2nd Archaeometry and Underwater Archaeology "Sebastiano Tusa"

Summer School

Favignana (TP) 6 - 12 September 2020

Proceeding

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Eugenio Caponetti

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2nd Archaeometry and Underwater Archaeology “Sebastiano Tusa” Summer School

A cura di Eugenio Caponetti

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Area Marina Protetta “Isole Egadi”

Associazione Italiana di Archeometria -AIAr

Dipartimento STEBICEF Università degli Studi di Palermo

Dear Sebastiano,

the second edition of the Archaeometry and Underwater Archaeology Summer School took place in a fortunate time window, despite the vicissitudes of the corona virus, as you might see. The event was successful, even having faced few inconvenient.

Despite your absence you were still with us. Anyway, the school, maybe undeservedly, bears your name.

An affectionate hug,

Eugenio

"The role of natural as well as physical and chemical sciences to identify the real nature of objects, their provenance and manufacturing processes, is now essential and became so tied with the normal archaeological way of running the research. The time in which those sciences were called "scienze sussidiarie all'archeologia" is gone. Now the various researchers must work side by side since the beginning of any archaeological project. A real continuous process of hypothesis and deduction between different professionals must be carried out at any stage of any archaeological research".

Sebastiano Tusa

PREFACE

The deepening of the historical, artistic and material knowledge of a find, sometimes unique, is functional to its enhancement as it facilitates and strengthens its use. The complex world of Cultural Heritage in every aspect requires collaboration between different professional figures, where collaborating does not mean putting together the contribution of each, but creating a synergistic activity through the use of a language that is as shared as possible.

Speaking about the underwater cultural heritage, nowadays a wide series of discovered wrecks stand around the entire Mediterranean Sea and particularly around the Sicilian seabed. These wrecks reveal a wide variety of artifacts such as anchors, amphorae containing different types of food, military equipment, such as helmets and swords, bronze artifacts, stones, marble sculptures and other types of objects. One of the main goal of the archaeology is the historical reconstruction, that need as many information as we can. Therefore the study of such important finds it is crucial to understand their stylistic and chronological features and especially the characteristic of materials, where they were originated from as well as how and when they were manufactured. The effective collaboration between the professionals involved is mandatory to guarantee the greatest effectiveness and efficiency from the discovery of the find to its museum settlement through its restauration, conservation, and valorisation.

This school follows the first edition held in Sicily on an itinerant basis in various museums and archaeological parks. It was originated from a strong and proficient collaboration with Sebastiano Tusa.

The goal of the summer school "Archaeometry and Underwater Archeology - Sebastiano Tusa" is to help promote dialogue between "hard science" operators and humanities researchers. to encourage and deepen the knowledge of students and operators in the sector, offering them a vision, even if partial and limited, of the variety and richness of the cultural heritage found or originating from the sea and of the means to deepen their knowledge. The enhancement of these museum exhibits can help encourage the participation of civil society, increase local interest in this type of cultural heritage and give a good boost to the local economy.

The choice of the places where the school takes place is not accidental, but is due to the fact that the *Museum former Stabilimento Florio delle tonnare di Favignana e Formica*, a true jewel of industrial archeology, was the place where the equipment, anchors and boats were kept togheter and became a thriving tuna processing and conservation industry. Today it is rich in artifacts such as beaks, helmets, amphorae, and other finds, many of which are related to the Battle of the Egadi which took place between Favignana and Marettimo, ended on 10 March 241 with the victory of the Roman fleet over the Carthaginian one, placing end to the first Punic War. The reconstruction of the Battle of the Egadi is linked to the extraordinary underwater archaeological discoveries of Sebastiano Tusa.

Proponents of law enforcement, armed forces, public and research institutions involved in various ways in the discovery, recovery, conservation, enhancement and management of the underwater cultural heritage were invited to participate to the *Round Table "Problems and perspectives for better management, protection, conservation and enhancement of finds from the sea"* that was planned at the beginning of the school. The involvement of representatives of all these institutions was done with the aim of strengthening existing collaborations and creating new ones among those involved in various capacities in the finds that at present are or have been taken from the seabed.

We are grateful to all institutions that allowed the fulfilment of the School, to all people involved in the organization, to the scholars for having accepted to participate and mainly to the students for being here.

We conclude with the hope that this School named after Sebastiano Tusa could become an annual or biennial appointment to increase the knowledge of the archaeology of the underwater world and of the methods of archaeometry applied to the study of the underwater finds from our sea, and last but not least to remember all that Sebastiano Tusa has done for the development of this and all the sectors related to it.

Eugenio Caponetti

It is a great honour for me to inaugurate the second edition of “Archaeometry and Underwater Archaeology - Sebastiano Tusa” Summer school.

The school aims to encourage the synergy between humanistic and hard science, founding Sicily as the best meeting ground. The Sicilian scientific community has done a great work, from the late Sebastiano Tusa, former Cultural Heritage Assessor, to the chemists from the University of Palermo, working in the cultural heritage field and coordinated by Eugenio Caponetti.

This collaboration led to numerous initiatives, whose spearhead was the Summer School first edition. It is an excellent outlook to keep pursing Sebastiano’s project, hoping it could become a periodic meeting for the cultural heritage community.

I wish to all participants, students and faculties, a fruitful work, and I thank Professor Eugenio Caponetti and Dott. Valeria Patrizia Livigni for arranging the school.

You have all my best wishes in your work.

È per me un grande piacere dare il via ai lavori della seconda erdizione della Summer School “Archaeometry and Underwater Archaeology - Sebastiano Tusa”.

Nata dalla volontà di promuovere un dialogo costruttivo tra il mondo degli studiosi delle scienze umanistiche e quello delle scienze “dure”, ha trovato terreno fertile nell’incontro tra il contesto scientifico siciliano, rappresentato da Sebastiano Tusa, e alcuni chimici dell'Università degli Studi di Palermo impegnati in tematiche connesse ai beni culturali, coordinati da Eugenio Caponetti.

Questa collaborazione, che ha permesso di realizzare nel tempo numerose iniziative comuni, è culminata nell'organizzazione della prima edizione della summer school. È sicuramente un eccellente modo per continuare nell’opera tracciata da Sebastiano far si che questa iniziativa possa continuare in futuro assumendo, magari, un carattere periodico.

Concludo augurando a tutti i partecipanti, discenti e docenti, un proficuo lavoro e ringraziando il Prof. Eugenio Caponetti e la Dott.ssa Valeria Patrizia Livigni per aver organizzato questa scuola.

Buon lavoro a tutti

L’Assessore dei Beni Culturali e dell’Identità Siciliana

Alberto Samonà

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2^{nd} Summer School

Archeologia e Archeometria Subacquea "Sebastiano Tusa"

Programma

Domenica 6 Settembre

17:00 Registrazione Studenti
17.30 Assemblea soci Associazione Archaeometry Summer School, prima convocazione

Lunedì 7 Settembre

09:00 Assemblea soci Associazione Archaeometry Summer School, seconda convocazione
Conosciamoci
Presentazione degli studenti: ciascuno in 6-8 minuti racconta la propria esperienza formativa

10:30 ***Saluti istituzionali***

Alberto Samonà	Assessore ai Beni Culturali e l'Identità Siciliana
Valeria Patrizia Li Vigni	Soprintendente del Mare
Roberto Garufi	Direttore del Museo Regionale di Trapani "Agostino Pepoli"
Enrico Caruso	Direttore del Parco Archeologico di Lilibeo-Marsala
Salvatore Livreri Consoli	Direttore Area Protetta di Favignana
Maria Guccione	Erudito locale, già assessore del comune di Favignana

10.45 *Presentazione della scuola e introduzione alla Tavola Rotonda*
Eugenio Caponetti Labor Artis CR Diagnostica – Già P.O. UNIPA

11.00 Tavola Rotonda

Problematiche e prospettive per una migliore gestione, tutela, conservazione e valorizzazione dei reperti provenienti dal mare

Coordina Eugenio Caponetti

Valeria Patrizia Li Vigni	Soprintendente del mare
Ugo Picarelli	Direttore Borsa del turismo Peastum
Enrico Caruso	Direttore del Parco archeologico di Lilibeo
Enzo Ruvolo	Direttore UOC Area Mare ARPA Sicilia
Manuela Falautano	ISPRA
Lorenzo Appolonia	Direttore laboratori scientifici CCR Venaria Reale
Stephan Doempke	Word Heritage Watch, Berlin anticipa
Franco Andaloro	Stazione zoologica Anton Dohrn
Contrammiraglio Andrea Cottini	Comandante del Comando Marittimo della Sicilia
Contrammiraglio Roberto Isidori	Direttore Marittimo della Sicilia Occidentale
Contrammiraglio Giancarlo Russo	Direttore Marittimo della Sicilia Orientale
Generale Div. Riccardo Rapanotti	Comandante Regionale Sicilia Guardia di Finanza
Colonnello Andrea Martinengo	Comandante Reparto Operativo Aereonavale Sicilia
Tenente Colonello Valerio Marra	Comandante del Gruppo Carabinieri T.P.C di Roma.
Colonnello Gianluca Vitagliano	Comandante Provinciale dei Carabinieri di Trapani
Luogotenente Angelo Busciglio	Comandante del Nucleo T.P.C. di Palermo.

Conclusioni
Alberto Samonà Assessore ai Beni Culturali e all'Identità della Regione Siciliana

13.30 *Pausa pranzo*

15.30 *Archeologia subacquea. Storia, ricerche e prospettive.*
Edoardo Tortorici Già P.O. UNICT

16:15 *La battaglia delle Egadi*
Valeria Patrizia Li Vigni Soprintendente del Mare

17:00 *Fine Giornata*

Martedì 8 Settembre

9.00 *The Role of Cultural Heritage for Sustainable Development*
Stephan Doempke Word Heritage Watch, Berlin

9.35 *Il contributo delle indagini chimico fisiche alla lettura dei reperti provenienti dal mare*
Eugenio Caponetti Labor Artis CR Diagnostica - Già P.O. UNIPA

10.10 *Archeoecologia*
Franco Andaloro Stazione zoologica Anton Dohrn

10.45 *Pausa*

11.00 *Tecniche elettrochimiche per la diagnostica nei beni culturali*
Mario Berrettoni Università di Camerino

11.35 *Conoscere per conservare: metodi per valutare il rapporto materiali/ambiente*
Lorenzo Appolonia Direttore laboratori scientifici CCR Venaria Reale

12.10 *La ricerca archeologica subacquea in altofondale e le nuove metodologie multidisciplinari basate sull'interazione tra osservazione diretta e sistemi remoti: i relitti di Panarea e la Battaglia delle Egadi.*
Roberto La Rocca Archeologo subacqueo, Dipartimento Beni Culturali

12.45 *Pausa*

15.00 *La fotografia subacquea in campo archeometrico, dal rilievo tradizionale al rilievo 3D*
Salvo Emma Assessorato dei Beni Culturali e dell'identità siciliana

15:25 *Introduzione alla Spettroscopia XRF e sue applicazioni*
Maria Luisa Saladino Dipartimento STEBICEF – UNIPA

15.50 *Laboratorio di Spettroscopia XRF*
Gabriella Chirco Studente PhD Dip. Culture e Società - UNIPA

Mercoledì 9 Settembre

9.00 *Scienza e Archeologia: esperienze di ricerca congiunta* *on line*
Monica de Cesare Dipartimento Cultura e Società UNIPA

9.35 *Sistemi diagnostici per lo studio dei processi di degrado di reperti metallici*

Maria Pia Casaletto ISMN-CNR Palermo

10.10 *La metallografia, uno strumento per ricostruire i processi metallurgici antichi dei manufatti di interesse storico*
Justine Vernet ICMATE-CNR Genova

11.00 *Moderni metodi per l'analisi di vetri archeologici antichi* on line
Cristina Leonelli Dipartimento "Enzo Ferrari" UNIMORE
Cristina Boschetti IRAMAT-CEB, UMR5060, CNRS/Université d'Orléans France

11.35 *Dalla cultura materiale ai miti del mare*
Francesca Oliveri Archeologa Soprintendenza del Mare

12.10 *Recenti scoperte di archeologia subacquea nei mari di Sicilia*
Nicolò Bruno Archeologo Soprintendenza del Mare

13.00 Visita del museo Ex Stabilimento Florio delle tonnare di Favignana e Formica

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9:00 *Indagini con fasci di neutroni di ritrovamenti metallici archeologici* on line
Francesco Armetta Dipartimento STEBICEF – UNIPA

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Fabrizio Lo Celso Dipartimento STEBICEF – UNIPA

10:10 *Relitto A di Lido Signorino (Marsala). Analisi archeometriche e ricerca archeologica sul*
Filippo Pisciotta PhD candidate Université Aix-Marseille e UNIPA

10.45 *Visita Guidata al Museo alla sala GranTorino ed alla sala multimedialedella Battaglia delle Egadi*

12:30 *pausa*

14.00 *Approccio multianalitico allo studio dei reperti provenienti dal mare.*
Eugenio Caponetti Labor Artis CR Diagnostica – Già P.O. UNIPA

14.20 *Introduzione alla MO ed alla Spettroscopia Fors e sue applicazioni*
Maria Luisa Saladino Dipartimento STEBICEF – UNIPA

14:40 *Laboratorio di Spettroscopia FORS e MO*
Veronica Ciaramitaro Dipartimento STEBICEF – UNIPA

15.10 *Scansioni laser e tecniche digitali fotogrammetriche in campo archeometrico*
Laboratorio laser scanner
Dario Giuffrida IPCF-CNR Messina

Venerdì 11 Settembre

9.00 *Analisi Multivariata nel Campo dei Beni Culturali*
Sebastiano Trusso ICPF-CNR Messina

9.35 *Geoarcheologia di mare profondo e innalzamento del livello marino nel Mediterraneo*
Francesco Torre Già P.O. UNIBO

10.10 *Itinerari culturali subacquei in Sicilia - Musei sommersi e nuove tecnologie*
Pietro Selvaggio Soprintendenza del Mare
Floriana Agneto Soprintendenza del Mare

11.00 *La Nave punica di Lilibeo: nuovi dati e ipotesi per la ricerca archeologica*
Maria Grazia Griffo Parco archeologico di Lilibeo-Marsala

11.35 *La Nave punica: storia e restauro dal ritrovamento alla presentazione nel Museo Lilibeo*
Enrico Caruso Parco archeologico di Lilibeo-Marsala

12.10 *Studio dello stato di conservazione e dell'efficacia degli interventi conservativi su legni archeologici mediante tecniche di spettroscopia NMR in stato solido*
Alberto Spinella Aten Center - UNIPA

12.45 *Pausa*

14.00 *Introduzione alla spettroscopia Raman e sue applicazioni*
Rosina Celeste Ponterio IPCF-CNR Messina

Laboratorio Applicazioni Spettroscopia Raman
Viviana Mollica Nado IPCF-CNR Messina

15:00 *Introduzione alla Spettroscopia infrarossa e sue applicazioni*
Laboratorio Applicazioni Spettroscopia Infrarossa
Vincenzo Renda UOC Area Mare ARPA Sicilia

19:30 *I Beni Archeologici subacquei e gli Habitat di insediamento: quale modello per la gestione congiunta?*
Alessandro Agate Area Marina Protetta Isole Egadi

19:45 *20 anni di esplorazione, documentazione e studio del patrimonio culturale sommerso della Sicilia: le attività della Global Underwater Explorers insieme alla Soprintendenza del Mare*
Francesco Spaggiari Global Underwater Explorers
Mario Arena Global Underwater Explorers

Sabato 12 Settembre

10.00 *Riflessioni finali da parte di tutti i presenti*

11.00 *Consegna degli attestati di partecipazione*

12:00 Chiusura della Scuola.

Resume on student meeting

At the School opening, we took a time entirely dedicated to the students enrolled in the program, where each one of them had the opportunity to introduce themselves by presenting their training path and subsequent experiences.
The Summer Schools was open to Archaeologists and also professional profiles working the field of cultural heritage with a different background, in order to create a meeting point between the Archeologic universe and the galaxy of applied sciences, whose progression often provides new tools and methodologies for the preservation of artefacts. This edition welcomed 11 (10 planned) participants well-fitting the mission of the school, both because they came from various Italian universities and research institutions located in various cities such as Turin, Genoa, Bologna, Rome, Messina, Catania and Palermo, and also because of a rather varied cultural background.
Dario Giuffrida and Viviana Mollica Nardo are PhD students and researchers at the CNR of Messina, the first deals with digital archaeological survey, the second with spectroscopic techniques applied to problems concerning Cultural Heritage; Justine Vernet, post doctorate of the CNR of Genoa, deals with archaeomaterials; Veronica Ciaramitaro fellow UNIPA student, deals with the characterization of stone protective on stones and their interactions with the stone substrate; Aurelio Bonasera researcher (UNIPA) deals with a new generation solar cells based on organic dyes; Antonella Privitera is a PhD student in *Matter Sciences, Nanotechnologies and Complex Systems* (UniRomaTre); Rosalinda Sciacca, PhD student in *Analytical Chemistry,* with her doctoral thesis she is involved also with electrochemical methodologies applied to the study of finds of historical and artistic interest; - Dario Giuliano, Archaeologist and PhD student in *Cultural Sciences* (UNIPA); - Emilia De Paolo and Silvia Pariti, archaeology students (UNITED), are diving experts specifically interested in the school's themes; Gabriella Chirco, restorer with experience also in the field of conservation and diagnostics applied to cultural heritage, she is a PhD student in *Human Sciences: dynamics of systems, cultural heritage and cultural studies* (UNIPA). During the introduction each student presented a poster with the results of their most recent scientific activities. Some of those participants shared their expertise with short talks or laboratory activities as part of the main program of the school. All of them aimed at the exchange of knowledge, in order to encourage the integration of different points of view and technical background. As a final result, the multidisciplinary background of the students underlined how it is important to put in close contact different areas of the Scientific Research to provide the best tools for characterizing artefacts and preserving their status as long as possible. Student posters and their profile are shown at the end of this volume.

Resumè by Gabriella Chirco and Antonella Privitera


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Brief notes on Round Table

"Problems and prospects for a better management, protection, conservation and enhancement of finds from the seabed"

These brief notes summarize the work of the round table reporting the main topics addressed, not considering single interventions. The need for collaboration between the so-called hard sciences and the humanities was the common thread of the whole event. Particularly, the most common topics among the interventions were the collaboration between the archaeologists and the diagnosticians, and memories about Sebastiano Tusa.

Representatives from the armed forces and law enforcement agencies highlighted how their administrations have logistically supported and still support the work of the archaeologists during the discovery and recovery of new finds, and how they daily monitor the treasures under the sea in order to avoid illegal recovery actions by the grave robbers of the sea.

The work of the *Sea Area of ARPA Sicilia* is among the support actions, it combines the role of safeguarding the environment with the interest for the rediscovery of the past, the emotion for the discovery of an artifact and the consequent passionate work of reconstruction and historical contextualization of the discovery. Among other things, the equipments and professional skills at the head of the structure are at complete disposal for any study, management, protection and enhancement of the underwater heritage that requires them.

It was emphasized that the discovery of an artefact in shallow and deep waters is the result of human skills and the increasing contribution of sophisticated and efficient technologies, but in most of the cases, however, the human contribution remains fundamental. The discovery, however, is just the initial act of a series of operations. If there are no conditions to leave the finds in the place of discovery with the creation of marine archaeological parks, they can be preserved or exhibited in suitable structures, possibly around the area where they were discovered. Both options have a positive impact on the touristic attraction of the involved places which can make the cultural asset a flywheel that generates resources for self-financing of conservation policies and for the region.

