once again, the investigations developed at HMS *Swift* are worth mentioning. They included the study of ship's equipment related to the anchoring, pumping, and steering systems; rigging components; ordnance and personal weapons; furniture; utensils related to food and kitchen; clothing and uniform accessories; and some personal belongings. Research has allowed for the gaining of novel information and discussing technical aspects related to the ship's characteristics, the artefacts used on board, and the technology of the wider society (e.g. Ciarlo 2014; Ciarlo et al. 2011, 2015a; De Rosa et al. 2011; Elkin et al. 2011).

Investigations can be grouped, according to the provenance of the materials, and the approach and scope of research, into three categories. First, studies on isolated (decontextualized) remains of museum collections (e.g. Svoboda et al. 2005; De Rosa et al. 2010;

⁵ Chile and Mexico are two other countries in Latin America where analyses of this kind were introduced in the last years for the study of shipwrecks.



Fig. 1 Copper-based fastenings from the French shipwreck *Fougueux* (1805): **a** front and right side view of two spikes; **b** sheathing tacks; **c** front, top, and right side view of a bolt with clinch ring; and **d** clinch rings (after Ciarlo 2016). Courtesy of the Centre for Underwater Archeology of the Andalusian Historical Heritage Institute (CAS-IAPH)

Ciarlo et al. 2011). Second, analysis of artefacts from a particular site, within an archaeological project (e.g. Lorusso et al. 2003; Ciarlo 2006; Ciarlo et al. 2016a, 2016b; De Rosa and Svoboda 2007; De Rosa et al. 2008, 2009, 2015; Marconetto et al. 2007; Murray et al. 2009). Third, research of naval technology (relative to metallurgy of warships) and the society of the time, drawing on the characterization of materials from several sites (e.g. Ciarlo 2015b, 2016; Ciarlo et al. 2014a, b).

The studies encompassed within the first category have been conducted sporadically and have essentially focused on the study of the formal and physicochemical features of the pieces. These analyses were motivated by different objectives, primarily the wish to recognize the manufacturing methods by which the materials were produced, and define their time and provenance. Some of the objects studied were considered relevant because of their likely association with iconic archaeological sites, or their technical or historical uniqueness. At this point, it is worth recalling that studies of isolated artefacts are heuristically limited for research, given materials have lost their original context.

Most of the studies on metallic remains from shipwrecks are clustered within the second category. Contrary to the case mentioned above, the latter deal with pieces that do possess contextual information from the sites and that have been or are being studied within archaeological projects. The analyses carried out were of great relevance during the initial stages of several projects, because they provided useful information to describe and identify the sites. The results obtained have contributed with lines of work related with nautical technology, as those dealing with artefact production, shipbuilding, technical and scientific knowledge available, performance of materials, and innovation processes.

The third category can be considered an extension of the second, as it mainly implies a change in scale. A prosperous future of the specialty lies in the investigations that place focus on the integration of information recovered from several shipwrecks, as well as on the re-examination of existing collections. The studies that meet these characteristics are recent, but most promising.⁶

Forging Bridges Between Specific Data and Archaeological Interpretations

Archaeometric studies provide valuable information regarding the microstructure and chemical composition of artefacts. The structure of metals comprises features observable at different magnitudes, such as dislocations, grains, inclusions, twins, shrinkage cavities, and pores. Usually, research involves analyses at more than one level, and thus different observation techniques are required. Specific studies help to recognize, for instance, the variability in constitutive elements and the thermo-mechanical and corrosive processes that transformed a given object. Among these techniques, metallography has played a leading role in the microstructural analysis of archaeological materials. This technique consists in the examination of the microstructure of metal artefacts by means of light microscopy (LM) and scanning electron microscopy (SEM), seeking to determine the type and morphology of the material's microconstituents (Fig. 2). The proportions, shapes, colours, and configuration in which these occur are strongly related with the composition and properties of the material, and they are the enduring evidence of some of the transformations that it suffered (see Scott 1991; Wayman 2004). Metallography allows reconstructing a sequence of events

⁶ A detailed account of the investigations conducted in Argentina on metal artefacts recovered from historical shipwrecks has been published previously (Ciarlo 2015a).