Deep attention was addressed to the protection of cultural heritage by countering all illegal operations ranging from illegal recovery to clandestine marketing, that sometimes involves supranational organizations. This contrast becomes effective when it manages the identification of the various protagonists of the steps that bring the object from the grave robber to the final buyer, managing to neutralize the entire chain. The commitment of the Carabinieri Command for the Protecting of the Cultural Heritage as a whole begins with the photographic cataloguing, up to the dismantling of international criminal organizations involved in the illegal marketing of finds to end with the material recovery of the property and its return to the territory where it has been removed. In this field, in addition to the investigative activity carried out by the special department of the Carabinieri in more than 50 years, considering that it was established on 3rd May 1969, one year before the signing in Paris of the 1970 UNESCO Convention, it is equally important to underline the role and function of the Database of Illegally Stolen Cultural Property. This is the largest database of works of art in the world, counting as today more than 1,280,000 cultural properties to still be searched. The Database also contains archaeological finds illegally excavated on land or fished out of the sea and illegally exported abroad, which are, of course, also the subject of research in the international field.

The preventive activity the Carabinieri Command for the Protection Cultural Heritage carries out, due to their exclusive competence in guaranteeing the safety of the national cultural heritage, as confirmed by the Decree of the Minister of the Interior of 15 August 2017, on the territory and therefore also in the marine archaeological areas, sees them directly involved together with the Carabinieri of the Underwater Unit and the Naval Service and the underwater archaeologists of the "Superintendence of the Sea". It is a constant monitoring activity that allows not only a cataloguing of the underwater cultural heritage, but also the prevention of possible criminal activities that "the grave robbers of the sea" can carry out. The hard sciences-archaeology interactions, the purpose of this school, must find fertile ground for meeting in the daily operations connected to the practical activity of all the skills involved in the management of cultural heritage "tout court". The contribution of diagnostics begins from the instant of discovery. Although the chemical-physical techniques that can be used in water are still under development, immediately after the artifact is taken out of the seawater the diagnostics occur and it is fundamental for the material knowledge of the object and its state of preservation. Furthermore, the diagnostics significantly contributes to the archaeometric study of the finds and provides the necessary information to operate in the best way to all the subjects who will interact with the object in the various stages of its new life following the discovery.

Starting from the axiom that any object of archaeological interest has its own specific material constitution, one can never ignore the contribution of hard sciences for a deeper knowledge and therefore it is needed its complete characterization to avoid loss of cultural heritage. Chemical-physical investigations are fundamental both to give ground information for a possible restoration of the find, and above all to establish the most suitable conditions for a correct conservation. Unsuitable conditions of conservation can cause greater damage rather than centuries and millennia on the seabed. The effective interaction among chemicals, physical and archaeological investigations, makes the archaeometric study effective and optimized, and it cannot be left to the good will of individual actors or to the far-sightedness of some. Sebastiano Tusa can certainly be considered a precursor, but he would have had to find an institutional framework that makes the interactions between these two souls the norm and not the uniqueness. Councillor of Assessorato ai Beni Culturali e l'Identità Siciliana, Alberto Samonà concluded the work by recalling the fundamental role of the Superintendence of the Sea of the Sicily region, strongly desired and fulfilled by Sebastiano Tusa; it constitutes a unique and true excellence whose model will be replicated on national scale. He emphasized the positive role of the cultural asset, which, if properly valued and "used", really constitutes a resource for the involved region. He also listed a series of projects managed by his department and concluded by thanking all the institutional and non-institutional subjects who in different ways contribute to the enhancement of the treasures that our seabed preserves.

Résumé by Mario Berrettoni and Eugenio Caponetti


STINTORE
POLVERE


2nd Archaeometry and Underwater
Archaeology Summer School
Sebastiano Tusa
Favignana 6 - 12 settembre 2020
CAUTION

General contributions

Archeologia subacquea. Storia, ricerche e prospettive.

Edoardo Tortorici

L'Archeologia subacquea non esiste, l'espressione è di A. Tchernia, uno dei più importanti archeologi subacquei degli anni Settanta del secolo scorso. Con questa frase lo studioso voleva sottolineare, per evitare fraintendimenti, che l'archeologia subacquea non è diversa, concettualmente e metodologicamente, dall'archeologia "terrestre"; cambia, ovviamente, l'ambiente in cui si svolge la ricerca, cioè l'acqua, e dunque l'uomo ha bisogno di particolari attrezzature per operare in immersione. La volontà/necessità da parte dell'uomo di estendere il proprio campo di indagine all'ambiente subacqueo risale ad epoca molto antica. Vale la pena di ricordare che già nel II millennio a.C., soldati assiri, impegnati in operazioni belliche, riuscivano a respirare sott'acqua da un otre di cuoio riempito d'aria; nel mondo romano esistevano corporazioni di *urinatores*, che si immergevano in apnea per recuperare il carico delle navi affondate. Nel XV e XVI secolo, alcune leggende di ambiente islamico fanno riferimento ad Alessandro Magno che si sarebbe fatto calare in mare entro un grande recipiente di vetro per ammirare e studiare l'ambiente e i fondali.

Nei secoli XVII e XVIII si deve al perfezionamento della campana batoscopica di E. Halley, la felice conclusione di alcune imprese subacquee, come quella del recupero dei cannoni bronzei dal relitto della grande nave da guerra svedese *Vasa*, affondata nel 1628 nel porto di Stoccolma subito dopo il varo. Ulteriori sperimentazioni porteranno alla definitiva realizzazione delle prime attrezzature per palombari (inizi del XIX secolo), fornendo decisamente ai ricercatori la possibilità di operare sott'acqua con sufficiente efficacia: i recuperi effettuati dai palombari nelle navi di Nemi (oggetti dell'attrezzatura e della decorazione bronzea, 1895), nei relitti di Anticitera in Grecia (1900-1901) e di Mahdia in Tunisia (1908-13), le scoperte fortuite e i recuperi di pregevoli opere d'arte greca (Efebo di Maratona, 1925; Posidone e "fanciullo fantino" di Capo Artemisio, 1928), ebbero grande risonanza e misero in evidenza l'importanza della ricerca archeologica sottomarina.

Le due grandi navi di Nemi, a cui si è accennato, attribuite all'imperatore Caligola, vennero poi scavate all'asciutto tra il 1928 e il 1932, addirittura abbassando, per lo scavo, il livello del lago (fig. 1).

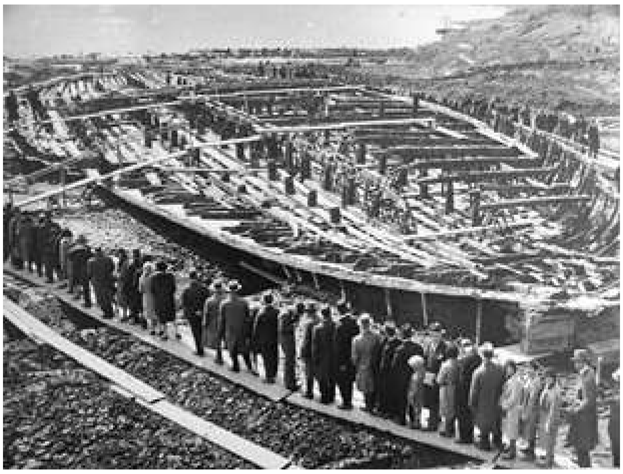

Fig. 1. Visita alle navi di Nemi in corso di scavo (1930) (da Ucelli 1940).

Le navi, vennero poi tirate in secco ed ospitate in una sorta di grande capannone in muratura, appositamente costruito sulla riva. La risonanza dell'impresa fu enorme: per la prima volta era stato possibile analizzare due relitti antichi perfettamente conservati, ottenendo fondamentali contributi conoscitivi per la tecnica di costruzione navale romana e per la stessa ricca decorazione bronzea del rivestimento. Durante la Seconda Guerra Mondiale, in circostanze non ancora chiarite completamente, le due imbarcazioni antiche vennero purtroppo completamente distrutte da un grande incendio, provocato dalle truppe tedesche in ritirata.

La possibilità di effettuare ricerche archeologiche, scavi e prospezioni subacquee divenne concreta con l'invenzione dell'autorespiratore ad aria (denominato *Aqua-lung*), progettato e realizzato nel 1942 da J. Cousteau ed E. Gagnan (fig. 2), che permetteva all'operatore in immersione una respirazione autonoma, non più dipendente dalla superficie: l'aria, compressa ad alta pressione (200 atm ca.) entro bombole poste sulle spalle del sommozzatore, veniva erogata alla stessa pressione ambientale (cioè in relazione alla profondità di esercizio), tramite un meccanismo (appunto l'erogatore) terminante in un boccaglio.

Fig. 2. J. Cousteau ed E. Gagnan a bordo della *Calipso* nel 1953 (RolexMagazine.com).

Questo sistema, in seguito continuamente perfezionato, determinò un vero e proprio salto di qualità, permettendo ad un numero sempre maggiore di persone di immergersi in sicurezza con un'attrezzatura notevolmente semplificata (maschera, pinne, muta in neoprene, cintura di zavorra) rispetto a quella dei palombari. La prima sperimentazione archeologica dell'autorespiratore ad aria venne condotta nel 1948 sul relitto di Mahdia, in Tunisia (J. Cousteau, Ph. Tailliez). Pressappoco negli stessi anni veniva definitivamente raggiunta la consapevolezza, per l'archeologia subacquea, che gli scavi e le ricerche dovevano rispondere agli stessi criteri di correttezza scientifica delle indagini condotte in terraferma. La nascita dell'archeologia subacquea moderna si può infatti fare risalire all'ottobre 1949, quando alcuni pescatori locali segnalarono al prof. Nino Lamboglia, la presenza di un relitto con carico di anfore vinarie al largo di Albenga. Lo scavo venne affidato alla Società

SO.RI.MA. (Società Ricuperi Marittimi) di Genova, che, con i palombari e la draga della nave *Artiglio*, aveva acquisito grande notorietà per il recupero dei lingotti d'oro del carico dell'imbarcazione inglese *Egypt*, affondata nell'Atlantico. La draga, in particolare, arrecò notevoli danni al giacimento di anfore e Lamboglia (fig. 3), tristemente, ebbe a commentare con grande senso di onestà*: Il cimitero di anfore provocato dalla "benna" a bordo della nave avrebbe turbato la coscienza di qualsiasi archeologo, e turbò assai la nostra*. Fu tuttavia proprio questa esperienza a chiarire definitivamente che gli scavi subacquei dovevano corrispondere agli stessi criteri di "*scientificità*" (il termine è di Lamboglia) degli scavi terrestri e spinse lo stesso Lamboglia all'impostazione di una metodologia di intervento che rimarrà fondamentale per il successivo sviluppo delle tecniche di scavo subacqueo.

Fig. 3. N. Lamboglia a bordo dell'*Artiglio*, osserva le prime anfore recuperate dalla nave di Albenga (da Gandolfi 2000).

La seconda campagna di intervento sulla nave di Albenga, condotta con l'impiego esclusivo di sommozzatori, venne infatti quasi totalmente dedicata alla realizzazione di un sistema di quadrettatura del relitto, da porre come base per la documentazione grafica e fotografica e per l'individuazione, il posizionamento e la numerazione dei singoli reperti del carico. Grande impulso alle ricerche venne inoltre dall'utilizzo di strumenti particolarmente adatti agli scavi sottomarini: tra il 1950 e il 1952 i relitti di Anthéor/Chrétienne A e Grand

Congloué, sulla costa meridionale francese, vennero infatti scavati impiegando per la prima volta la sorbona, ancora oggi in uso in tutti i cantieri. Si tratta di un sistema composto da un lungo tubo rigido o semirigido corrugato, nella cui parte iniziale, attraverso una manichetta, viene immessa aria in pressione che, risalendo violentemente verso la superficie, crea una forte aspirazione. Tale forza aspirante, che può essere regolata in intensità a seconda delle esigenze, viene sfruttata per rimuovere strati e materiali (sabbia, sedimenti, banchi di posidonia oceanica, ecc.) che ricoprono i resti archeologici (fig. 4).

Fig. 4. La sorbona impiegata nello scavo di Gela (da Vullo 2013).

Ancora nello stesso periodo (tra il 1954 e il 1957, nel corso dello scavo del relitto del Titan) vennero sperimentati sistemi di documentazione fotografica subacquea, con la realizzazione di un mosaico fotografico dell'intera area di ricerca. Si può affermare che, in definitiva, sul finire degli anni Cinquanta, erano ormai poste le basi metodologiche per il moderno scavo archeologico subacqueo.

Ulteriori contributi innovativi vennero forniti nel decennio successivo da alcuni importanti scavi condotti da ricercatori anglosassoni (G.F. Bass, F.H. van Doorninck). In tali cantieri (Capo Gelidonya, 1960; Yassi Ada I, 1961-64) tutte le operazioni subacquee furono svolte per la prima volta direttamente da archeologi e ricercatori e non da sommozzatori professionisti, come era avvenuto fino ad allora, con difficoltà notevoli nella conduzione, nel controllo e nella documentazione dei dati scientifici. Il relitto di Yassi Ada I, inoltre, costituisce il primo esempio di scavo subacqueo integrale ed estensivo, con il rilievo totale del carico e dello scafo ligneo, anche mediante l'impiego sperimentale della fotogrammetria subacquea, cioè di un sistema che permette di abbreviare notevolmente i tempi di esecuzione della documentazione grafica, ottenendo rilievi planimetrici da riprese fotografiche. In questo stesso periodo vennero affrontati anche i problemi legati al prolungamento dei tempi di immersione e alla sicurezza degli operatori, mediante l'impiego, prima sperimentale, poi ulteriormente perfezionato e adottato su larga scala, di camere di decompressione immerse e di campane batoscopiche (ad es., negli scavi dei relitti di Yassi Ada II, Punta Scaletta, Albenga). Notevole rilievo inoltre assunsero anche le ricerche volte a sperimentare e codificare tecniche di restauro e conservazione del materiale bagnato, con particolare riferimento alle strutture lignee delle imbarcazioni, alle ceramiche e al contenuto delle anfore da trasporto (relitto di Kyrenia). Si affermano in questo periodo la diffusione e la fortuna degli sport subacquei, anche con il contributo di film e racconti dedicati alle "avventure" sotto il mare.

A partire dagli anni Settanta, grazie alle conoscenze acquisite e ai risultati raggiunti, l'evoluzione delle tecniche di scavo subacqueo permise ormai di raccogliere dati e informazioni di assoluto rigore scientifico. Le iniziative di scavo di rilevante impegno logistico si moltiplicano, potendo ormai contare su strumenti di lavoro affidabili e collaudati (sorbona ad aria e ad acqua, lancia ad acqua), su condivise e generalizzate strategie di scavo (il sistema basato sulla quadrettatura e sui saggi regolari ripetuti), su avanzati sistemi di documentazione (grafica, fotografica, fotogrammetrica), su navi appositamente attrezzate per l'archeologia subacquea e su specialisti del settore di solida esperienza e di alta professionalità (fig. 5).

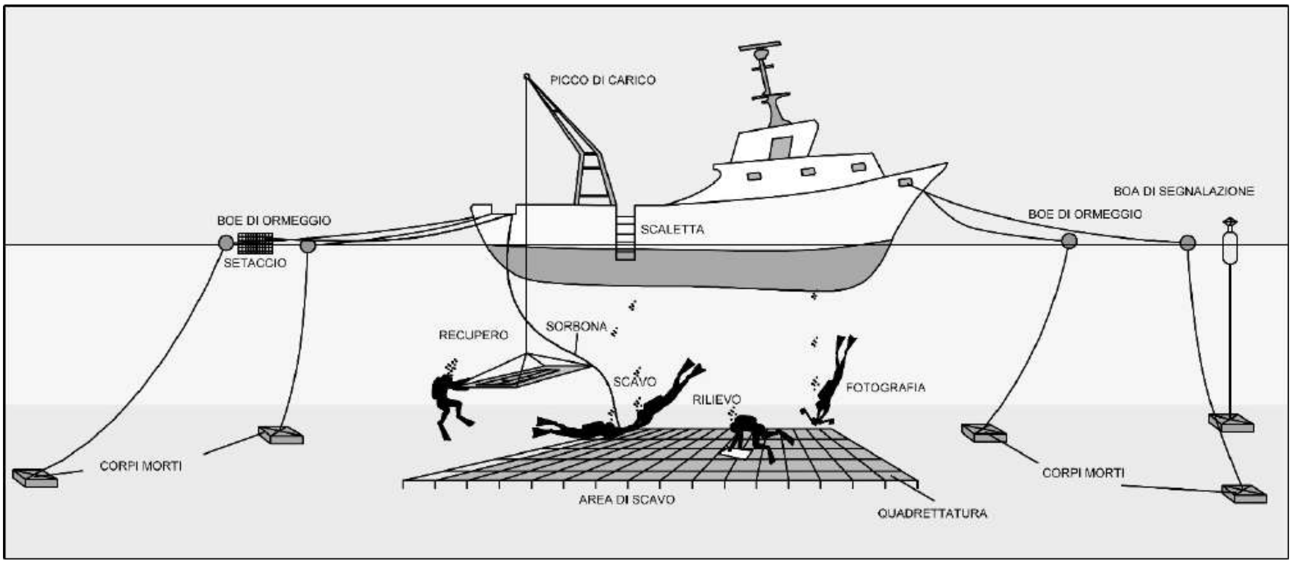

Fig. 5. Schema del cantiere in mare: imbarcazione appoggio e principali operazioni subacquee nell'area di scavo (da Vullo 2013).

In generale questo periodo è caratterizzato dall'introduzione di tecnologie e strumenti sempre più sofisticati, come l'impiego negli scavi di impianti a circuito chiuso per le riprese filmate, di telecamere e di cabine telefoniche sommerse per il collegamento continuo con la superficie, di sommergibili teleguidati per gli interventi e le ricognizioni ad alte profondità, di fotorestitutori per la traduzione grafica delle riprese stereoscopiche (Yassi Ada II, Planier III, Madrague de Giens). Di particolare rilievo è anche l'utilizzo sperimentale dell'informatica per l'archiviazione e la gestione dei dati di scavo (Planier III). Nel decennio successivo e ancora nei primi anni Novanta dello scorso secolo, pur aumentando considerevolmente il numero dei relitti e delle località sommerse scavati o in corso di scavo, non si sono registrate particolari novità nelle strategie, nelle tecniche e nei materiali impiegati, che sostanzialmente sono gli stessi sperimentati con successo negli anni Settanta. In questi ultimi anni l'interesse sembra rivolto alla messa a punto di metodologie di scavo subacqueo, in linea con le più moderne tecniche dello scavo stratigrafico terrestre, alla sperimentazione di mezzi e strumenti sempre più avanzati di documentazione (con particolare riguardo all'impiego della fotogrammetria e dell'informatica) e all'introduzione di condivise normative di intervento per i ritrovamenti ad alta profondità. Per quanto riguarda le tecniche di scavo, l'esigenza di un attento controllo della stratigrafia, in conformità con le esperienze acquisite negli scavi di terraferma, era già fortemente sentita negli anni Sessanta e Settanta. Su queste stesse basi e in rapporto alle odierne tendenze in questo campo (concetto di unità stratigrafica, analisi dei rapporti fisici tra gli strati, redazione del diagramma stratigrafico, documentazione imperniata sulle piante di strato, introduzione di un organico sistema di schedatura di strati e materiali, strategie di intervento per grandi aree, ecc.), e in riferimento alle necessità operative (ad es., negli scavi di Cala Culip e Grado), l'interesse verso gli aspetti metodologici sembra essere nuovamente di attualità. Le difficoltà relative all'ambiente di lavoro, alla conduzione delle operazioni di scavo e di documentazione e all'ordinata asportazione degli strati e dei materiali archeologici rendono ancora oggi insostituibile l'impiego della "quadrettatura". Si tratta in sostanza di suddividere l'area da scavare in una serie di quadrati uguali (per mezzo di un reticolo rigido o semirigido), singolarmente identificati con lettere e numeri. A tali quadrati si fa riferimento per programmare giornalmente i lavori di scavo in immersione, la documentazione grafica e fotografica, il controllo della provenienza dei materiali archeologici, ecc. Secondo tale sistema gli strati possono essere numerati e scavati uno alla volta ed un quadrato per volta, riconosciuti e asportati secondo superfici reali e seguendo l'ordine inverso a quello in cui si sono formati. Lo stesso ordine può essere seguito per lo svolgimento delle operazioni di documentazione grafica e fotografica. La redazione contestuale del diagramma stratigrafico (matrix) si rivela di estrema utilità per il controllo della sequenza stratigrafica. Il grande numero di dati scientifici prodotto giornalmente da un moderno scavo stratigrafico rende necessario l'allestimento e l'organizzazione coordinata e contemporanea di più cantieri, in mare e a terra. In mare aperto, ad esempio, il cantiere è organizzato in due settori tra di loro interdipendenti: l'imbarcazione appoggio in superficie e l'area di scavo vera e propria sott'acqua. Navi appositamente armate e attrezzate per la ricerca hanno fatto la storia dell'archeologia subacquea (basti pensare alle navi Daino, *Cycnus* e *Cycnulus* dell'Istituto Sperimentale di Archeologia Sottomarina e *Archéonaute* della Direction des Recherches Archéologiques Sous-marines). Spesso si tratta di veri e propri laboratori galleggianti con strumenti ad alto contenuto tecnologico per lo scavo, la ricerca e la sicurezza degli operatori (sorbona, compressori a bassa e alta pressione, telecamere e terminali di linee telefoniche a circuito chiuso, camere iperbariche pluriposto, attrezzature per la fotogrammetria e per la documentazione grafica informatizzata, ecc.), che costituiscono il punto di riferimento logistico di tutti i lavori che si svolgono sul fondo. La complessità di alcuni interventi rende necessaria la presenza, sulla terraferma, di un'ulteriore serie di supporti logistici per la gestione contestuale dei dati e dei materiali archeologici e per la manutenzione delle attrezzature (magazzino/laboratorio per i primi interventi di restauro e per la documentazione dei materiali archeologici; magazzino/officina per il deposito e la manutenzione di strumenti e materiali; centrale operativa di raccolta ed elaborazione dei dati provenienti giornalmente dallo scavo e di preparazione di materiali e programmi per la prosecuzione dell'intervento). Un intervento archeologico condotto correttamente non può presentare carenze, approssimazioni o lacune nella documentazione, sia generale che di dettaglio. Per questo motivo è attualmente adottato un articolato sistema, comprendente un'analitica documentazione per schede di strati e materiali, oltre alla tradizionale documentazione grafica e fotografica. Riguardo alla documentazione grafica, l'utilizzo di moderni programmi di grafica automatizzata CAD (Computer Aided Design) ha permesso che i rilievi effettuati venissero immediatamente trasferiti su computer, ottenendo planimetrie aggiornate generali e di dettaglio rielaborabili e stampabili, relative alle situazioni stratigrafiche e allo stato di fatto delle varie fasi dello scavo (l'impiego dei supporti indeformabili in poliestere consente ormai agli operatori subacquei di disegnare direttamente sott'acqua con gli stessi livelli qualitativi della documentazione di uno scavo terrestre). Le tradizionali riprese con macchine fotografiche subacquee, o poste entro custodie stagne, sono ancora oggi strumento fondamentale della documentazione. Ad esempio, l'unione delle riprese di ogni singolo quadrato di scavo consente la realizzazione di un mosaico fotografico dell'intera area. Ugualmente le foto di dettaglio in cui è evidenziata la stratigrafia sono di estrema utilità per la comprensione delle vicende stratigrafiche del relitto o del sito sommerso in corso di scavo. Lo sviluppo dei sistemi informatici di questi ultimi anni ha inoltre aperto nuove possibilità di gestione, elaborazione e archiviazione delle immagini. Di grande importanza è l'impiego, introdotto e sperimentato già a partire dagli anni Settanta, di un sistema di rilevamento indiretto basato sulla fotogrammetria. Si tratta, in sostanza, di utilizzare coppie di foto stereoscopiche (effettuate con fotocamere metriche che riprendono la stessa porzione di scavo da due punti differenti, posti su uno stesso asse e alla medesima quota) per ottenere, tramite apposite sofisticate apparecchiature di restituzione analitica e analogica, rilievi quotati. Sono attualmente in corso di sperimentazione per l'archeologia subacquea sistemi volti a semplificare ulteriormente le operazioni di ripresa, impiegando fotografie scattate da macchine non metriche e restituite da avanzati strumenti analitici. Di grande utilità, infine, risulta l'utilizzo della documentazione filmata, effettuata con telecamere fisse o mobili. La necessità, largamente condivisa, di fare riferimento a comuni metodi di lavoro si fa particolarmente stringente nel campo degli interventi ad alta profondità, sempre più frequenti ormai, anche in considerazione dello sviluppo di mezzi e tecnologie, che consente agli archeologi subacquei nuove possibilità di indagine. Si notano a questo proposito difformità evidenti, dal punto di vista dell'approccio culturale, nelle finalità e nei metodi di indagine. Ad esempio, un intervento (1997) di un gruppo di ricercatori statunitensi nel Canale di Sicilia, effettuato a quote operative di 800 m di profondità, ha evidenziato come, a fronte di un imponente dispiego di mezzi e tecnologie (è stato addirittura impiegato un sommergibile a propulsione nucleare), non sempre corrispondano risultati scientificamente apprezzabili e metodologicamente corretti: da alcuni relitti individuati sono stati indiscriminatamente prelevati anfore e altri oggetti senza alcuna attenzione verso i contesti stratigrafici. Viceversa, in alcuni interventi recenti da parte di ricercatori francesi nel Golfo del Leone (relitto Arles 4, a 600 m di profondità), si sono privilegiate le indagini non distruttive nel rispetto dell'integrità dei giacimenti, concentrando l'interesse sugli aspetti della documentazione, mediante l'impiego della restituzione fotogrammetrica assistita dal computer e con interessanti esperimenti di ricostruzione virtuale in tre dimensioni (fig. 6).

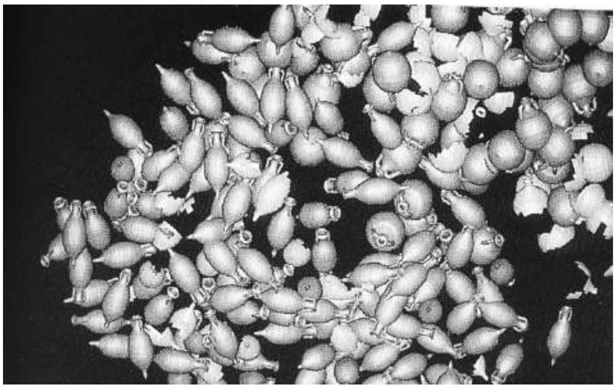

Fig. 6. Il relitto Plage d’Arles 4. Restituzione in 3D (da Long 1998).

La storia dell'archeologia subacquea è fatta non solo di scoperte, mezzi e tecnologie, ma di uomini, veri e propri pionieri dell'archeologia subacquea, a cui si debbono numerosi progressi metodologici, tecnici e numerose scoperte fondamentali; di molte di queste personalità, si è già parlato in precedenza; alcuni sacrificarono addirittura la vita per la ricerca. L'archeologia subacquea tedesca infatti subì una grave battuta di arresto nel 1970, per il tragico incidente sul relitto della Secca di Capistello, a Lipari, in cui persero la vita in immersione, Helmuth Schlager ed Ugo Graf, dell'Istituto Archeologico Germanico di Roma.

Fra i pionieri dell'archeologia subacquea occorre ancora ricordare la figura di Honor Frost (fig. 7), che divenne famosa ed apprezzata, anche nel nostro paese, per gli importanti studi sulle ancore votive in pietra e soprattutto per la scoperta, lo scavo ed il restauro della nave da guerra punica di Marsala.

Fig. 7. Honor Frost (wordpress.com).

Fu tra le prime archeologhe a sperimentare la tecnica del PEG (glicole polietilenico) per il restauro del legno bagnato. Ideò e realizzò il primo itinerario subacqueo italiano all'isola di Ustica.

La figura più importante nel panorama dell'archeologia subacquea degli ultimi decenni è senza dubbio quella di Sebastiano Tusa. Archeologo completo, laureato alla Università di Roma La Sapienza, docente universitario, dedicò gran parte della sua vita professionale alla sua terra di origine: la Sicilia. In Sicilia ricoprì praticamente tutti i più importanti incarichi nell'ambito dell'Amministrazione Regionale dei Beni culturali: Soprintendente a Trapani, fondò e diresse per molti anni la prima Soprintendenza del Mare d'Italia. Grande organizzatore e tessitore di rapporti umani (dal subacqueo locale alle più prestigiose Università americane), innumerevoli furono le nuove scoperte e gli scavi intrapresi, anche in alta profondità. Recentissima è la scoperta del vero sito della Battaglia delle Egadi, che chiuse la Prima Guerra Punica (fig. 8).

Fig. 8. Sebastiano Tusa con gli elmi della Battaglia delle Egadi (Soprintendenza del Mare).

Proprio per la sua indiscussa fama di studioso di livello internazionale, venne nominato nel 2018, Assessore ai Beni Culturali per la Regione Siciliana. Grande fu lo sconcerto della comunità scientifica in occasione della sua tragica morte, avvenuta il 10 marzo 2019, per un incidente aereo sui cieli dell'Etiopia.

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The tree levels multianalytical approach appliaed to finds from the seabed. Gela orichalcum ingots case study.

Eugenio Caponetti[1,2] and Francesco Armetta[1]

[1] Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche -STEBICEF, Università di Palermo, Viale delle Scienze pad.17, Palermo I-90128, Italy

[2] Labor Artis CR diagnostica s.r.l., via Celona 19 Palermo I90145, Italy

eugenio.caponetti@unipa.it, phone: +39 3402484708.

Abstract

The function of diagnostics in the study of objects of historical and artistic interest is increasingly recognized nowadays, but from a practical point of view it does not have the right space it deserves, see for example the calls for the restoration of public works. By studying an object of historical and/or artistic interest, the information we are looking for depend on the purpose of the study and it is different according to the type of object under investigation.

In this presentation we will show, from a methodological point of view, that a three levels multi-analytical non-invasive, micro-invasive and micro-destructive approach, can be applied to different types of artifacts and for different purposes.

The study of Gela orichalcum ingots will be presented as a case study, in order to show a practical application of what we call the three level multi-analytical approach.

Non invasive and non destructive techniques are used in the first level by using portable instrumentation. The obtained informations provide a variety of other informations and pose new questions. The information are useful to design the second level of the investigations, according to the specific questions raised during the first survey.

In the second level micro-samples are required to be taken from the artwork and are analyzed with laboratory equipment; therefore these kind of analysis are micro-invasive or micro-destructive. The obtained information are preparatory in order to plan more specific investigations that are part of the third level. These investigations are carried out in laboratories specialized in particular analyzes (such as workshops for isotopic composition, wood dating and more, or in international facilities such as the ones that make use of neutron or synchrotron light.)

KEYWORDS: non-invasive, micro-invasive, micro-destructive techniques; portable strumentations;

1. Introduction

The deepening of knowledge (historical, artistic and material) of a relic, sometimes unique, is functional to its enhancement as it facilitates and strengthens its use. The role of natural, chemical and physical sciences in identifying the real nature of objects, their origin and production processes, is indispensable today and must be the basis of the current way of carrying out archaeological research. The multidisciplinary approach not only provide the stylistic and chronological characteristics of the finds, but also the nature of the materials that compose it and its state of conservation.

In particular, the chemical-physical study is useful in order to increase knowledge of the matter nature of the find under investigation. In addition the knowledge of phenomena, occurring in the core and mainly at the interface, due to the interaction of the artwork with the environment, may lead to a proper understanding of the changes produced by natural or accidental events and can help for planning its appropriate conservation in an adequate environment and for planning their monitoring over time.

The deterioration nowadays includes not just a macroscopic alteration that can be valued by visual or tactile interactions, but also primarily any molecular or microstructural irreversible alteration of the materials constituting the item under investigation. Therefore, its conservation status must be evaluated in an objective way analyzing the integrity of the materials and investigating the change of the physical-chemical properties at atomic level [1].

2. The investigation techniques

Facing the study of an object of historical and/or artistic interest, the questions we ask ourselves, and therefore the information we are looking for, may be relate to the knowledge of the nature of the materials constituting the artwork (elemental composition and molecular composition) their spatial organization (cristalline structure), the production and/or execution technique, the origin of the materials, its state of conservation, the processing or execution technique, its history, origin of materials, age, authentication. All these elements are useful for planning the conservation and, in case it is necessary, the restoration.

Today we have available a very large number of techniques that can be effectively used for the study of materials, and therefore for the investigation on artifacts of historical and/or artistic interest. There are many ways to classify the investigation techniques, for example bulk and surface techniques, organic and inorganic techniques, elementary analysis techniques, molecular analysis techniques structural investigation techniques and so on.

Dealing whith cultural heritage artefacts, the classification usually made is: i) non-invasive and non-destructive techniques that do not require the instrumentation to come into contact with the work, ii) micro-invasive and non-destructive techniques: these techniques require the taking of a micro-sample that remains unchanged after the analysis, iii) micro-destructive techniques: in this case the micro-sample is sacrificed to carry out the analysis.

Anyway, it is important to underline that modern equipments require sampling from ever smaller amount of matter, sometimes even a few milligrams. In the field of cultural heritage, a conservative position authorizes only non-invasive and non-destructive analyzes, but a long discussion can be opened on this. Starting from the axiom that it is not possible to obtain information about an object without interacting with it and that this interaction inevitably modifies the object under investigation, we assert that it is not possible to generalize, but, for each specific case it is necessary to consider costs and benefits. In this evaluation, the costs may also include the economic ones necessary to carry out the analysis, but they consist mainly on the "damage" (possible modification) that we might cause to the object under investigation. The benefits consist of the usefulness of the obtained information, the increase of knowledge of the object under analysis and the importance of the knowledge acquired.

3. The three levels multi-analytical approach

In this presentation we will show that, from a methodological point of view, a common multi-analytical non-invasive, micro-invasive and micro-destructive approach can be applied to different types of artifacts and different purpose for each artifact.

The three levels approach is comprised by a multi-analytical non-invasive, micro-invasive and micro-destructive study of an artwork implying a number of tasks with a strict order of compilation. The order of compilation is strictly related to the amount of information that is possibly gathered from the analyses and the harmfulness to the work of art of the various analytical techniques. It is not the same thing if we first apply non-destructive, non-invasive techniques, and then techniques requiring a sampling, rather than the opposite.

A proper protocol of investigation involves a first level of analysis performed by using non-invasive and non-destructive techniques with portable instrumentations. It is a screening phase to get basic information about the object and individuate the main characteristic. Although much information can be inferred from the results obtained by applying the above techniques, new questions often arise and more specific investigations are required. In the second level a micro-sampling is required in order to analyze micro portions of the artifact under investigation in scientific laboratories, using micro-invasive and or micro-destructive techniques. In the third level more specific analyses are required. These analyses can be performed in international large facilities or highly specialized laboratories where specific measurement can be performed on selected sampled of high value or representative of huge set.

First level. The three levels multi-analytical investigation approach involves a first screening by using non-invasive techniques by using portable instrumentations.

Some of the possible techniques, due to their characteristics, will be the subject of practical demonstrations during this summer school:

- 3D reconstruction of an object for the production of virtual model, useful for restoration and museum exibition;
- X Ray Fluorescence Analysis (XRF) for qualitative a semi quantitative determination of elemental composition of the object;
- Fourier Transform Infrared Spectroscopy (FTIR) mainly for the determination of organic, but also for inorganic compounds;
- RAMAN Spectroscopy for the determination of inorganic and organic compounds in support of FTIR investigation.

The use of portable equipment, such as the ones related to XRF, FTIR and RAMAN techniques, has a huge versatility and great advantages, first of all it is not necessary to bring the work to the laboratory, but the other way around, to bring the laboratory where it is located the artifact. The use of these techniques provides the possibility to get a wide variety of information without 'touching' the object. This first screening is usually not very expensive and does not cause any modification in the artifacts. The obtained information can sometimes give enough information to answer our question, but they very often raise new questions. In this case they are useful to plan a subsequent stage of analysis that requires the taking of micro-samples from the artifact under investigation.

Second Level. In the second of the three levels multi-analytical investigation approach, a motivated micro-sampling is performed. The obtained samples are analyzed in research laboratories using micro-invasive and/or micro-destructive techniques.

Such second stage is carried on only when it is deemed necessary and it has to be performed in the best respect of the integrity of the artifacts.

Laboratory equipment compared to portable equipment have a higher performance and gives more and more detailed information. Even if a portable equipment does not provide sufficient information for our needs and it is therefore necessary to carry out some samples, we must underline that the results provided by portable equipment allow us to select, and therefore minimize, the sampling points on which to carry out micro-invasive and micro-destructive analyzes. In this way we reduce the cost of the analyzes, but above all we can limit the "damage" caused to the artwork under investigation to a minimum.

For all the techniques that use a portable equipment, there is a corresponding laboratory equipment. There are a huge number of techniques that use laboratory equipment, here we mention only those that have been talked about in the frame of this school or were used in the case study that we are going to present.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) can determine the main and trace elements of an alloy respectively. One of the advantages of using these techniques is the higher detection power attained, resulting in a more improved limit of quantification, which can be particularly relevant for elements present at trace levels.

X-ray photoelectron spectroscopy (XPS) is a technique for analysing the first atomic layers of specimen giving information on the elements present and their chemical state.

Electrochemical techniques can provide deeper information about the degradation processes, especially for metal objects. A global overview of this kind of relic's degradation can be performed by metallographic analysis, which also reveals the structural feature of the metal bulk.

All these techniques can produce a very large dataset that originates by performing measurement on several objects and/or at different sampling points of the same objects. Collection of very large dataset, in fact, is not uncommon in the cultural heritage field. In this situation, it could be difficult to extract clear and well defined information, a statistical view and more specifically chemometric approaches can help to highlight similitudes and differences in the analyzed samples, and at the same time emphasize the importance of some parameters.

Principal component analysis (PCA), beside other multivariate statistical methods, is nowadays one of the most important and widely used statistical techniques in many fields. As a matter of fact it starts to be considered a useful tool in the cultural heritage field. For example, a set of the same type of finds can be grouped for similitudes and differences as a result of the application of chemometric analyses. The obtained similitudes can be ascribable, for example to same raw materials, manufacture or origin, which are fundamental information both for archaeological studies and for a representative sample selection to be used for deepen characterization by means of techniques of the third level. Therefore, the second level analysis obtained information that can be preparatory to plan more specific investigation.

Third Level. In the last level, we include both non-invasive and micro-invasive analyzes to be performed in international large facilities or highly specialized laboratories. These analyzes are grouped together because they involve financial and / or logistical problems. The access to the equipment in international facilities is subject to the presentation of a formal proposal whose acceptance is decided by a panel of scientists, which evaluate the necessity to apply the requested technique to the specific case study. In the case of non-invasive analysis, the costs for the analysis itself are a combination of transport and insurance costs, much needed in order to move the relic to the specific laboratory.

Neutron and synchrotron light facility provides a large set of techniques, which allow studying the core of the sample in a non-invasive way, revealing internal features. I.e. tomography is able to show the inner of an object, unveil the hidden parts while diffraction provides information about the structure of organized materials, which is strictly connected to the manufacture processes.

A high level of accuracy in the determination of isotopes is often used in order to demonstrate the provenience materials constituent the relic. The analysis of lead isotope is a consolidate way to determine the cave provenience of raw materials for metal production.

Another important and interesting analysis is Radiocarbon dating (also referred to as carbon dating or carbon-14 dating), it is a method for determining the age of an object containing organic material by using the properties of radiocarbon, a radioactive isotope of carbon.