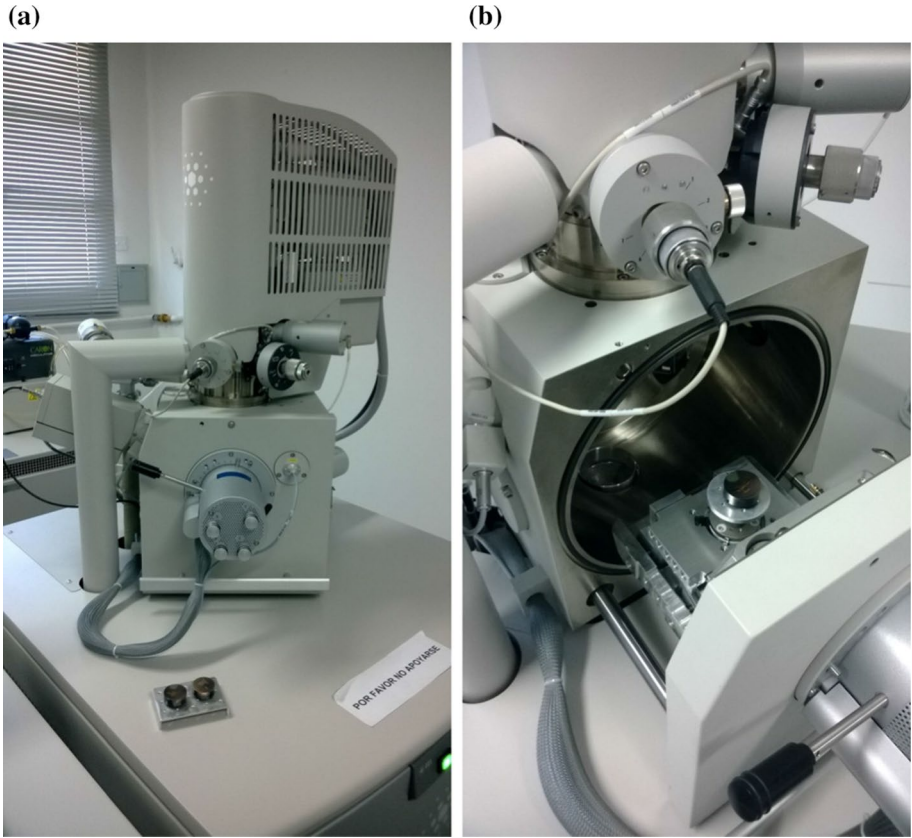


Fig. 2 Scanning electron microscope used for metallography: **a** SEM *QUANTA FEG 250* and **b** view of the chamber where a metal sample is placed. Courtesy of the National Institute of Industrial Technology (INTI)

associated to different moments of the artefacts' life histories (Rehren and Pernicka 2008: 239).

Many of the referred features are related, in one way or another, to past human activities. As a consequence, they provide an outstanding means to access them. In short, the aim of characterization studies is to understand how those properties were linked with the social life of people (Jones 2004). The aim is to establish a connection between data that may be considered mainly technical (i.e. physicochemical properties of metals) and social aspects that were somehow involved in the configuration of those archaeological materials. Data derived from these analyses contribute to an investigation of greater scope, where different sources of information are combined to shed light on human past. Objects and subjects do not exist as exclusive entities; they are and have always been inextricably intertwined.

In Argentina, research on metallic materials from historical shipwrecks has followed two approaches on the interpretation of analytical results. At an initial phase, a deductive reasoning is generally used. A link is established between certain features of the materials (e.g. grain structures, non-metallic inclusion arrangement, presence of one or various phases, alloy composition and hardness) and the thermo-mechanical (e.g. temperature reached, cooling speed, and deformation extent) and corrosive (e.g. localized,