The use of these techniques often highlights peculiar request and provides accurate response to archaeologists; some techniques of the third level have been topics of lectures of the school.

4. Gela orichalcum ingots.

The study of Gela orichalcum ingots will be presented as a case study in order to show a practical application of what we call the three level multi-analytical investigation approach.

The ingots (Fig. 1) were found and recovered from the seabed near Gela, a major harbour of Sicily, during two different times, in an area with remains of a ship and earthenware dated around the end of the VI century BC. In the VI century BC, Gela was the most powerful town of blooming Sicily, and a major trading centre of the Mediterranean Sea.

Figure 1 Part of the ingots exposed at the Gela Museum

It is not a surprise that the entire gulf of Gela is an archaeologist's paradise; three full shipwrecks of the Greek period have been located, and one of them has been already recovered and restored.

The first ingots discovery (2014) consists in 40 pieces, while during the second discovery (2017) other 47 ingots were found. During the first attempt, five ingots were analysed by means of X-Ray Fluorescence technique in order to determine the elemental composition and to identify the type of alloy. Presence of copper and zinc were analysed to be main elements, indicating an alloy similar to the legendary orichalcum, a very precious alloy of ancient times.

Plato describes the ports and forts of Atlantis, the legendary ancient town, as covered by a rare metal called ὀρείχαλκος [2]. The Greek word ὀρείχαλκος (ὄρος, upstream and χαλκός, Copper) is attested in several literary sources like the pseudo-Homeric Hymn to Aphrodite, where the birth of Aphrodite is described.

Considering that the archaeological evidence of orichalcum objects is very unusual, in connection to the Atlantis myth, the discovery has received high attention from the mass media, which diffuse the news all around the world increasing the interest of archaeological community (Fig. 2).

Figure 2 Recording of the visual examination

Therefore, we started a systematic study on these finding with the aim to determine all the information about the source and the production of this rare alloy.

First level. The first step involved a scrupulous visual examination; the ingots morphology suggested a casting mono-valve mold production (Fig. 3).

Figure 3 Photographic recognition at the museum

The mold contact surface is poorly defined, indicating the use of a rough finish ot the mono-valve refractory material. It can be excluded that two ingots were prepared by using the same mold. The presence of ripples on the surface exposed to the air during the cooling process, consequence of a rapid solidification of the melted alloy, indicated that the temperature was near the melting temperature.

The first of all the XRF investigation was extended to all the first discovery ingots, and only later to the second set, with the aim of performing a comparison between them, once determined the elemental composition. Results evidenced that all the ingots are constitutes by an alloy whose major elements are copper and zinc, with considerable amount of lead. The lead concentrations ranging from 1.1% to 6.8%w/w, implies a voluntary addition of the metal, very certain at least for the higher concentrations.

The weight ratio between the two metals, Cu/Zn, varing between 2.7 and 5.7, well matched the composition of the notorious orichalcum. In particular the zinc content, lower than 26% w/w, is compatible with the brass production using the cementation process. In fact, it has been claimed that it is impossible to attain a Zn concentration > 32 w/w with the cementation process that was used until the industrial revolution; this limit, also known as the magical limit, helps to discriminate modern brass artefacts.

These results maintained the hypothesis that, the precious ingot cargo was transported in an ancient ship dated to the end of VI century BC. Moreover, the composition variability allows us to make some hypothesis about the production and the familiarity of the ingots. I.e. the manufacturer had not a preferential value of composition, or a reliable way to control it; alternatively, the ingots came from different furnaces, possibly using raw minerals from different geographical areas. [3]

Second level. Information about the origin of the raw materials and the production technique could be obtained by more sophisticated analyses able to determine trace elements. This is very important because it gives us an accurate multi-elemental fingerprint of the each sample [4,5] In order to perform this kind of analysis, micro-samples of a few milligram are needed from each ingot. For this purpose, it was important that the authorities recognized that the acquired knowledge is worth the sacrifice and therefore it allowed us to make a withdrawal. This particular step was filmed by a troupe of the National Geographic, confirming the mass media interest to the discovery.

The analysis of main and trace elements was performed by ICP-OES and ICP-MS techniques. The obtained elements were: Cu, Zn, Mn, Fe, Ni, Co, As, Ag, Cd, Sn, Sb, Te, Bi, Pb, Li, Al, V, Cr, Rb, Sr, Ba. As an example, results from few ingots are reported in Table 1.

Table 1: Elemental composition of some of the ingots

Sample	Cu	Zn	Pb	Fe	Ni	Ag	Sb	As	Co	Cd	Sn	Te	Bi	Mn	Li	Al	V	Cr	Rb	Sr	Ba
	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
S01	73.02	20.61	5.60	0.30	580.42	146.29	55.65	9.85	2.79	12.19	9.70	0.57	41.35	19.94	5.55	11.48	3.71	3.17	0.08	1.00	0.19
S02	86.58	15.63	4.29	0.53	534.01	199.17	132.34	36.40	8.44	19.99	4.80	1.00	72.84	20.83	2.17	4.46	1.55	1.31	0.07	0.15	0.18
S03	73.25	28.46	5.91	0.78	450.57	131.06	105.63	23.78	8.47	16.51	6.70	0.64	28.98	15.75	4.00	8.89	3.33	2.70	0.14	8.90	0.35
S04	80.21	20.41	6.17	0.39	557.63	171.22	69.96	11.05	4.83	11.87	9.34	0.82	60.73	23.16	6.16	13.76	6.08	4.91	0.14	0.29	0.39
S05	78.09	22.18	3.87	0.55	512.95	156.48	67.00	14.47	6.49	5.30	7.69	0.58	58.66	23.27	3.87	11.65	4.38	3.69	0.12	0.91	0.45
S06	80.80	21.71	6.51	0.19	578.63	158.81	60.30	8.32	1.88	9.63	8.54	0.96	61.35	15.66	2.12	4.36	2.29	1.90	0.11	0.45	0.75
S07	74.91	19.89	6.45	0.33	559.28	130.31	107.63	21.01	3.37	11.63	17.56	0.80	51.00	22.31	1.75	5.50	2.16	1.57	0.13	0.34	0.50
S08	81.69	24.00	6.13	0.31	548.09	159.53	75.44	9.66	3.19	7.61	6.98	0.83	58.51	23.71	1.99	13.28	3.55	2.36	0.11	1.45	0.26
S09	79.76	18.29	4.63	0.44	481.85	158.88	109.29	24.21	5.28	30.50	3.92	0.91	91.30	23.69	1.69	8.40	2.70	1.78	0.07	0.11	0.43
S10	71.89	28.20	5.92	0.76	434.52	104.66	111.57	23.53	8.29	16.24	6.65	0.61	27.55	19.48	1.23	6.77	2.00	1.41	0.12	0.21	0.30

The variability of main elements confirms a rough production of manufactures. The different trace elements among the ingots and their different concentration are probably due to different metal minerals accompanying raw materials or to their introduction by handling methodologies, therefore the adequate analysis of the trace elements could be useful in pinpointing the provenance of the materials or technological differences.

Considering the number of ingot and the number of determined elements, about 1600 values were obtained. In order to get a better insight on such amount of analytical data, they were examined by means of the multivariate analysis that is one of the chemometric method presented during his lecture by Doctor Sebastiano Trusso [6].

As a result of the statistical analysis the dendrogram obtained by the Ward's method is reported in Fig. 4. It displays the hierarchical relationship between the ingots identified by a similarity parameter. It is noteworthy to point out that some of the impurities (trace elements), not the main components, have the highest influence in the determination of such classification.

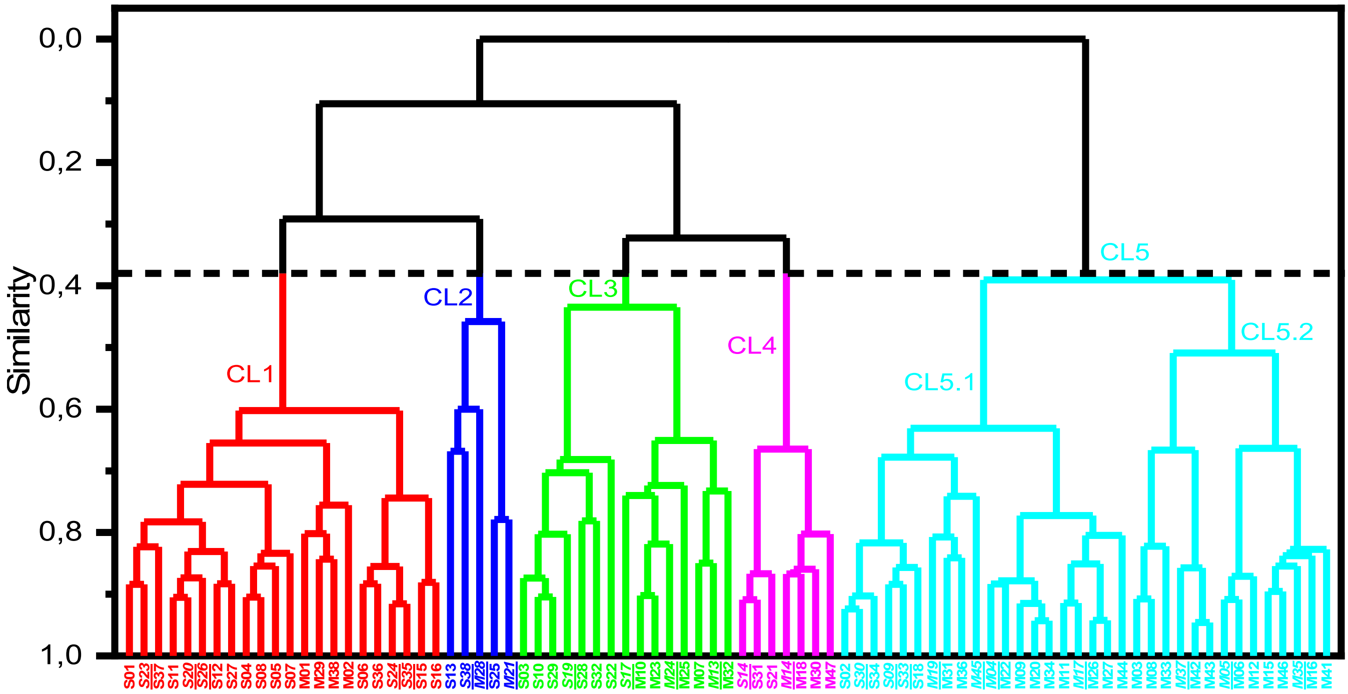

Figure 4: Ward's cluster of robust scaled data. Italic underlined abscissa labels indicate those samples for which the Pb isotopic ratios were determined.

The dendrogram divides the whole amount of ingots in five clusters. The mixing of ingots of the first (S) and the second (M) discovery in the same clusters confirms that the whole number of ingots belongs to the same naval load. The three main clusters, CL1, CL3, and CL5, represent the 87% of the total number of ingots. The existence of different clusters is an interesting result for the archaeological as well as historical interpretation of this important discovery [7].

As a matter of fact their presence could be ascribed to different manufactures in the production methods and/or to the different provenience of the minerals. In any case it strengthens the evidence of the different origins of the ingots because the morphological aspects can only be ascribed to the casting procedure adopted by the furnaces.

In order to try to give an answer to the specific questions raised about the manufacture and the provenience, it was decided to analyse the ingots with more peculiar techniques of the third level such as the ones that allow us to determine the core structure and the Lead isotopic ratio.

Since it is not possible to analyse all the ingots, the identification of the five clusters was very useful in order to select a limited but representative number of ingots.

Third Level. A series of 11 representative orichalcum ingots was selected on the basis of the classification and a systematic non-invasive micro-structural study was undertaken by means of Time of Flight Neutron Diffraction (ToF-ND) at the ISIS Spallation Neutron Source of the Appleton Rutherford laboratory, UK. This technique allows us to investigate of the ingot core revealing its homogeneity, the phase composition, the presence of strain and texture without the sampling associated with traditional invasive techniques like metallography.

The phases composition, the microstructure results and the crystals parameters obtained by the analysis of the neutron patterns, suggested that the ingots were made by roughly controlling the thermic parameters of the casting procedure according to an ancient and a not well handles technology.

It has been done the hypothesis that the driving force of the grouping ability can be the provenance of the raw materials used for the production of the ingots. Among the methods to disclose the provenance of some metals the lead isotopic ratio analysis is particularly developed and utilized [8,9]. It has been demonstrated that the lead isotopic ratio analysis is the most powerful method for provenance attribution of this metal. This because the lead isotopic ratios of the mines used in different historical periods are known and are collected in accessible databases. The same information is not available for others elements such Copper and Zinc.
On the base of these considerations, while aware that Lead is only one of the three elements constituting the alloy, and in particular that it is the one in lower concentration, we performed the analysis of the Lead isotopic ratio on 24 ingots chosen as representative of the 5 groups obtained by the statistical analysis. The obtained results assign the Lead probable origin to Greece (Crete), Italy (Sardinia) and Spain (Sierra Morena), with the presence of two well defined Italian groups.

Even if we can predict the geographical origins of the lead from a probabilistic point of view, the obtained results allowed us to exclude others suitable regions as origin.

All these finding are useful data for the archaeologists also in order to pursue a deeper study on the orichalcum trade in the Mediterranean area.

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The Battle of the Egadi Islands

Valeria Li Vigni Tusa

Soprintendenza del Mare, Regione Siciliana, Palemo
vpatrizia.livigni@gmail.com

A Sebastiano

Non c'è esempio così prestigioso di metodologia scientifica di ricerca come la scoperta sensazionale di una nuova pagina di storia riscritta da Sebastiano Tusa con l'esatta ricostruzione del luogo dove si combattè e delle strategie di combattimento utilizzate dai romani nella vittoria della I Guerra Punica nel corso della Battaglia delle Egadi.

Uomo capace e sensibile grande archeologo, Sebastiano aveva dato prova dalla sua genialità e competenza quando appena trentenne scrisse il primo saggio di Preistoria che per anni, e ancora oggi, è la base su cui studiano i giovani archeologi all'Università.

E' interessante ripercorrere sinteticamente la ricostruzione che Sebastiano fa dalle fonti fornendoci le strategie, gli equilibri le alleanze e lo stato di coinvolgimento di truppe mercenarie che sicuramente contribuì alla sconfitta della flotta cartaginese

I romani erano sicuramente più coinvolti in una guerra che aveva visto tutti privarsi dei propri averi per una causa fondamentale. Basti pensare che i rostri furono costruiti grazie alle donazioni dei Romani.

Tutto inizia nel 289 a.C con la morte di Agatocle, tiranno di Siracusa, quando un gruppo di mercenari italici, rimasti senza lavoro, il 288 a.C. conquistò Messina creando una vera e propria struttura statale con a capo due *meddices* (termine osco) e si autonominarono Mamertini.

Costoro, dalla base di Messina, saccheggiavano il territorio circostante e divennero ben presto un serio problema per Siracusa.

I Siracusani si affidarono a Gerone che dopo alterne vicende riuscì a sconfiggere i Mamertini a Milazzo ponendo Messina sotto assedio. I Mamertini, bisognosi di aiuto militare, inviarono due delegazioni, contemporaneamente, a Roma e a Cartagine.

Cartagine fu la prima a rispondere inviando le truppe che conquistarono Messina e le loro navi furono dislocate nel porto a meno di tre miglia dalla costa italiana.

Per i Romani l'eccessiva vicinanza dei Cartaginesi al territorio fu determinante per intraprendere un'azione di tutela e controllo totale della Sicilia.

Roma si alleò con i Mamertini e nel 264 a.C. inviò truppe in Sicilia. Era la prima volta che forze romane uscivano dalla penisola italiana.

Gerone II, essendo alleato a Cartagine, dovette fronteggiare le legioni di Valerio Messala. Fu sconfitto e ottenne la pace versando 100 talenti, e divenne un fedele alleato di Roma.

Rimasero in campo solo i due eserciti romano e cartaginese in lotta per il possesso della Sicilia, grande produttrice di grano e testa di ponte di entrambe le potenze per il controllo commerciale e militare del Mediterraneo centrale.

A questo punto i trattati furono infranti, e si interruppe una plurisecolare amicizia fra le due città dando inizio alla prima guerra punica.

265 a.C. - I Mamertini, attaccati da Gerone II di Siracusa, chiedono assistenza a Roma e a Cartagine. Roma risponde solo dopo Cartagine

264 a.C. – i Romani, comandati dal console Appio Claudio, sbarcano in Sicilia. I Cartaginesi assediano Messina

263 a.C. - Gerone II è sconfitto dal console Manio Valerio Messalla ed è costretto ad un'alleanza con Roma

262 a.C. - Le forze cartaginesi si rinchiudono ad Agrigento, la città è assediata dai Romani. Segesta si allea con Roma

261 a.C. - Conquista romana di Agrigento. Roma si dota di una flotta. Si costruiscono 100 quinqueremi e 20 triremi nei cantieri delle città greche. 30.000 rematori, in gran parte contadini italici, sono addestrati a remare su "navi virtuali".

260 a.C. - Battaglia delle Lipari disastrosa per i Romani. Subito dopo il console Gaio Duilio vince la battaglia di Milazzo con l'aiuto dei "corvi" (ponti levatoi che agganciandosi alla nave nemica costituivano una passerella per combattere corpo a corpo.

259 a.C. – Conquista di Alalia

258 a.C. - Battaglia navale e vittoria romana di Sulci

257 a.C. - Battaglia navale e vittoria romana di Tindaride. è apprestata una flotta di 230 quinqueremi (97.000 uomini)

256 a.C. – I Romani tentano di invadere l'Africa. Cartagine oppone una flotta di 250 navi (150.000 uomini). Scontro a Capo Ecnomo con vittoria romana guidata dai consoli Lucio Manlio Vulsone e Marco Attilio Regolo. Le truppe romane sbarcano in Africa, a Clupea, e avanzano verso Cartagine. La battaglia di Adys e l'espugnazione di Tunisi da parte dei 15.000 uomini di Attilio Regolo segna il primo successo romano in Africa e Cartagine chiede la pace senza esito

255 a.C. - I Cartaginesi con il generale spartano Santippo organizzano la difesa. Battaglia di Tunisi. Il comandante Attilio Regolo è catturato, le truppe romane sopravvissute (solo 2.000 uomini) raggiungono Clupea e vengono evacuate dalla flotta di 350 navi distrutta durante il viaggio di ritorno verso la Sicilia

254 a.C. - Nuova flotta di 220 navi e apertura di una leva per un nuovo esercito. I Romani vincono a Palermo (27.000 prigionieri di cui 13.000 venduti come schiavi). Contrattacco cartaginese respinto dalle forze di Cecilio Metello. Cinque città greche in Sicilia passano da Cartagine a Roma

253 a.C. - Dopo un anno di stallo lungo le coste della Sirte la flotta romana ritorna in patria e perde 150 navi nella tempesta.

251 a.C. - Vittoria romana a Palermo contro i Cartaginesi condotti da Asdrubale. Cartagine rinforza la guarnigione in Sicilia e riconquista Agrigento

250 a.C. - I Romani costruiscono la strada fra Agrigento e Palermo iniziano l'assedio di Lilibeo con forze di terra e 200 navi

249 a.C. – Roma forza il porto di Drepanum , perde quasi tutta la flotta al comando del console Claudio Pulcro. Il console Giunio Pullo perde in una tempesta la flotta ma riesce a conquistare Erice. Aulo Atilio Calatino nominato dittatore in Sicilia.

248 a.C. - 243 a.C. - Scorrerie di entrambi i contendenti in territorio nemico. A causa delle condizioni economiche disastrose, Cartagine non riesce ad ottenere da Tolomeo Filadelfo, re dell'Egitto, un prestito di 2.000 talenti. Ma anche Roma non naviga nell'oro e per contenere le spese limita le unità necessarie a 60 navi. Amilcare Barca compie vittoriose incursioni in Sicilia

242 Con un estremo sforzo Roma costruisce una nuova flotta ricorrendo anche a finanziamenti privati. Vengono allestite 219 navi. I Romani riescono a occupare Trapani e il Lilibeo viene bloccato

241 a.C. - Il 10 marzo avviene la battaglia delle Egadi con la decisiva vittoria di Roma. I Romani impiegano (Polibio) 200 navi da guerra (quinqueremi a vela). Le 200 per Polibio, 250 per Cassiodione, navi cartaginesi da guerra cariche di rifornimenti destinati per la guarnigione cartaginese di Amilcare assediata sul Monte San Giuliano non riescono a manovrare e fuggono. Cartagine perde 120 navi e 10.000 uomini sono catturati. Il comandante Annone finisce sotto processo per la sconfitta e è condannato a morte. Cartagine è forzata ad accettare le condizioni di pace.

La Battaglia delle Egadi è stata la grande scoperta di Sebastiano Tusa, una grande ricerca sviluppata su vari livelli dallo studio delle fonti alla ricerca sul campo alle operazioni di intelligence. Va ricordato che il primo rostro fu ritrovato da Sebastiano, con l’aiuto del nucleo TPC presso lo studio di un dentista che lo aveva ricevuto come compenso per una prestazione professionale. Tale fortunato recupero andava a intrecciarsi con i racconti che negli anni aveva ascoltato Sebastiano dai pescatori e dai pionieri della subacquea che in quel luogo avevano trovato innumerevoli ancore in piombo. Fu proprio Cecè Paladino, a confessargli che in passato, molti subacquei, avevano recuperato dalla zona di Cala Minnola numerose ancore in piombo che venivano recuperate per venderle e fonderle per farne pesi di rete.

Unica interpretazione plausibile di questa imponente presenza di ancore era quella di trovarsi nel sito dell’evento bellico e strategico.

“I ceppi d’ancora dovevano essere alcune centinaia a giudicare dai racconti dei vecchi pescatori e vennero tutti ,o quasi, fusi per farne piombo per le reti. Erano le ancore della flotta romana di Lutazio Catulo che, al fine di infliggere ai Cartaginesi un colpo ferale sul fianco della loro flotta sfruttò l’elemento sorpresa, dando l’ordine di tagliare le cime e non perdere tempo nel recuperare le ancora issandole a bordo”.

La battaglia navale delle Egadi che si concluse il 10 marzo del 241 con la vittoria della flotta romana è sicuramente la più nota battaglia combattuta nell’antichità, quella che più di ogni altra ha avuto l’onore della cronaca per le interessanti scoperte archeologiche subacquee di Sebastiano Tusa che ha saputo fornire, con grande tenacia, capacità e metodo scientifico, risultati che hanno radicalmente mutato una storiografia stratificata da tempo su erronee attribuzioni e indebite asserzioni.

Questo particolare assembramento di ancore, in un luogo che non era una zona portuale né di scarico merci, in quanto sempre attraversata da correnti violente e da venti burrascosi che determinavano immediate condizioni di mare mosso e pericoloso, fece riflettere Sebastiano sulla possibilità di un ancoraggio di fortuna dovuto a un evento fortuito sopraggiunto improvvisamente, intuì che la flotta romana, appostata nella cala recise le cime delle ancore per sferrare l'assalto alla flotta cartaginese che si dirigeva da Marettimo verso il porto di Trapani per portare i rifornimenti ad Amilcare. Il Generale Lutazio Catulo sferrò l'attacco decisivo a sorpresa sconfiggendo le truppe nemiche che non arrivarono mai alla meta, Monte San Giuliano e dovettero tornare in patria. Il generale Annone fu ucciso ma portò in salvo alcune navi mentre Lutazio Catulo tornò vittorioso a Roma e fece erigere il Tempio a Giuturna nel Campo Marzio a Largo di Torre Argentina.

Da queste considerazioni è partita la ricerca subacquea tradizionale e in un secondo momento la ricerca subacquea con l'utilizzo delle nuove tecnologie per ricostruire le strategie di una guerra combattuta dal 264 al 241 a.C., conclusasi il 10 marzo del 241 a.C. nel mare delle Egadi dopo ventitre anni di scontri mortali tra Roma e Cartagine.

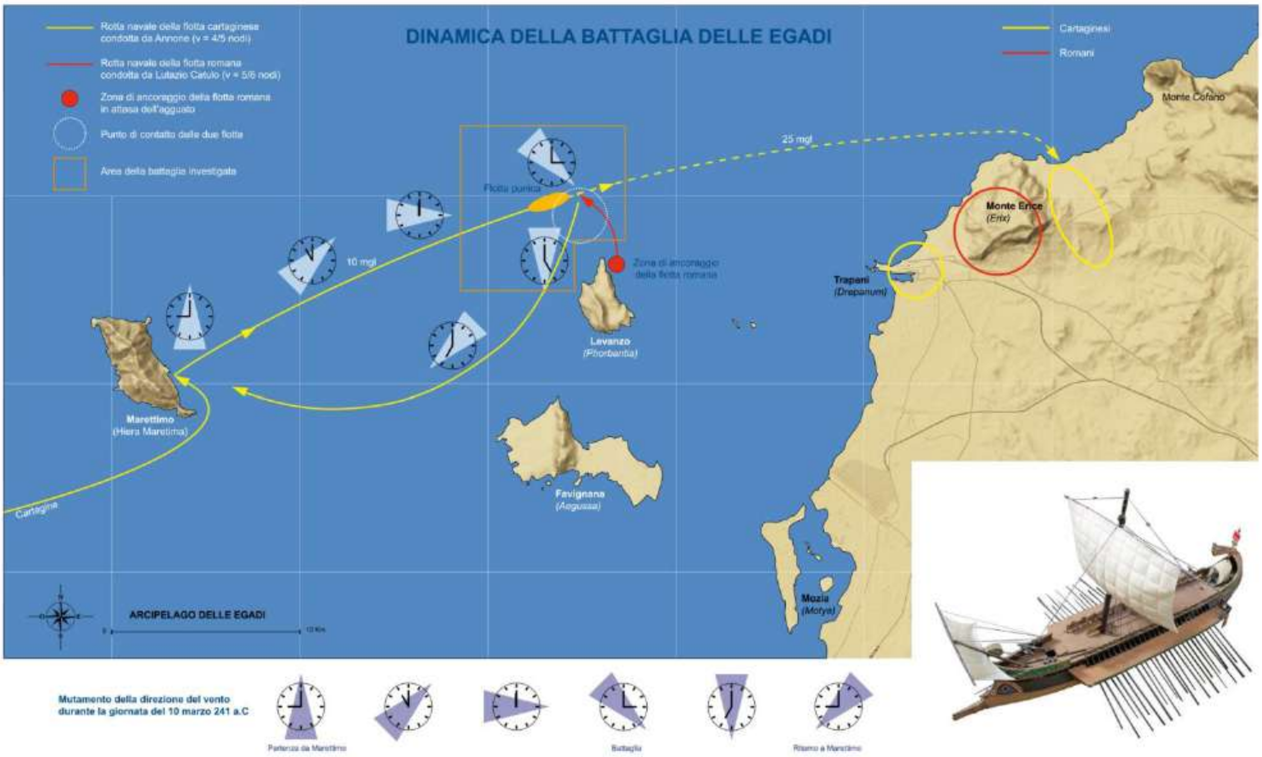

Figura 1 Dinamica della Battaglia delle Egadi

Secondo la dinamica della battaglia ricostruita da Sebastiano (FIG.1), dovette influire in maniera preponderante, oltre l'effetto sorpresa con cui le navi onerarie dei cartaginesi furono colte, il repentino cambiamento dei venti a favore della flotta romana ancorata a ridosso di Capo Grosso che, con le condizioni favorevoli si lanciarono contro la flotta cartaginese sconfiggendola.

Le nuove tecnologie, il multibeam a trasmissione acustica ad alta risoluzione, il Side Scan Sonar a trasmissione acustica, il sonar ad alta risoluzione, il magnetometro sincronizzato, gradiometro marino orizzontale a trasmissioni magnetiche, il multibeam interferometrico e il Laser Scann Sonaro, furono gli strumenti utilizzati per mappare la vasta area marina delle isole Egadi e fornirono i risultati eccellenti a noi noti.

La ricerca sistematica e tecnologicamente avanzata condotta dalla Soprintendenza del Mare della Regione Siciliana in collaborazione con la RPM Nautical Foundation, nel mare delle Egadi ha consentito, in Sicilia il recupero di ben 23 Rostri, nel resto del mondo ne esisto soltanto 3 (Athlit-1, Bremenhafen-1, Pireo-1).

Dei 23 rostri ritrovati ben 22 sono rostri a tridente romani, con le iscrizioni che testimoniano la certificazione da parte dei Seviri o questori artefici del finanziamento (FIG 2)

Figura 2 Rostro romano 1

e uno punico che reca, sulla guaina, un'iscrizione in punico inneggiante a Baal affinché faccia penetrare il rostro nella nave nemica (FIG.3)

Figura 3 Rostro Punico

Il rostro si fissava, coprendola, sull'intersezione di due elementi lignei convergenti che erano il dritto di prua e la chiglia ed erano assicurati alla parte lignea dello scafo mediante numerosi chiodi.

La parte anteriore del rostro era costituita da un possente fendente verticale rafforzato da ben tre fendenti laminari orizzontali

Dei 20 elmi del tipo Montefortino ritrovati, 4 sono mostrati in Fig 4.

Figura 4 Elmi del tipo Montefortino

Tale ritrovamento ha sancito la prova dell'esattezza del luogo dello scontro indicato nell'area a Nord di Capo Grosso di Levanzo.

Fondamentale è la valenza che ha assunto l'intera area che ha fornito elementi fondamentali per la ricerca in un contesto naturalistico incontaminato quale è quello del mare delle Egadi e dove è stato realizzato il Parco subacqueo delle Egadi che non si limita alle testimonianze relative alla storica battaglia bensì ai numerosi relitti. Tra essi ricordiamo il relitto di Cala Minnola con anfore del tipo greco-italico datato al I sec a.C. che trasportava vino dal Lazio appartenente alla famiglia dei Papia, come si evince dai bolli sulle anfore, i relitti con piatti ed anfore di Punta Altarella e Secca Scaletta a Levanzo. A Favignana vi sono i relitti di San Nicola, un cargo romano imperiale fra Punta Marsala e Punta Cala Rossa Interessante è il relitto di una nave che trasportava tegole, brocche, boccali, piatti ed anfore di piccole dimensioni, naufragata presso la Secca del Toro al largo di Punta Galera di Favignana. A Marettimo ricordiamo il relitto di Cala Mugnone e presso Cala Spalmatore si trovano numerosi cannoni pertinenti una nave pirata del XVII secolo, colata a picco laddove si era nascosta prima di sferrare un attacco sulla costa siciliana. Nello stagnone presso l'Isola Longa, Punta Scario, vi sono relitti con carichi di mattoni e tegole e anfore.

Tali relitti costituiscono altrettante tappe del suddetto Parco organizzato con gli itinerari sommersi, in linea con la normativa UNESCO legata alla tutela e valorizzazione "in situ" dei beni sommersi, nel nostro Parco arricchito dalla possibilità della visita a distanza attraverso il sistema di telerilevamento.

Il grande Parco Archeologico Sottomarino delle Isole Egadi rappresenta un variegato microcosmo, un'area idonea alle indagini sistematiche con approcci interdisciplinari. Questo mare ha avuto una grande importanza strategica perché ha rappresentato il passaggio obbligato sulle rotte che collegavano l'Europa all'Africa.

Il patrimonio naturalistico incontaminato di questo arcipelago ha conservato il patrimonio archeologico in un contesto immutato consentendo la migliore interpretazione delle dinamiche storiche.

Nello spazio dell'ex Stabilimento Florio, la musealizzazione degli importanti ritrovamenti inerenti la Battaglia e la videoinstallazione consentono al visitatore di immergesi nel racconto della battaglia in una "cattedrale del lavoro" che rivive attraverso le innumerevoli storie dei tonnaroti che accompagnano virtualmente il visitatore alla scoperta della pesca del tonno, della lavorazione, salagione o inscatolamento, un museo che trasmette saperi attraverso lo stupore e il divertimento.

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Fonti antiche

Polybe, *Histoires* Zonara, *Epitomé historíon*

Le aree marine protette: gestione proattiva per la tutela dell’ambiente marino e lo sviluppo sostenibile

Salvatore Livreri Console, Alessandro Egidio Agate

A.M.P. “Isole Egadi”

Ubicato nell’estremità occidentale della Sicilia, l’arcipelago delle Egadi rappresenta da sempre, un luogo estremamente importante per le sue particolari caratteristiche ambientali e storiche. È qui che nel 1991, il Ministero per l’Ambiente e la Tutela del Territorio e del Mare, ha istituito una delle Aree Marine Protette più grandi d’Europa con i suoi 54.000 ettari di estensione, affidandone la gestione al Comune di Favignana.

Ad oggi, le Egadi possono essere considerate due volte area protetta, infatti, l’A.M.P. coincide anche con la ZSC ITA010024 “Fondali dell’arcipelago delle isole Egadi”, uno dei più grandi siti Marini della Rete Natura 2000, avviata nel 1992 dall’Unione Europea, a dimostrazione dell’importanza che i fondali dell’arcipelago ricoprono per lo sviluppo della vita di flora e fauna.

La particolarità che rende uniche le acque ed i fondali dell’Area Marina Protetta delle Isole Egadi è la presenza della più estesa prateria di posidonia oceanica del Mediterraneo (12.536 ettari).

Questa pianta marina, effettuando la fotosintesi clorofilliana, libera ossigeno nell'ambiente creando i presupposti per lo sviluppo degli organismi marini, inoltre con le sue lunghe foglie, che in alcuni casi raggiungono anche i 2 metri di lunghezza, offre rifugio per le innumerevoli specie faunistiche che abitano i nostri mari. Nelle acque della A.M.P., infatti, sono presenti circa il 22-25% delle specie protette o vulnerabili del Mediterraneo. La posidonia

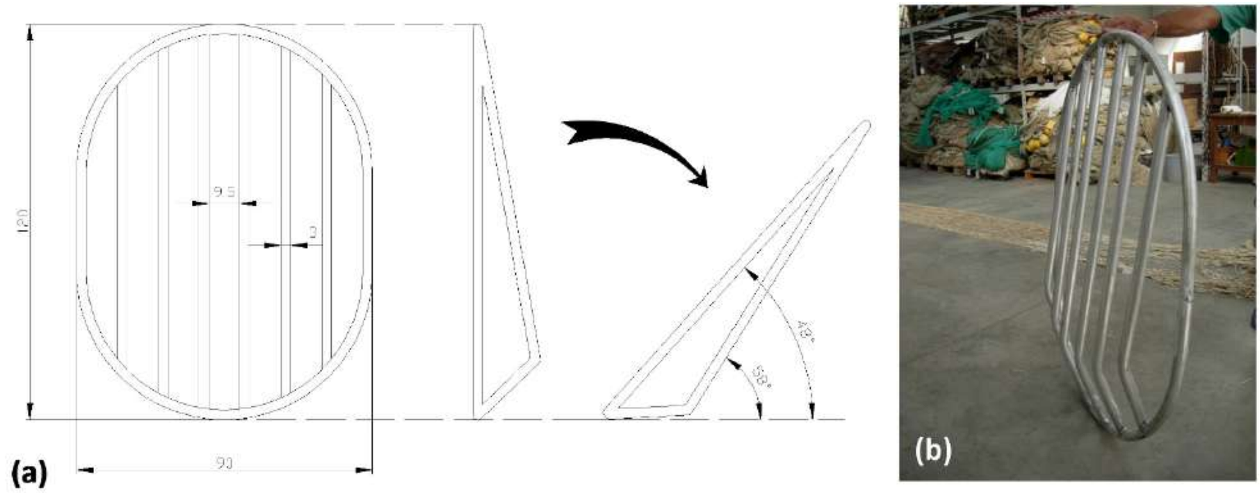
oceanica non rappresenta però l'unico tratto distintivo dell'Area Marina, si annoverano, infatti, numerose specie protette che qui trascorrono parte della loro vita, come la tartaruga *Caretta caretta*, che proprio a Favignana viene ulteriormente tutelata grazie al Centro di Recupero Tartarughe Marine instituito e gestito dall'Area Marina Protetta, dove oltre alla salvaguardia di questa specie in via d'estinzione, si svolgono attività di sensibilizzazione ed educazione ambientale.

La tutela ambientale ed il contingentamento dei flussi nautici hanno creato le condizioni ideali per il ritorno della Foca Monaca nelle acque dell'A.M.P., prove inconfutabili della sua presenza sono le immagini scattate tramite speciali macchine fotografiche, "foto trappole", sensibili al movimento, posizionate all'interno di alcune grotte rappresentanti l'habitat ideale per la sosta di questa specie sfuggente che non ama molto la presenza dell'uomo.

Infine, ma non per ordine d'importanza, si possono ricordare tante altre specie quali cetacei, squali, aquile di mare e alcune tipologie di uccelli come l'uccello delle tempeste che si lasciano ammirare durante le immersioni subacquee o navigando nelle acque dell'arcipelago.

La protezione del mare e delle sue specie non può prescindere dalla regolamentazione delle attività di pesca professionale. Molte sono le attività che l'Area Marina svolge in sinergia con la marineria del territorio, infatti, i pescatori delle tre isole sono stati coinvolti, nel corso degli anni, in vari progetti con finalità di tutela ambientale e monitoraggio delle specie a rischio come “Vedette del mare”, “Progetto TartaLife”, “Pescatori e delfini” volti a sensibilizzare le marinerie su argomenti delicati quali la protezione di tartarughe, delfini e altri cetacei, o come “Marine Litter” diretto, invece, alla tutela ambientale sul fronte inquinamento da plastiche o altro materiale galleggiante.

In concomitanza con le attività descritte, l’equipe di biologi dell’Area Marina Protetta lavora sulla progettazione di sistemi sperimentali di pesca sostenibile con lo scopo di ridurre



la pressione sulle specie a rischio, un esempio è il TED, una griglia fissata all’imboccatura delle reti a strascico che permette la cattura delle specie target ma preserva la vita delle tartarughe che riescono ad allontanarsi senza essere inghiottite dalla sacca della rete stessa.

Lo strascico non rappresenta solamente un pericolo per le tartarughe, ma è anche uno dei principali fattori di depauperamento del fondale e della distruzione della prateria di posidonia oceanica. Per impedire la progressione di tale fenomeno, l’A.M.P. ha posizionato, tra il 2013 ed il 2017, in alcune aree specifiche dei “dissuasori

antistrascico”, grandi blocchi di cemento eco-friendly muniti di uncini metallici destinati a recidere le reti, fungendo così da deterrente per la pesca illegale. I risultati raggiunti sono eccellenti: i blocchi sono diventati parte integrante del fondale venendo colonizzati da una moltitudine di organismi marini e la prateria di posidonia è tornata ad espandersi considerevolmente. Altro fattore di stress per la posidonia oceanica è il turismo nautico, che soprattutto durante i mesi estivi, riversa nei mari antistanti le Egadi migliaia di imbarcazioni e natanti che con le loro ancore producono notevoli danni. Per tale ragione le cale più rappresentative dell'arcipelago sono state munite di campi ormeggio gestiti dal personale dell'A.M.P. In totale si contano all'incirca 180 gavitelli, che stanno contribuendo al ripascimento della prateria di posidonia anche dove sembrava ormai in forte regressione.