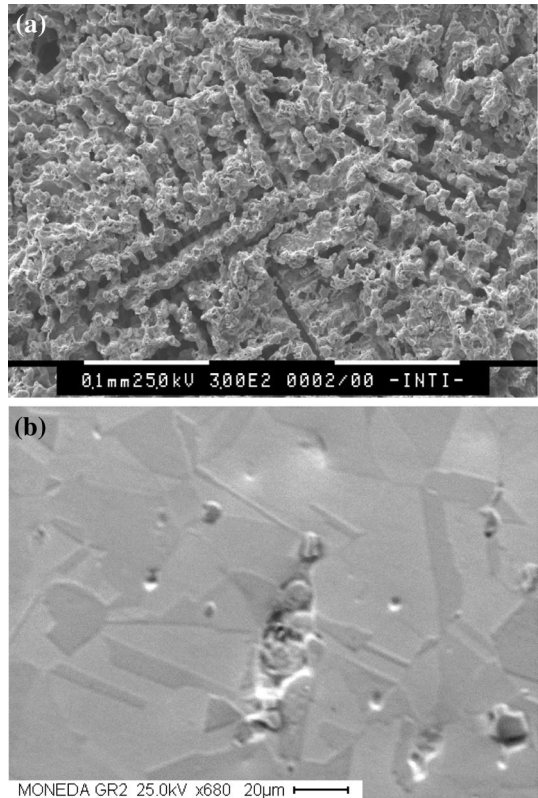
galvanic, and intergranular) processes that resulted in their final configuration. In turn, relying on the current empirical and theoretical knowledge of metallurgy, this may be rendered into significant information regarding specific activities. Thereby, it is possible to account for the characteristics of the methods involved in artefact production in detail.

To circumscribe the spatial and temporal coordinates of the materials, the previous stage tends to be followed by one of a different nature. It is defined by an analogical (direct) reasoning method, in which available historical and/or archaeological information on each site, as well as the contexts of raw material sourcing, production and use of artefacts, are altogether taken into account. Based on this data, a correlation between the transformations to which materials were subject, on one side, and technological practices developed within a particular historical context, on the other, is established. These archaeological statements about metallurgy are relative to factors such as the questions posed (i.e., the focus and scope of the research), the degree to which contextual relations of artefacts can be relied upon, and the methodological approach adopted by specialists.

Let us consider a brief example to illustrate the latter. In 1999, during the excavations conducted at the stern of HMS *Swift*, six metallic discs—preliminarily identified as coins—were recovered. On the basis of the original plans of the *Swift*, the location of the finds seemed to correspond to one of the cabins located in the lower deck and belonging to the officers. Three halfpennies and a farthing of George Rex were analysed non-destructively using scanning electron microscope with energy dispersive X-ray spectroscopy (SEM–EDS) and wavelength dispersive x-ray fluorescence (WDXRF), on their surfaces. This allowed the alloy composition and manufacturing process to be determined and the quality of the coins to be evaluated. According to the regal standards of that time, during the reigns of George II (1727–1760) and George III (1760–1820), low value coins such as halfpennies and farthings manufactured in Great Britain were made of laminated sheets of pure copper which were cut as discs (blanks) that were later coined. The farthing was made of pure copper, as was expected. The three halfpennies, instead, exhibited a dendritic microstructure, due to casting in a mould, and a chemical composition of copper with tin, zinc, iron and lead, added in different quantities (Fig. 3). Both the raw material and the manufacturing method used for these coins did not fulfil the official standards of the time. Therefore, the main conclusion was that the three halfpennies were counterfeits. Thereupon, the presence of this type of coins on board a Royal Navy ship was discussed taking into account the historical circumstances, in particular the habitual use of cash, the regulations concerning its production, the practice of copper coin counterfeiting, and the widespread use of these products in Great Britain and their overseas colonies (see Ciarlo et al. 2015a).

It is in the quest to answer some socio-cultural enquiries about the human past that the results of metallurgical analyses truly fulfil the aims of archaeological research. In Argentina, even if this premise is generally abided by, it has sometimes been partially neglected because of the specificity of some studies, mainly focused on technical matters. For the knowledge of ships and nautical activities, as was referred to above, great potential lies in comparative analyses of sites. Regarding goals to be achieved, Catsambis et al. (2011) stated that the future of maritime archaeology “rests on synthesis—synthesis of geographically and chronologically diverse archaeological data; synthesis and evolution of concepts; synthesis of archaeological subdisciplines and maritime sciences” (Catsambis et al. 2011: xiii). In other words, they revealed the need to integrate diverse scales of analysis, cogitate on the theoretical foundations of the specialty, and foster the articulation of diverse methods, techniques and expertise from other disciplines.