Infine, un discorso a sé merita il tonno rosso (*Blue Fin Tuna*) la cui presenza ha scandito per secoli la vita delle isole, esso, per le comunità egadine, ha rappresentato la principale fonte di sostentamento. La pesca del tonno ha origini antichissime persino le raffigurazioni rupestri presenti all'interno della Grotta del Genovese (Levanzo) risalenti al 2400-2200 a.C., fase finale dell'epoca neolitica, mostrano una figura facilmente identificabile con la sagoma di un tonno. Nel corso dei secoli la comunità delle isole Egadi è riuscita, grazie a famiglie dalle spiccate attitudini imprenditoriali, i Florio prima e i Parodi poi, ad utilizzare al meglio questa risorsa. La prova evidente è il grande Stabilimento Florio delle Tonnare di Favignana e Formica, industria conserviera che ha vissuto i suoi fasti tra il XVIII ed il XIX secolo, dove nei periodi di massima espansione lavoravano circa

800 persone le cui mansioni spaziavano dalla pesca "mattanza" alla manutenzione dei vascelli fino all'inscatolamento del tonno.

Luogo di grande fascino ed esempio di archeologia industriale di alto profilo, oggi è la sede del Museo della tonnara, gestito dall'Area Marina Protetta, meta di migliaia di visitatori nonché luogo di occupazione per molti giovani che svolgono attività di dimostratori della struttura e dei suoi contenuti. Il Museo, oltre alla collezione relativa alla filiera della lavorazione del tonno, vanta al suo interno un antiquarium dove è possibile ammirare reperti archeologici rinvenuti nei fondali delle isole Egadi (ancore ed anfore). L'ex falegnameria dello Stabilimento ospita, invece, i rostri appartenuti alle navi romane e cartaginesi che si affrontarono nel 241 a.C. a Nord di Capo Grosso (Levanzo) nello scontro decisivo per la conclusione della Prima Guerra Punica, la famosissima "Battaglia delle Egadi", che sancì la vittoria di Roma su Cartagine, l'annessione della Sicilia all'impero ed il conseguente cambio di egemonia sul Mediterraneo.

Insieme allo Stabilimento Florio, l'A.M.P. gestisce, da quest'anno, anche il Castello di Punta Troia sito presso l'Isola di Marettimo, la più occidentale delle isole dell'arcipelago. Costruito, intorno al IX sec., con funzione di torre di avvistamento saracena, è giunto fino ai nostri giorni passando sotto varie dominazioni fino alla definitiva chiusura voluta dal Re delle Due Sicilie Federico II di Borbone nell'anno 1844. Nel corso degli ultimi anni, il Comune di Favignana ne ha predisposto la riapertura dopo alcuni interventi di ristrutturazione. Al suo interno sono visitabili le antiche prigioni e l'Osservatorio Foca Monaca dell'Area Marina Protetta, si è così creato un connubio perfetto tra storia e ricerca scientifica legata a questa straordinaria specie protetta.

L'area Marina Protetta quindi si pone nel territorio come una Agenzia Culturale, ancor prima che un Ente di Conservazione; le interazioni culturali sempre più frequenti tra i fruitori dei percorsi sovra e subacquei naturalistici con quelli etno-antropologici, rendono ricca di contaminazione e di spunti la gestione degli ambienti costieri, sempre più improntata alla integrazione delle politiche attive nei confronti degli stakeholder pubblici e privati, e quindi per una *governance* della spazio marittimo che sia sempre più aderente allo spirito della Convenzione di Barcellona.

The Role of Cultural Heritage for Sustainable Development

Stephan Doempke

Definitions

Cultural Heritage is any and all tangible and intangible product of human aesthetic creativity which an individual or a group of people has inherited from past generations and considers it as such.

The official UN definition of Sustainable Development, which is used here, is: "Sustainable Development is development which meets the needs of the present without compromising the ability of future generations to meet their needs." (Brundtland Commission 1987)

The Sustainable Development Goals

End Poverty in all its forms everywhere

End Hunger, Achieve food security and improved nutrition, and Promote Sustainable Agriculture

Ensure healthy lives and Promote well-being for all at all ages

Ensure inclusive and equitable quality education and Promote Iifelong learning opportunities for all

Achieve gender equality and empower all women and girls

Ensure availability and sustainable management of water and sanitation for all

Ensure Access to affordable, reliable, sustainable and modern energy for all

Promote sustained, inclusive and sustainable economic growth, full and productive employment and decent work for all

Build resilient infrastructure, Promote sustainable industrialization and foster innovation

Reduce inequality within and among countries

Make cities inclusive, safe, resilient and sustainable

Ensure sustainable consumption and production patterns

Take urgent action to combat climate change and its impacts

Conserve and sustainably use the oceans, seas and marine resources for sustainable development

Protect, restore and promote sustainable use of terrestrial ecosystems, Sustainably manage forests, Combat desertification, Halt and reverse land degradation, and Halt biodiversity loss

Promote peaceful and inclusive societies for sustainable development, Provide access to justice for all, and Build effective, accountable and inclusive institutions at all levels

Strengthen the means of implementation and Revitalize the global partnership for sustainable development (United Nations 2015)

Every member country of the UN is obliged to implement these goals until 2030 and to report about the results.

On the face of it, none of these Goals seem to have much to do with cultural heritage. Cultural Heritage is mentioned only in one of the 167 sub-goals, or targets, which break down each of the 17 Goals to more detail. Target 11.4 (under Goal 11) reads: Strengthen Efforts to Protect and Safeguard the World's Cultural and Natural Heritage.

How Do Cultural and Heritage Contribute to Sustainable Development?

The international community of heritage experts claims that cultural heritage contributes to sustainable development, but I have heard little about how exactly this happens beyond the fact that cultural heritage sites contribute to the global economy. That, however, is a consideration which addresses only one of the two aspects of cultural heritage, its economic value. Never have I heard anything about how the intrinsic value of culture and heritage contributes to sustainable development. So what could that contribution be? Isn't cultural heritage a nice but rather insignificant part of our lives?

In this very short presentation I would Iike to offer here two hypotheses:

1. Heritage and tradition are a fundamental part of every human society. Abolishing them will lead to their disintegration.

In order to make my case, I will start with an observation concerning a fundamental difference between the anorganic and the organic world. The German-American psychoanalyst Kurt R. Eissler mentions the principle of invariance which is valid throughout the anorganic world: "The physicist ... can be sure that the behavior of one electron ... is the same for all electrons. ... It is irrelevant which electron among billions of others finds his attention since what is valid for one electron is valid for all others as well." (Kurt R. Eissler 1980, p. 66, translation mine). Eissler then continues to say that the rigid identity of physical structures in the anorganic world is abandoned in the organic world where a second principle is added, that of variation. It is this novel principle on the organic level which allows evolution. Citing Handler (1970, p. 165, translation mine): "The unique attribute of living matter ... is its ability of self-duplication, paired with mutation."

How deeply the duality of invariance and variation, or continuity and change, runs through everything in our world is becoming immediately clear when we look at some essentials in our life:

- On the structural level: All biological species follow the same fundamental genetic design. All human beings have two legs, two arms and one head, and they grow to a clear minimum and maximum size. And yet, within this invariance, the variation of physiognomy is endless: No human being is exactly the same as another one.

- On the functional level: The heartbeat is completely invariant throughout our lives; if this were not the case for even a short time, we would die in a very short time. For each heartbeat, however, we also observe typical variations of speed, length of the curve etc.

- Most interesting, however, is this phenomenon on the psychological level, in the human personality, and in particular in what we call the Ego in psychoanalysis. At this point we are entering the sphere of cultural evolution which distinguishes the human being from all other organic life. The Ego is a psychic institution which is not innate; it develops over several years and its full development marks the end of childhood before reaching puberty. We are all aware of our Ego since this is what we perceive of ourselves in our normal state of consciousness. The Ego is a remarkably stable institution, and our element of continuity, although it has never been located in our body. We keep it for the rest of our lives, and it ensures that in our self-perception we always remain the same person in spite of the fact that we also change throughout our lives, both physically and psychologically, in our aging and maturing process.

Can we say that we are the same person that we were 20 years ago? Yes and no. How is this possible? It is this mysterious institution inside which says "yes, that's me" or "no, that's not me" to everything we experience, and integrates all those experiences into our personality: This is how identity is created. That answer "yes" or "no" to something also changes over time - we may like rock music or impressionists for a time but later prefer opera and renaissance. But we always feel that we continue to be the same person through all our changes.

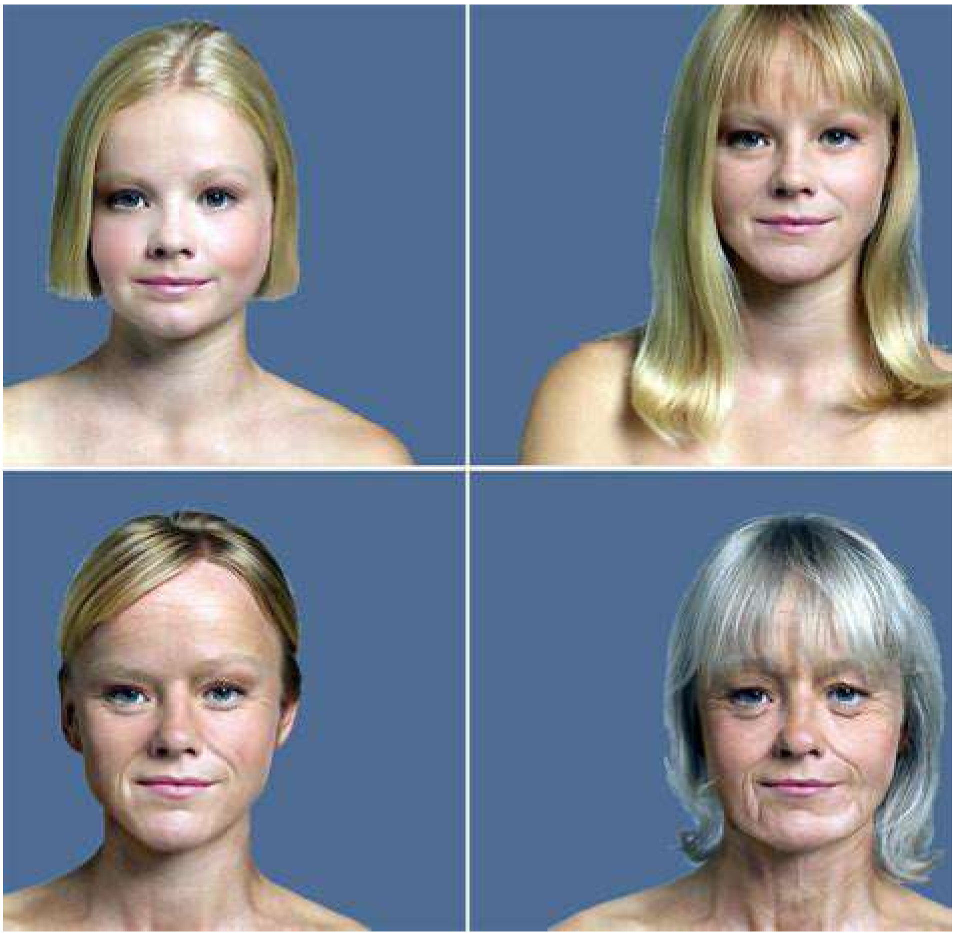


Fig. 2: Although humans undergo fundamental changes both physically and psychologically, there is something inside us that makes sure that we feel that we have remained the same person. Photo: Getty Images

We can take the observation of continuity and change even further, to human societies. All groups of people, from the earliest dawn of the human species until today, have had a set of rules, traditions and customary practices which were observed by all of its individuals and which ensured that they would survive as individuals and live together in peace as a community. At the same time, their ways of life was also subject to permanent change elicited by changing natural environments, progress in technology, exchange with others, new insights and the ingenuity of their members. As a result, societies which live exclusively in the continuity of their traditions and are unable to adapt and embrace change will become stiff and ritualistic, and will eventually break apart. On the other hand, societies which change all the time and don't have common principles, standards and traditions that guide them will lose their internal structure and end up in chaos.

In this context it is of some concern when we observe that in our Western industrialized societies almost exclusive priority is given to the new and the innovative while heritage and tradition seem to have a negative connotation (with the exception for tourism). lnnovation is becoming a value in itself, an obsession, and tradition is considered something bad in itself, worthless for today's world. We are witnessing the paradox situation that the biggest innovation today could be not to be innovative. For a healthy - sustainable - society we need a balance of continuity / tradition / heritage on the one hand and change / evolution / innovation on the other hand.

And at this point we can see very clearly that cultural heritage is not only important but actually essential for the sustainable development of humanity. Being one of the two pillars of human societies, it is dangerous to obliterate it since without it they will probably disintegrate.

2. Sustainable development - a development in lasting harmony among people and between people and other living beings - requires people cultivated by aesthetic education through cultural heritage.

The German poet, playwright and philosopher Friedrich von Schiller (1759 - 1805) was, together with his friend Johann Wolfgang von Goethe, one of the most prominent figures of the Weimar Classic and maybe the most important promoter and advocate of classical Greco-Roman culture and arts. He is famous for the Ode to Joy, the words to the last movement in Beethoven's Ninth Symphony.

Schiller was a strong supporter of the French Revolution and its ideals of freedom and human rights, but then was disgusted when he saw how the same people who fought for these ideals then returned their country to barbary and bondage. In a series of letters to his donor (Schiller 1793-1794), he expressed disgust of both the "raw, lawless drives" among the lower classes and the even "more revolting sight of atony, weakness of mind, and decline of character" in the civilized classes. The age of enlightenment, which seemd to have led to the victory of reason, has remained a theory which failed to refine the character of humanity.

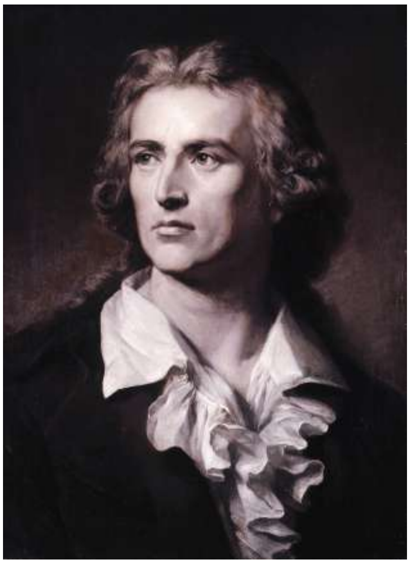


Fig. 3: Friedrich Schiller. Unnown painter, c. 1790. Photo: prabook.com

Schiller concluded that humankind was neither worthy nor ready for a state based on freedom and reason since "only the character of the citizens creates and maintains the state, and allows for political and civil freedom": First one would have to create citizens for a constitution before one can give the citizens a constitution. He immediately realized that this statement included a circular argument: The character of citizens depends on the constitution as much as the constitution depends on the character of the citizens. In order to escape this vicious circle, one would have to find ways and means to improve the people's character without requring the involvement of the state.

Schiller found the most effective instrument for the refinement of character to be aesthetic education: art, taste and beauty should lift people to a refined sensitivity, and they are independent from politics and the state. However, he warned that the arts must avoid declining to a mimicry of the Zeitgeist which, on the opposite, they should elevate to their heights. For that, the arts need ideals in the highest beauty as embodied in the immortal works of the Greek and related geniuses.

In a stringent and compelling argument, written in the most elegant style, Schiller has told us once and forever that the eternal beauty of cultural heritage lies at the basis of lifting humankind to a condition which will make it ready to appreciate the values of freedom and reason, and create constitutions, states and ways of life built on these values.

Dealing with culture and the arts makes people more sensitive and peaceful, educates people who will not follow their destructive instincts, not kill other people or other living beings, and rather create a "Monarchy of Reason" which leads them to a state of self-chosen freedom. Even only going into a museum and exposing yourself to the eternal beauty of sculptures and other works of art would contribute to this.

Realizing how important culture and heritage are for sustainable societies, what should follow from this for our work on cultural heritage?

1. Obviously, we have to defend, safeguard and promote the cultural heritage itself; not as an economic asset but for its intrinsic value for the higher development of mankind.

2. Every child should grow up with its cultural heritage. Cultural heritage and aesthetics should have a strong position in primary and secondary education, as well as in non-formal education.

3. Therefore, we should make our cultural heritage accessible to everyone, and a part of life of our societies and of every individual person. Politicians, scientists and businesses should engage in philanthropy to encourage the population to engage in culture and heritage.

4. As societies we should offer many more opportunities for the broad population to interact with cultural heritage, including the creation of studies and jobs in culture and heritage-related fields, both professional and vocational.

Fig. 4: People should be exposed to the works of immortal beauty from an early age.

Photo: iStockphoto.commonkeybusinessimages or Sarakatsani children on their national gathering in 2014 near Tsepelovo, Greece. Photo: Stephan Doempke

I would like to remind here of the original meaning of the word culture, from Latin colere: to cultivate, to take care of, and to honour. Each of the three aspects of the word touches important parts of how cultural heritage can become a living part of our societies: First, we have to cultivate, to refine and improve everything which becomes the object of our activity, including ourselves. Secondly, we have to maintain what we have created. There is no culture without maintenance, or taking care of things. Take the olive tree: the wild olive tree doesn't need care but the cultivated one needs it. The need for care is the fundamental difference between the wild and the cultivated. And thirdly we have to learn and appreciate again the value of both the objects of our activities and the way we deal with them.

All this means that we have to plant the appreciation for culture and heritage in wide sectors of the common people. Someone who hasn't been brought up with arts or theatre or archeology will not appreciate it when being grown up, and will not easily being convinced later to pay taxes for it. But someone for whom this has been part of her/his life - both as an individual and a part of a community - will easily understand when you explain why our heritage needs to be protected.

Postscript: Thoughts on identity

We are Europeans. This is a reality, we cannot change it, and we cannot escape it. Everything we do must be seen in this perspective. No matter what the bureaucrats in Brussels do, Europe is much more than that, and all the heritage of Sicily is always a European heritage, too, and cannot be separated from Europe. The European Union has been a huge success story - even for those who don't realize or deny this. And we should consider how our heritage, in addition to Iocal, regional and national heritage, can be seen as our common European heritage and contribute to an emerging European identity.

The idea and the project of Europe will ultimately be successful only if we - all Europeans together - will be able to create a European identity. I believe that Sicily, Iooking at its history and heritage, has a huge potential to contribute to this, and I am sure that this would be very much also Sebastiano Tusa's opinion. The origins of Europe are not in Germany, England or France. They are in the Mediterranean, today ignorantly labelled as "crisis countries", and we should do much more to expose, promote and celebrate the ancient origins of Europe from the cult of Pan and Demeter in Greece to iso-polyphonic singing in Albania, to the Launeddas of Sardegna and the Talayotic sites in Minorca.

We understand that some political forces are trying to use the concept of identity to divide us, implying that there is something like a pure culture and identity, and the identity of one group excludes the identity of another group. Both Germans and Sicilians know better: Our original cultures and peoples, through the course of history, have been undergoing more outside influences than we can enumerate. But while our nations and cultures are, as a result, composite nations and cultures, they still remain distinctly German and Sicilian. The phenomenon is the same that I mentioned above when I explained the Ego: there is change and variation all the time, but there is a hidden underlying continuity which ensures that it still remains the same person or the same culture. Once an American politician remarked about pornography: "l cannot explain it in words, but I know it when I see it." In the same way, while it may be difficult to define German or Sicilian culture in a textbook or political statement, you will always recognize when you see it.

In order to create that European identity we must bring people together and expose them to the variety of European cultures. One of my most rewarding experiences was my work with the organization "Cultural Heritage without Borders" (CHwB). During the Balkan Wars of the 1990s, cultural heritage objects became targets of warfare. Christian Serbs destroyed mosques, and Albanian Muslims destroyed churches. When the wars were over and the countries needed to be rebuilt, members of the Swedish Parliament established CHwB in order to support the restoration of these buildings, but they used this program to bring people of different cultures together. ln two-week socalled "Restoration Camps", young people from all these enemy countries would come together, receive education and training from the best Euopean experts, and implement small interventions at local historic buildings.