Fig. 3 SEM images of two copper-based coins: **a** dendritic microstructure of a copper-alloy halfpenny recovered from HMS *Swift* and **b** microstructure of equiaxed grains and annealing twins observed in a regal copper halfpenny sampled from a numismatic collection. Courtesy of the National Institute of Industrial Technology (INTI)



Maritime and Beyond: The Significance of Comparative Studies of Shipwrecks

Based on Muckelroy's seminal work, Pomey stated that a ship is:

“...a complex machine that floats and moves in a way that is both autonomous and controlled, and constitutes an architectural system coupled with a technical system. The ship is an instrument adapted to a function. The instrument is designed to respond to precise needs arising from a political, economic, and military system. This instrument constitutes a functional system. The ship is the living and working environment of a micro-society. It is, however, a closed society whose hierarchy, beliefs, rules, rhythms of life, and tools make up a particular social system” (Pomey 2011: 26).

In this sense, nautical activities are typically designed for specific tasks and environment, i.e. the sea, or other aquatic setting, and sailing. At the same time, however, they maintain an umbilical relationship with the mainland society. Ships are a particular manifestation of a wider social, economic, political and symbolic system, with characteristics of its own. The potential of shipwrecks as sources of anthropological knowledge of people on board the ships and, by extension, of the mainland society, was stated on several occasions (e.g. Cockrell 1983; Lenihan 1983; Adams 2001; Martin 2011). For instance, Gould referred briefly to the wrought iron shipbuilding industry during mid-to-late 19th century,

which played a central role in the transition from sail to steam. The historical documents on the production processes and application of this material within the nautical industry are abundant. Nonetheless, many questions regarding social and economic processes behind this change remain to be answered. Analysing how wrought iron production, which was based in a craft modality, reached an industrial scale is of particular interest. Unlike steel, the procurement of in such amounts was an extremely laborious task, that required micro and macro organization, and special qualifications that are not well known yet (Gould 2000: 27). In this regard, research conducted by McCarthy and other specialists on iron and steel shipwrecks located in Australia is worth mentioning (see McCarthy 2009).

An approach of great potential lies in the analysis of shipwrecks at a regional and diachronic perspective. During the last years, several researchers have explored the relationship between the material evidence at the sites—singular entities—and the larger context, considering both the distinctive aspects of social life as their articulation with more extensive processes. Concerning shipwrecks, investigations range from the study of the evidence from a particular vessel to the analysis of several, either because they belong to a certain period, geographical area or wider historical topic (Delgado 2000: 10, 11). In this regard, Cockrell (1983) suggested a system to analyse shipwrecks and the mainland society to which they were related. The classification is useful as it allows handling complex data, and encompassing and organizing diverse relations, according to the research subject. Depending on how the information is structured, the studies can be classified in the following analytical dimensions: intrasite (refers to studies at a single shipwreck); intersite (comprises comparative works between vessels from the same period and different provenance, or from the same region but different period); intrafleet (when dealing with vessels contemporary and of the same fleet); and interfleet (research focused on fleets of similar or different origin, whether or not from the same period). The possibilities that the latter level of analysis provide are, according to the author, virtually unlimited. If the link that connected the ships with their parental context is considered as well, it is possible to extend the analyses even further (Cockrell 1983: 215). In retrospect, research within the first level has predominated, resulting in abundant reports of extraordinary quality (e.g. Stanbury 1994; Breen et al. 2001; Gardiner and Allen 2005; Cederlung and Hocker 2006; Bingeman 2010; Elkin et al. 2011; Nieto et al. 2016; to name but a few historical sites). Studies that combine information from different sites are much less copious (e.g. L'Hour and Veyrat 2000–2004; Grenier et al. 2007).

In sum, a diachronic analysis of artefacts from shipwrecks of different provenance stands as a remarkable means to contribute to the knowledge of technological changes within a particular maritime scenario, and also beyond its limits. A case studied at the Archaeometallurgy Group will now be introduced as an example of technological analyses in metallurgy that transcend the coordinates of a singular shipwreck (Ciarlo et al. 2014a, 2015b). This and other issues were addressed in the Ph.D. dissertation of one of the authors (Ciarlo 2016).⁷

⁷ Ciarlo's dissertation deals with the analysis of technological innovations and conflict of naval powers from mid-18th to early 19th centuries, with focus on the applications of metallurgy to warships. An array of metal artefacts from British, French and Spanish shipwrecks from this period was characterized, and special attention was paid to objects related to structural fastenings, sheathing, nautical equipment, and ordnance. Based on the application of different instrumental techniques and the information recovered from documentary sources and other well studied archaeological sites, changes in metallurgy and warships of the main European navies were analyzed. A discussion concerning technology transfer, the role of empirical techniques and scientific knowledge, as well as the implications that war between the mentioned states had on developments, allow for light to be shed on the dynamics of the innovation processes during this period.

On Studying Technological Change: The Case of Iron for Cannonballs

The iron ordnance used by maritime powers such as Great Britain, France, and Spain, played an important role in conflicts for the supremacy of seas. Within this context, cannons and cannonballs demanded much of the iron production of the time, along with other manufacturing destined to naval construction and equipment such as fastenings, ironwork, and anchors.⁸ Iron ordnance received special attention and capital investment, and was subjected to diverse innovation processes in manufacturing techniques and materials in order to improve their quality (Torrejón Chaves 1997). As for cannonballs, according to documentary evidence, their making did not require the same care and attention as cannons. Operations associated with the production of cast iron cannons were very delicate. As pointed out by José Alcalá-Zamora y Queipo de Llano “a miniscule negligence when weighing the loads of the ore, a small excess of flux, the poor preparation of the sand of a mold, a careless blow when hand debarking, irremediably rendered the piece useless” (Alcalá-Zamora y Queipo de Llano 2004: 80; translated by authors).

Given the function to which cannonballs were destined, the use of poor quality iron obtained in the first blast furnaces castings seems to have been common practice for its production in some foundries, as is stated in the *Compendio de matemáticas* (Compendium of mathematics) of Rovira (1787). Therefore, it is likely that cannonball quality was markedly heterogeneous. During its heyday, iron produced in the noted Spanish facilities was the grey type, with an average specific gravity of 6.9–7 g/cm³, according to tests with 17th century cannonballs. It should be noted that the reported value is lower than the value stated in Muller’s *A Treatise of Artillery* (1768) (cast iron: 7.425 g/cm³), suggesting that artefacts from Liérganes and La Cavada, when equivalent in size, were lighter than the British ones of the time. In projectile diameter versus weight tables, discrepancies can also be noted between English and French cannonballs of the same calibre. The values expressed by Muller suggest that French pieces were sometimes relatively heavier than English ones, while in other cases it was the other way round. It can be argued that the discrepancy in the weight-diameter relationship in projectiles belonging to each navy partly responded to the fact that the cast iron used had different characteristics. In this regard, the microstructure exhibited in them can be observed to understand the metallurgical characteristics of the cast iron production in this period.

For cannonballs from the 17th to 19th centuries, the progressive employment of grey iron (carbon in graphite state) instead of white iron (with carbon in the form of cementite) has been acknowledged (e.g. Bethencourt et al. 2013). Technical advantages of grey iron were double. The risk of fracture of shot made with this material was lower given their superior tenacity, thus they could withstand a larger load of powder charge. Besides, grey iron was ca. 5–10% lighter than white iron, varying according to the carbon content (the greater the amount of carbon, the lighter the material), so vessels’ shot cargo would be also lighter, and ultimately the ships themselves easier to manoeuvre.⁹ Taking into account the huge amount of ammunition usually carried on board a warship (or a ship transport), the implications of this discrepancy must have been relevant at this time, and people probably

⁸ For instance, see Alcalá-Zamora y Queipo de Llano (1999), Corbera Millán (1999), and Rodríguez-Villasanté Prieto (1999) on the case of iron destined to the navy in Spain during the 18th century.

⁹ White iron has a density of 7.7 g/cm³, while gray iron presents a range of 6.95–7.35 g/cm³. In other words, a cubic metre of gray iron would weigh between 750 and 350 kg less than the same volume of white iron.



Fig. 4 Wooden boxes for ammunition from the cargo of the *Deltebre I* (1813) site. Courtesy of the Catalan Centre for Underwater Archeology (CASC-MAC)

were aware about them. Both aspects seem to have been well understood by the practical metallurgists. They may have been well aware that if they used grey iron shot, they could use a larger load of powder charge; vessels cargo would be lighter, and thus the vessels themselves easier to manoeuvre (technical advantages, as these were especially significant for cannons). From the latter, a key question arose: what can cannonballs from mid-18th to early 19th century European warships tell us about cast iron production and the dynamic of this innovative process?