Fig. 5: CHwB Restoration Camp in Gjirokastra, Albania, 2012. Photo: Stephan Doempke

lmagine to see a young Serbian restore an Albanian house, or a Greek cooperate with a Macedonian! When you see how they had a lot of fun together and no problems with each other at all you will be able to believe that a united Europe is a realistic prospect, and the shared values of cultural heritage can be one of the most effective tools to achieve it. Cultural Heritage can bring us together rather than separate us, and to demonstrate this through our programs and projects is our most noble mission.

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Sea Researches

La ricerca archeologica in altofondale e le nuove metodologie multidisciplinari basate sull'interazione tra osservazione diretta e sistemi remoti: la Battaglia delle Egadi

Roberto La Rocca

Archeologo, Regione Siciliana - Assessorato dei Beni Culturali e dell'Identità Siciliana

robertolarocca66@libero.it

Il settore della ricerca archeologica subacquea strumentale, grazie all'importanza assunta dall'impiego di tecniche ed attrezzature sempre più sofisticate, si è andato sempre più affermando, soprattutto in seguito all'utilizzo di strumentazioni acustiche e magnetometriche derivate da ambiti militari e petroliferi offshore. Tali indagini, ormai ampiamente utilizzate in ambito archeologico, consentono di coprire aree molto grandi in tempi relativamente brevi, arrivando facilmente anche ad alte profondità. È per questo motivo che ultimamente hanno assunto un ruolo determinante nell'indagine ad ampia scala, delegando ai metodi d'indagine visiva diretta un ruolo successivo di controllo puntuale ed accurato dei target individuati (Fig. 1).

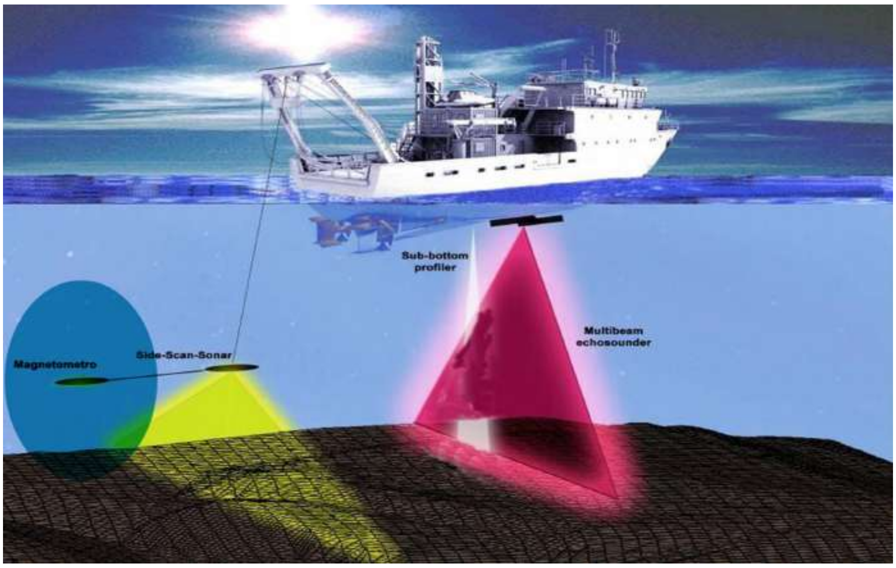


Figura 1 - Nave attrezzata per indagini geofisiche in ambito archeologico

Il progetto "ArcheoEgadi" di cui vedremo le linee principali, rappresenta un significativo esempio dell'utilizzo delle più moderne tecnologie e della cooperazione di istituti nazionali ed internazionali di ricerca, Forze dell'Ordine e privati nella ricerca archeologica subacquea moderna in Sicilia.

Il supporto delle indagini geofisiche è, comunque, solo uno dei momenti in una corretta programmazione della strategia da applicare nella ricerca archeologica, restando indispensabile acquisire conoscenze di carattere storico, archeologico, meteorologico e geografico. Il concorso di diversi approcci metodologici crea un corretto equilibrio tra tecnologia avanzata e ricerca tradizionale basata sulla risorsa umana, poiché il rilevamento elettroacustico non può sostituire l'occhio umano, soprattutto in presenza di fondali articolati. L'ausilio di metodologie geofisiche, possibilmente abbinate all'utilizzo delle prospezioni tradizionali, è in grado di rilevare in modo speditivo preciso ed affidabile evidenze antropiche.

La scelta della strumentazione da adoperare è basata sulla conoscenza acquisita durante la fase di progettazione, poiché ogni strumento d'indagine ha caratteristiche proprie che ne delimitano il campo d'applicazione. Una buona conoscenza della strumentazione è, pertanto, un requisito indispensabile per poter stabilire quali mezzi adottare in relazione agli obiettivi e al contesto.

Molteplici ricerche sono state eseguite nel corso degli anni nelle acque delle Egadi, ma a parte qualche raro caso non sono state interessate dall'utilizzo di moderne strumentazioni geofisiche.

Con le dovute cautele e distanze dai retorici resoconti sul valore epocale della battaglia, certamente ebbe effetti talassocratici diretti sul Mediterraneo dei secoli successivi, dove l'acquisita autorevolezza di grande potenza navale mediterranea consentì al mondo romano di avviarsi verso quella fisionomia imperialista che l'ha connotato nei secoli successivi. L'indubbio potere evocativo connesso con la battaglia che il 10 marzo del 241 a.C. si consumò in queste acque, ha fatto da motore per l'avvio di esplorazioni archeologiche sistematiche subacquee, sia tradizionali sia strumentali, ad opera della Regione Siciliana.

La costituzione di un gruppo di ricerca multidisciplinare non ha costituito soltanto un fattore determinante per l'efficacia e la completezza del risultato, ma è stato anche una garanzia di equilibrio tra le varie componenti, sia in fase di metodologia di approccio sia nella redazione del prodotto di sintesi finale. E' proprio grazie al concorso di diversi approcci metodologici, desunti dal confronto tra operatori di varie discipline chiamati a partecipare alla ricerca, che è stato possibile strategicamente puntare al raggiungimento di un corretto equilibrio tra tecnologia avanzata e ricerca tradizionale basata sulla risorsa umana.

La prima fase della ricerca si è articolata nella raccolta di dati storici, sia antichi che recenti, che potessero evidenziare la presenza di emergenze archeologiche subacquee nell'ambito dell'arcipelago delle Egadi. Si sono rilette le fonti classiche e si è approfondito lo studio della bibliografia specialistica. Già da queste fasi preliminari sono scaturite molteplici notizie su potenziali areali e siti d'interesse archeologico che sono serviti per pianificare ed ottimizzare la seconda fase costituita dalla ricognizione effettiva dei luoghi. La seconda fase è stata eseguita sia strumentalmente (indagini elettroacustiche) che direttamente mediante immersione umana ricognitiva, così da localizzare target potenzialmente indicatori di emergenze archeologiche. La terza fase, puntando direttamente ai siti e ai target precedentemente individuati, ha concesso di raggiungere il massimo dettaglio analizzando le caratteristiche effettive delle singole emergenze archeologiche.

Il progetto, in particolare, prevedeva la caratterizzazione dell'eventuale presenza di reperti archeologici nelle acque dell'arcipelago delle Egadi attraverso l'effettuazione di:

1. rilievi geomorfologici finalizzati essenzialmente all'identificazione della morfologia dei

fondali e di eventuali bersagli archeologici emergenti dal fondo;
2. rilievi stratigrafici finalizzati all'identificazione di eventuali presenze archeologiche celate sotto strati, più o meno spessi, di sedimento del fondale;
3. rilievi batimetrici finalizzati a realizzare immagini ad alta risoluzione di siti di rilevante interesse archeologico;
4. rilievi magnetometrici differenziali mediante gradiometro mirati ad identificare masse metalliche, o di qualsiasi altra natura, purché con caratteristiche geologiche e mineralogiche diverse da quelle dei sedimenti circostanti.

Le indagini sono state effettuate con l'ausilio di strumentazioni che, come già accennato, sono direttamente derivate dalla ricerca geofisica e messe a punto per motivi scientifici, soprattutto nell'indagine petrolifera offshore: il Multibeam Echo Sounder (MBES), il Side Scan Sonar (SSS), il Sub buttom Profiler (SBP), il Magnetometro e Gradiometro, ma anche il Remotley Operated Vehicle (ROV) e l'Autonomous Underwater Vehicles (AUV).

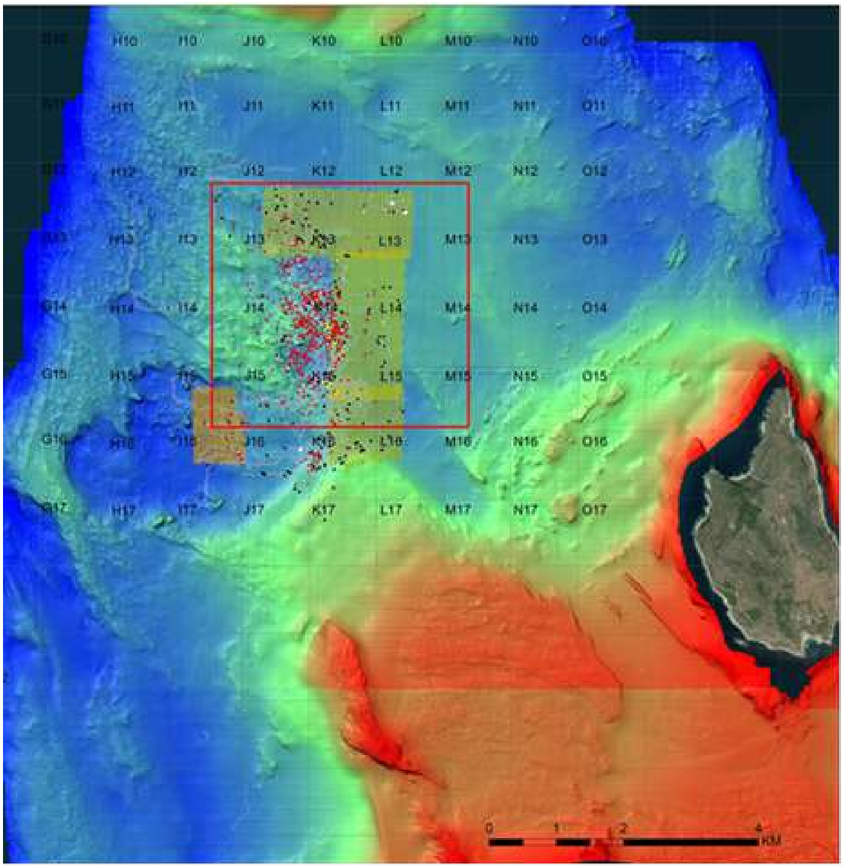


Figura 2 - Distribuzione areale dei target individuati.

Le analisi storiche e la ricostruzione della dinamica della battaglia, così come oggi avvalorata dalle indagini archeologiche effettuate, consentono di affermare che non esiste soltanto un limitato areale dove individuare le evidenze subacquee delle navi perdute nel corso della battaglia. La difficoltà di individuare il luogo dello scontro scaturiva da diverse considerazioni. Il convoglio cartaginese, poiché navigava a vela, si presume fosse distribuito lungo un vasto specchio di mare, reso ancora più ampio dalla dinamica stessa dello scontro che dovette parcellizzare il convoglio in molteplici duelli tra singole imbarcazioni. Areale ancora più evanescente considerando anche il mutare del vento pomeridiano e le forti correnti che poterono conferire lunghe derive alla lenta dinamica di affondamento dei resti lignei delle navi (Figura 2).

Si è privilegiata nelle ricognizioni subacquee tradizionali l'area costiera orientale (Cala Minnola, Punta Altarella e Secca Scaletta) e lo specchio di mare antistante l'estremità settentrionale (Capo Grosso) dell'isola di Levanzo. Qui sono stati rinvenuti numerosi elementi, tra cui un gruppo di ceppi plumbei cronologicamente e tipologicamente coerenti, che inducono a validare l'ipotesi che questo fosse il luogo del potenziale ancoraggio della flotta romana prima dell'agguato alla flotta cartaginese.

Senza escludere che anche altri siti possano avere contribuito al ricovero di parti della flotta romana, l'ipotesi che questa fu una delle basi principali per l'attacco, è sostenuta anche dal fatto che, con ogni probabilità, la rotta della flotta cartaginese, avendo come scopo quello di portare aiuto alla guarnigione punica asserragliata ad Erice, si dirigesse a Nord di Levanzo, doppiando Capo Grosso. D'altronde, l'esigenza di tenere una rotta sicura, difficilmente li avrebbe indotti a tagliare la rotta lungo il canale tra le due isole o, peggio, tra l'arcipelago e la costa siciliana, sia per il probabile pattugliamento nemico sia per le pericolose rade sabbiose prossime alla costa.

La flotta romana, con ogni probabilità, attese il convoglio cartaginese alla fonda all'ombra di Capo Grosso. Qui, per recuperare attimi preziosi, è possibile che tagliarono addirittura le cime delle ancore e, data la loro posizione, sbarrarono la strada ai nemici, sopraggiungendo con rapidità sulla flotta cartaginese assolutamente impreparata.

Per verificare la dinamica dello scontro ed individuare l'area su cui concentrare le ricerche, si è proceduto anche allo studio comparativo sulle condizioni ambientali dell'epoca. Al fine di poter confermare la dinamica della deriva delle navi coinvolte nella battaglia e quale potesse essere stato lo scarroccio subito, si è preso in esame il regime correntometrico dell'area e, su base comparativa, il regime eolico nel periodo e nelle ore dell'evento.

L'utilizzo di strumentazione derivata dalla ricerca geofisica ha sicuramente consentito di verificare che l'elettroacustica è in grado di ricostruire l'andamento morfologico e batimetrico del fondale con una risoluzione idonea ad identificare "anomalie di conformazione" che facciano ipotizzare la presenza di evidenze di natura archeologica. Consentendo di indagare aree molto ampie in tempi relativamente brevi, ha offerto la possibilità di concentrare l'attenzione solo dove si sono riscontrate le anomalie più significative. In tal modo, limitando i metodi tradizionali visivi soltanto per i controlli più accurati sui targets sospetti, si è ottenuta una sensibile riduzione dei costi di gestione.

Sino al 2016, la ricerca alle Egadi ha previsto un limitato impiego dell'immersione diretta profonda dell'uomo sul fondale, che nello specchio acqueo oggetto d'indagine oscilla intorno ai 90/100 metri di profondità. È solo a partire dal 2017 che, grazie alla collaborazione della GUE (Global Underwater Explorers), sono stati impiegati dei subacquei specializzati in immersioni in alto fondale per completare il quadro delle tecnologie e professionalità impiegabili.

L'integrazione tra la campagna di ricerca strumentale e gli operatori subacquei in immersione diretta è stata altamente proficua, incrementando sensibilmente il dettaglio della ricerca stessa e portando a localizzare una serie di reperti diagnostici di minori dimensioni, non visibili all'occhio strumentale, ma di grande importanza diagnostica.

È stata, però, la campagna di prospezioni del 2019 che ha visto per la prima volta l'impiego simultaneo all'interno dello stesso contesto archeologico della nave oceanografica Hercules (RPM Nautical Foundation) e gli operatori scientifici subacquei della GUE, ponendo le basi per la sperimentazione su alto fondale di una metodologia di ricerca che vede impiegati contemporaneamente sistemi di indagine strumentale, sistemi di indagine remota e operatori subacquei all'interno di un sito archeologico in alto fondale.

Questo approccio metodologico sperimentale, almeno sull'alto fondale, ha consentito il ritrovamento di un insieme di reperti tra i quali la prima arma: una spada sepolta appena sotto la superficie sabbiosa in prossimità del rostro Egadi 16, all'epoca ancora in *situ* (Figura 3).

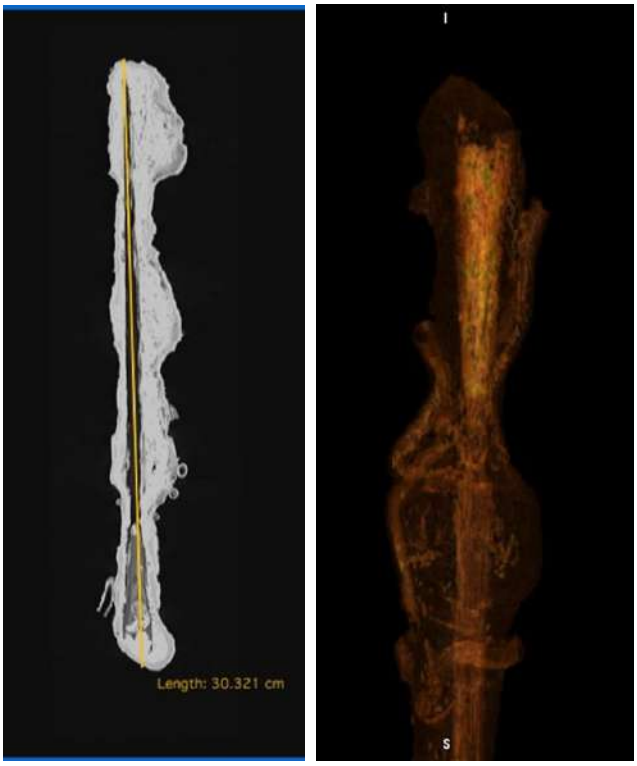


Figura 3 - Immagine radiografica della spada individuata nel 2019.

In tale occasione, le prospezioni sono state condotte con l'ausilio di metal detector di nuova generazione che, per la prima volta, hanno consentito d'indagare sotto lo strato sabbioso superficiale con risultati che, per numero e tipologia, ci confermano come quanto individuato sino ad oggi rappresenti solo in minima parte ciò che giace appena sotto lo strato superficiale sabbioso (Figure 4 e 5). I risultati delle


Figure 4 e 5 - Elmo tipo "Montefortino" con applique sommitale che riproduce una pelle di leone in rilievo che sembra abbracciare la pigna centrale.

recenti campagne, quindi, seppur ovvie sul basso fondale, ci confermano come la componente umana rimanga determinante anche in quella nicchia di ricerca archeologica subacquea rappresentata dall’alto fondale.

Underwater photography in the archaeometric field from traditional survey to 3d survey

Salvatore Emma

Regione Siciliana - Assessorato dei Beni culturali e dell'Identità siciliana

s.emma@regione.sicilia.it

Since the birth of underwater archaeology, man has felt the need to document underwater finds. A necessity that became indispensable when underwater archeology was transformed from the first pioneering recoveries of artifacts, to a structured scientific discipline and therefore with the need for timely documentation and as closely as possible to the truth. When it was practiced as a science, the need for precise documentation was considered indispensable, also in consideration that the archaeological site, following the excavation, is inevitably destroyed. Hence the need to carry out metric surveys and report, at the beginning on paper and subsequently on computer supports, the state of the archaeological site step by step.

In the first experiences of underwater surveying, systems already used on land were tested, therefore the use of meters and metric rollers. The measures marked on paper, however, inevitably suffered from errors due to a survey system not yet fully tested. The applications of terrestrial topography had not yet been applied underwater and, moreover, the archaeology of those years did not require a precision and detail which subsequently became fundamental for the study of submerged sites. From the 1970s the technique was perfected thanks to the use of underwater technicians, often topographers and draftsman, who with a good degree of precision were able to produce technical documents useful both for the study of sites and finds by scholars, and for the conducting an underwater archaeological excavation according to the stratigraphy system.