Research was focused on artefacts recovered from the sloop-of-war *HMS Swift* (1770), the Spanish 74-gun ship *Triunfante* (1795), the French 80-gun ship *Bucentaure* (1805), and the *Deltebre I* (1813), a site identified as a cargo ship belonging to the Royal Navy (see Martí 2006; Elkin et al. 2011; Vivar et al. 2013; Nieto et al. 2016; for a detailed historical and archaeological account of the mentioned ships), among other vessels considered for comparison. The latter, studied by the Centre for Underwater Archeology of the Archaeological Museum of Catalonia (CASC-MAC) under the direction of Gustau Vivar, is worth mentioning given that a significant part of the ship's cargo consisted of ammunition for artillery: mortar bombs, grenades, round shots, and canister shots (Fig. 4). Different spherical projectiles were analysed: round shot, grape shot and case or canister shot.¹⁰ Samples and comparative material considered cover a time span of about a century. After

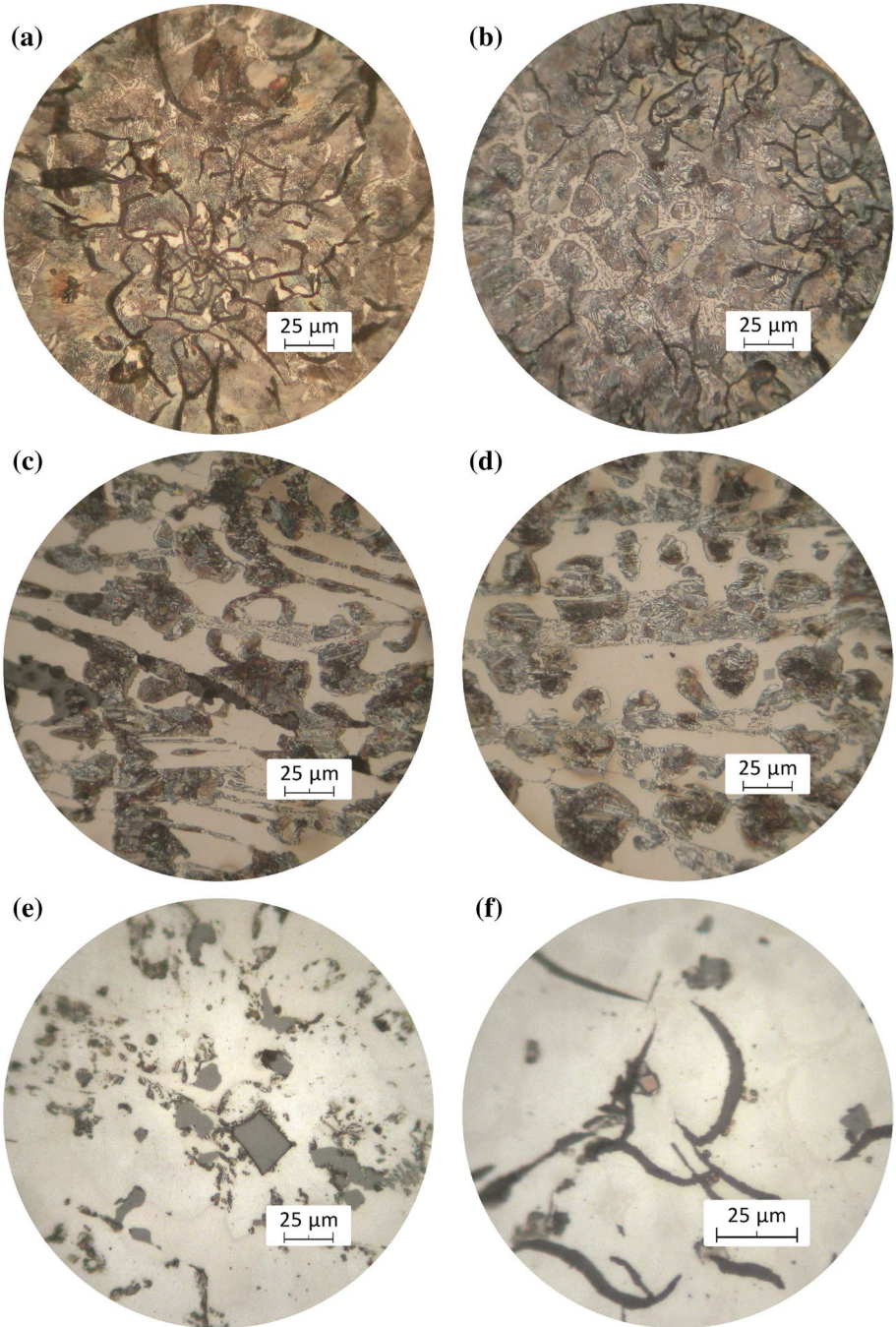
¹⁰ A wide variety of projectiles, depending on the objectives pursued when challenging an enemy (e.g., inflict damage on the hull, rigging and sails, or its crew) could be fired from cannons. For instance, round shot were those used primarily to produce damage to the hull, aiming to sink the ship. This kind of projectile could also be heated (red hot shot) or covered with a flammable preparation (fire ball) in order to set fire to the decks or make ammunition storage area (magazine) blow up. On the other hand, grapeshot and canister shot projectiles, frequently spherical shots, provoked a far reaching spray with a broad scope of action, very effective in producing casualties in the crew (see Falconer 1780; Moore 1801; O'Scanlan 1831).

Fig. 5 Photomicrographs of canister shot samples recovered from the Deltebre I (1813) site: **a** and **b** microstructure of gray pearlitic iron with steadite (samples no. 1 and 5; diameter: 24.8 mm and 25 mm); **c** and **d** microstructure of white iron, formed by cementite (with a columnar radial orientation), colonies of pearlite and some amount of steadite (samples no. 2 and 3, diameter: 28 mm and 35.5 mm); **e** grey particles of manganese sulfide—MnS—(sample no. 8, diameter: 29 mm); and **f** reddish particles of titanium compounds (sample no. 6, diameter: 29 mm). Samples **a** to **d**, etched with Nital 2%; **e** and **f**, unetched (after Ciarlo 2016)

a macroscopic identification and recording of the artefacts' main characteristics, a metallographic analysis by means of LM and SEM–EDS was performed. It was determined that the samples were made by casting. For the manufacturing of round shot, as well as some grape and case shot projectiles, individual moulds were generally used (a few pieces show macroscopic evidence of serial casting). The microstructural characteristics allowed mainly three types of materials to be differentiated: white, grey and, to a lesser extent, mottled iron. Leaving aside early sites, where white iron shot predominates, projectiles recovered from the shipwrecks analysed here exhibit different microstructures (see Ciarlo 2016, for a detailed account of the metallographic examination).

This remarkable variability does not seem to be related to the different types of projectiles in question. For instance, shot from HMS *Swift* are of white iron, irrespective of their size. The latter can also be appreciated in the Deltebre I site, where shot of similar diameter show markedly different microstructures. Generally, grey and white iron balls recovered from this shipwreck have particles of sulphides and titanium compounds, for which there is scarce evidence in the samples from earlier ships. Phosphorus contents of these projectiles, bearing in mind the presence of steadite in both grey and white iron microstructures, are also noteworthy. This element (as well as sulphur) was present in high ranges in British irons. Both used to be one of the fundamental challenges of the smiths, due to the detrimental effects on the mechanical properties when used to make wrought iron, but not as troublesome for its casting. Indeed, the content of phosphorus would have improved the castability of the material during the manufacture of shot. Regarding pouring temperature and cooling rate, it is worth noting that some samples of white iron present porosity and shrinkages. On the other hand, various grey iron projectiles exhibit microshrinkages in different quantities. Grape shot projectiles from the *Bucentaure* and round shot from the Deltebre I site, exhibit a complex microstructure. They have a core of grey iron, a band of white iron on their periphery, and a zone of mottled iron in between. This distribution indicates that the surface of these pieces was cooled rapidly. The use of an iron mould (shell), instead of a sand one, could account for this evidence. If the porosity and other macroscopic imperfections (e.g. the sprue) are also considered, a relatively poor control of the quality of these artefacts during its manufacture can be stated as well. This may have been a corollary of mass production of this kind of artefacts.

Although a certain tendency can be appreciated when artefacts from different periods are compared, such as an increasing use of grey iron for shot, this interdisciplinary approach made it possible to appreciate that this trend was not a regular process. Indeed, the analysed evidence indicates that the use of grey iron shot does not seem to have been homogeneous up to (at least) the early 19th century. As was already mentioned, artefacts from the Deltebre I site (even those projectiles of similar size) present different microstructures. Along with samples that have a microstructure of grey pearlitic iron with steadite, shot with a structure of cementite, pearlite and to some extent of steadite were recovered, so far appearing in similar quantity. Several particles of sulfides and a few of titanium compounds type (such as titanium carbide—CTi—and titanium carbide nitride—CNTi—),



were also observed in various samples (Fig. 5). The variability observed suggests that, despite the well-known advantages of grey iron in the 18th century, a regular introduction of ammunition produced with this material was partially constrained by a number of

factors. Some immediate concerns such as technical issues, the characteristics of the blast furnace technology and the variability associated with the manufacturing methods (e.g., the use of different moulds and a relative poor control of the quality during the process) may have accounted for this delay.

Regarding the latter, blast furnaces had a decisive role. Since the early Modern period, charcoal was used as fuel and reductant and operated mainly with acid slag and in low temperatures, which tended to produce white iron (with carbon combined in the shape of cementite). In this sense, the blast furnace technology impeded to some degree the possibility to produce ammunition of grey iron regularly. But with the improvements of furnaces during the 18th century, such as the gradual increase of the blasts height, the introduction of coke instead of charcoal (mainly in Great Britain), and the use of more efficient blowing systems, higher temperatures began to be reached and the tendency switched towards the obtention of more basic slag. These features allowed for a greater amount of silicon to be dissolved into the alloy, resulting in a process by which grey iron (carbon in graphite state) was more easily obtained (see Tylecote 1976).

By this parallel development, a technical constraint was beaten, and the regular manufacturing of projectiles of desired characteristics ceased to be a sought-after ideal of quality and became a concrete possibility in the foundries. As usual, the aspirations of craftsman were limited by the available means, and they could only apply certain novel ideas when appropriate technical conditions were materialized.

Concluding Observations

The account of the state of archaeometric research on shipwrecks in Argentina, and the studies described, have proven they offer great scientific potential for the field. The analyses based on knowledge and analytical methods and techniques from natural and applied sciences have contributed or added to topics such as the identification of artefact function and use, technological assessment (primarily materials used and manufacture methods), site formation processes, deterioration dynamics, provenance, and dating. In general, investigations have shown an increasing amount of analytical techniques are being applied. The research performed on these sites has laid the groundwork for the region.

Despite the progress accomplished, many shipwreck sites and artefacts recovered from them have not been studied yet, and there are several analytical means that should be further explored. In this regard, archaeometric analyses conducted under a well-defined research program are an outstanding way to improve the existing picture of our history. The potential of studies developed from a comparative basis was highlighted. Bearing in mind the difficulties that this method usually faces in practice, a plea for the revision and analyses of existing archaeological collections using new available instrumentation is also made here. This would not only contribute to achieve a more solid and comprehensive knowledge of shipwrecks already studied, but stand as a promising way to enrich the dialogue between the specialists of Latin America and abroad as well. A long and undoubtedly prosperous route towards scientific knowledge and preservation of maritime cultural heritage lies ahead. We have already taken fundamental steps, as the inter-communication and inclusion among the specialists and their complementary approaches are the key for success.

Within this context, investigations on metals from historical shipwrecks have played a significant role for the study of nautical technology. The research carried out by the Archaeometallurgy Group of Argentina stands out in the Latin American scenario. Their

interpretations, nonetheless, are mostly circumscribed to specific topics and contexts, which suggest that these studies are still at an incipient stage. Keeping in mind the results obtained and the potential provided by the available means of research, we urge for investigations to be carried out at a scale beyond that of the site and articulating evidence from a multiplicity of shipwrecks. Given the state of the art at our country, we consider this an exceptionally profitable road to follow in our quest for the understanding of the maritime activities of the past.

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