In the 90s the survey and documentation, thanks also to the progress of technology in the field of underwater photography, had a boost thanks to the use of modern diving photographic systems, accurate topographic survey techniques and the development of CAD design software which allowed the surveys carried out underwater to be returned in digital format. In the 2000s, 2D photomosaics began to be added to this type of survey thanks to the first software initially used in architecture and engineering, but which found an excellent use in metrically correct underwater surveying. Furthermore, photographic photo editing software and the birth of digital cameras with ever higher resolution, made it possible to obtain realistic results, also for dissemination and multimedia products.

In the meantime, archaeology had become a multidisciplinary science and more and more professional and technical photographers were employed in the topographical survey which brought that indispensable added value in a world which, up to that moment, had considered the survey and the restitution of submerged sites. an outline to all the operations carried out in an archaeological excavation.

So in the mid-2000s, from the two-dimensional relief plan, albeit quoted, we arrived at a survey system through the creation of photos which, appropriately treated by dedicated software, are able to reconstruct a three-dimensional model of both individual archaeological finds portions of the seabed, wrecks and entire submerged sites. A revolution that has made it possible to carry out measurements and surveys in far shorter times than traditional systems that involved the use of many divers for long diving times.

So, underwater photogrammetry began to appear in a sector firmly anchored to classical methodologies but which, by translating the 3D survey techniques used on land, took the opportunity to implement a modern, precise and fast system that has provided great help to the underwater archaeology.

SOME PHOTOGRAMMETRIC SURVEYS MADE IN SICILY

The "Sottomonastero roman harbour" in Lipari

In 2014 and 2015, the Soprintendenza del Mare of the Sicilian Region, with the University of Sassari, the CNR of Catania, the Museum of Lipari and the III Nucleo Sommozzatori Guardia Costiera di Messina, starded in Lipari, in the Aeolian Islands, the excavation campaigns of the so-called "Sottomonastero roman harbour", identified in 2008 at about nine meters deep thanks to the dredging of the port. On this occasion it was decided to use the three-dimensional photogrammetric technique for the first time as the only means of surveying the excavation. The need arose from the need to carry out a quick survey on a large site, having little time available due to the position of the archaeological site, inside the port of Lipari and in the immediate vicinity of the hydrofoil dock. For the survey of the site, two divers were engaged for two shifts of about an hour. 782 high resolution digital photographs were taken, processed with Agisoft Photoscan software.

(1)

(2)

The "Cala Minnola Roman wreck" in Levanzo, the "Helphis" wreck" and the "Carmelo Lo Porto" wreck in Favignana

In 2015, as part of the European project "Arrows - ARchaeological RObot systems for the World's Seas", the Soprintendenza del Mare created three three-dimensional models by photogrammetric survey of three submerged wrecks. The site of Cala Minnola, with the cargo of a roman ship consisting of about 90 amphorae, two lead anchors and a lead bilge pipe at a depth of 27 meters; the wreck of the ship "Elphis", about 50 meters long, sunk in 1978 between the islets of Formica and Maraone in the Egadi Islands and lying at a depth of 20 meters; the wreck of the merchant ship “Carmelo Lo Porto”, sunk in 1971 off the coast of Favignana, which lies broken in two sections at a depth of 18 meters.

The aim of the project was the comparison between the three-dimensional models obtained through the survey made directly by a diver with photographic footage and subsequently processed with "image based" software capable of returning a 3D model, and the 3D models returned by Multibeam at high resolution and three-dimensional obtained by processing high resolution satellite images.

(3)

(4)

(5)

The “Capomulini wreck” in Acitrezza (CT)

The wreck was discovered at a depth of between 55 and 80 meters in 2009 and systematically studied in the following years. The cargo of 303 intact amphorae is still in place and many amphorae are still in the loading position. There are also two lead anchor stocks and a bilge pipe more than four meters long. In 2016, in order to study cargo dispersion and monitor the wreck, a 3D model was made. Given the considerable depth of the wreck and the difficulty of diving due to the strong currents present on the site, the realization of the images was entrusted to a professional underwater photographer who dived with a rebreather diving system. About 1500 photographs were taken, of which 250 were considered useful for the realization of the model using the Agisoft Photoscan software.

(6)

(7)

THE PHOTOGRAMMETRIC SURVEY OF INDIVIDUAL UNDERWATER FINDS

In research campaigns, the 3D survey of individual finds made with photographic images is of great use; a fast and highly accurate method that reduces the time required for carrying out operations. During the research campaigns carried out between Favignana and Levanzo, theater of the "Battle of the Egadi", an epic clash between the Roman and Carthaginian fleets, 3D models of the finds identified from time to time were made, in such a way as to offer archaeologists the possibility to evaluate the finds placed at a depth of about 80 meters in a few minutes. In this specific case, the Egadi12 Ram, was taken with about 200 high resolution photos. A few minutes after the dive, a 3D model was created, metrically correct thanks to the Agisoft Photoscan software, in order to immediately proceed with the classification of the find. A precise and fast method which, with a single dive, provided the possibility of creating an immediate metrically correct support for the study and which, with traditional technique, would have required many dives, measurements and creation of images.

(8)

3D MODELS MADE IN THE DEEP SEA BY DIVER

In 2014, thanks to the collaboration between the Soprintendenza del Mare and the GUE - Global Underwater Explorer, the first three-dimensional model of an ancient wreck in the deep sea was created using images taken by divers. Four dives to a depth of 114 meters were required by professional deep-sea divers who took high-resolution images of the Roman wreck called "Panarea III". Subsequently a 3D model was made with Agisoft Photoscan software. It is the first example of the realization of a three-dimensional model at high depth thanks to the possibility of remaining on the underwater site for operators using a rebreather diving system that allows the stay of about thirty minutes on the wreck, and therefore, the possibility of creating the necessary images to the elaboration of the model.

(9a)

(9b)

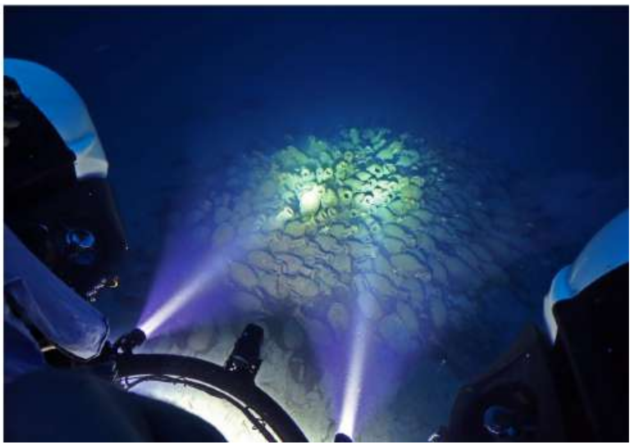
(9c)

(10)

3D MODELS MADE IN THE DEEP SEA WITH THE USE OF BATHYSCAPHE

In an exploration campaign in the Aeolian Islands carried out in 2015, dives were carried out at depths between 110 and 150 meters off the island of Panarea. Four Roman wrecks, identified in 2010 by the Aurora Trust, were carried out using the "U-Boat Worx's - Explorer 3" bathyscaphe made available by the American Aurora Trust. Thanks to a high resolution camera, positioned in the lower part of the bathyscaphe, photographic coverage of the four sites was carried out and the three-dimensional models were subsequently created. The lighting system of the bathyscaphe, used during the photographic shooting, allowed the return of the original texture by providing a model with the color of the finds perfectly identical to the original. A great opportunity therefore that opens up new frontiers in the realization of high-depth surveys.

(11)

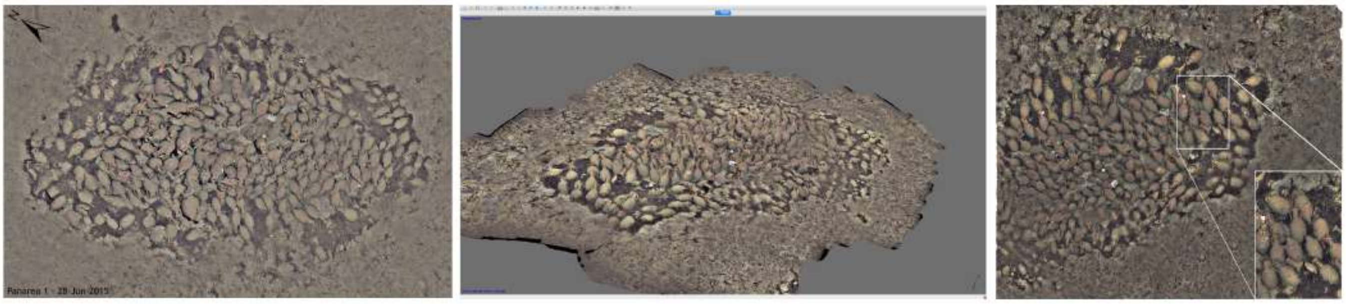


(12)

(13a)

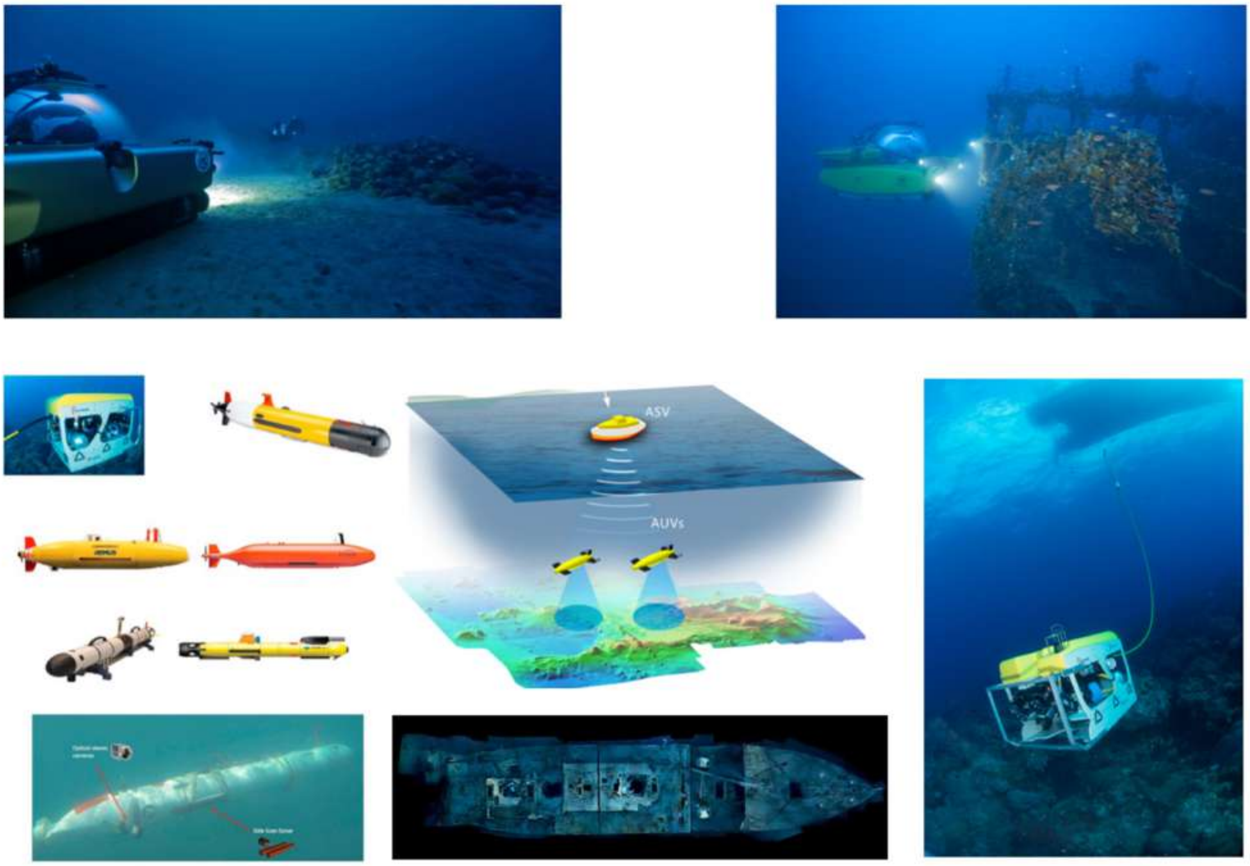
(13b)

(13c)



(14a) (14b) (14c)

Probably the future to carry out reliefs of wrecks and archaeological sites at great depth, is therefore the possibility of using the photogrammetric system also with submarines or underwater robots that can reach altitudes denied to man, but also through autonomous underwater vehicles (AUV) equipped with video, photographic and lighting systems. Hence an important reduction in construction times with a consequent economic saving, but above all the possibility of obtaining three-dimensional models that can be used for various uses, from a study tool for archaeologists, to the creation of informative products for the general public (immersive reality, 3D projections, use of augmented reality viewers). It is evident that the realization of high depth reliefs with submarines and mini-submarines represents the optimum both for quality and speed in the realization. The high cost of these technologies, however, justifies their use in archaeological missions of great economic commitment. The technologies that can be used at high depth remain, therefore, those linked to the use of ROVs (Remotely Operated Vehicles), wire-guided robots from the surface that allow high-resolution photographs and videos to be created, or AUVs (Autonomous Underwater Vehicles), autonomous underwater robots. That allow you to take photographs and videos, as well as the possibility of using instruments such as gps, multibeam or side scan sonar. New technologies and new techniques for archaeological survey at high depth: this is the new frontier of marine archaeology where man, with traditional techniques, cannot reach.



(15)

Photographic references:

1. Sottomonastero Lipari_3D processing Salvatore Emma-Soprintendenza del Mare

2. Sottomonastero Lipari_3D processing Salvatore Emma-Soprintendenza del Mare

3. Cala Minnola wreck_3D processing Salvatore Emma-Soprintendenza del Mare

4. Helphis wreck_3D processing Salvatore Emma-Soprintendenza del Mare

5. Carmelo Lo Porto wreck_3D processing Salvatore Emma-Soprintendenza del Mare

6. Capomulini wreck_3D processing Salvatore Emma-Soprintendenza del Mare

7. Capomulini wreck_3D processing Salvatore Emma-Soprintendenza del Mare

8. Egadi12 Ram_3D processing Salvatore Emma-Soprintendenza del Mare_photo Lundgren GUE

9a. Panarea III wreck_photographic footage of the wreck_photo Lundgren-GUE

9b. Panarea III wreck_photographic footage of the wreck_photo Provenzani-GUE

9c. Panarea III wreck_a diver shows an artifact to an archaeologist_photo Lundgren-Gue

10. Panarea III wreck_3D processing GUE

11. The bathyscaphe before the dive_photo Gabriele Galletta

12. Panarea I wreck _photo Salvatore Emma-Soprintendenza del Mare

13a. UBoatWorx before dive_photo Salvatore Emma-Soprintendenza del Mare

13b. Setting before diving_photo Salvatore Emma-Soprintendenza del Mare

13c. Detail of the camera_photo Salvatore Emma-Soprintendenza del Mare

14a. Panarea I wreck_2D photomosaic_3D processing Salvatore Emma/Gerhard Seiffert

14b. Panarea I wreck_3D model_3D processing Salvatore Emma/Gerhard Seiffert

14c. Panarea I wreck_Ortophoto from 3D model_3D processing Salvatore Emma/Gerhard Seiffert

15. Batyscaphe_ROV_AUV

Geoarchaeology of deep sea Sherki Bank and Black Sea

Francesco Torre

Università di Bologna
Francesco.torre2@unibo.it

Two scientific expeditions funded by the National Geographic Society will be discussed in which the undersigned participated, together with Harvard University, MIT of Boston, Pennsylvania University. A study of marine and terrestrial archaeology was carried out simultaneously to understand the rise in sea level from a geomorphological point of view and the history of the great emigrations of ancient Mediterranean populations.

The first site in Mediterranean Sea.

The Skerki Bank Project was the first interdisciplinary effort to determine the importance of the deep sea to the field of archaeology. Over a nine-year period from 1988 to 1997, its various field programs resulted in the discovery of the largest concentration of ancient ships ever found in the deep sea. In all, eight ships were located in an area of 210 km., including five of the Roman era spanning a period of time from 100 B.C. to 400 A.D., documenting the existence of a major trading route in the central Mediterranean Sea between ancient Carthage, Rome, Sicily, and Sardinia. The project involved the use of highly sophisticated deep submergence technologies including towed acoustic and visual search vehicles, a nuclear research submarine, and an advanced remotely operated vehicle. Precision navigation and control permitted rapid yet careful mapping, both visual and acoustic, of each site with a degree of precision never attained before. Advanced robotics permitted the recovery of selected objects for subsequent analysis without intrusive excavation. This multi-disciplinary effort of archaeologists, oceanographers, and ocean engineers demonstrated that deep water archaeology has great promise and can be done without the exploitation of ancient sites for private gains. The Project also demonstrated that in the absence of evolving laws of the sea, a great deal of human history may be at peril. The subject Geoarchaeology I taught at the Free University of Trapani from 1980 to 1987 in the Course of Cultural Heritage which is located at that University. It was then a great success. I continued to study it, and to apply it, as a geologist in the Archaeological Section at the Superintendency of Trapani. But how important it was for professional and scientific development and economics was made to me by the Americans during the last expedition in 1997 to Banco Skerki, an expedition in which I was lucky enough to participate. On board an oceanographic vessel and a nuclear submarine of the American Navy, staying with the latter for three days and three nights at a depth of 800 meters, I was able to study the seabed, and understand, as well as being an eyewitness, of how sediments begin to form at these depths, embryos of what our imposing limestone formations will be in the future. The rain of plankton, which illuminated it could be seen falling from above, was a scene that any geologist in the world should have witnessed. We were in the presence of the bing bang of the future geological formation. Billions and billions of plankton shells were depositing on the bottom surface marine and the impression was that everything remained flat and without thickness. Think that every thousand years the fund increases by only one centimeter. The submarine was advancing at 2 knots an hour, while I stuck to the porthole and saw all sorts of wonders coming towards it, shipwrecks, amphorae, valleys, bumps, large holes dug by whales that lay on the bottom, and then again everything flat for miles and miles, in a deathly silence, broken only by the beep of the on board sonar. Everything you see at those depths is wonderful, from the birth of a new volcano to the terrifying appearance of an abyssal fish near the porthole. The light is lost at about 350 meters, after which the on board lights control. The submarine explores the bottom standing about three meters from it but leaning and walking on the seabed, with wheels, when it is necessary to observe closely. The impression is that of being on the moon and the expedition is comparable to the space one. The water around the wrecks of the discovered ships was clear and crystalline, although they were hidden in perpetual darkness. This discovery opens a new era for the study of deep sea archaeology. A sunken ship is a moment of time enclosed in the depths of the sea, its animation has only been suspended. There are also many risks involved. Two nuclear submarines, before the construction of this one, exploded, as I will say below due to the strong pressure and hundreds of men perished at the bottom of the ocean. The Russian nuclear submarine Kursk sank just 100 meters deep in the Baltic Sea and no one was able to save the crew members. Imagine if this happened at a depth of 800 meters. We were aware of this but no one talked about it to his neighbors. The pressure at that depth is just under a ton per square centimeter, which means that if anything were to happen the men on board, coming out, would become jam. Eventually I received an honorary crew member certificate from Commander Richard for my courage. The submarine's sonars were able to detect objects tens of miles away and to know the nature, size and type of material of any type of object buried in marine sediments. The expedition was born in 1988 with the sole purpose of searching for American ships and German submarines sunk during the Second World War in the Mediterranean Sea. During the research Ballard discovers the wreck of a Roman ship, called ISIS, 70 miles off the Sicilian coast, that is, in international waters. Research began in 1989 and ended on June 29, 1997. During this long expedition, high-tech tools are used. Two robots, remote controlled vehicles, Medea and Jason, a nuclear submarine, the NR-1, and a research vessel the Carolyn Chouest (Fig. 1-2-3), on which there were all the research laboratories and the operational base. NR-1 is the most sophisticated submarine in the world today. 44.5 meters long, with a diameter of 3.8 meters and an immersion displacement of 400 tons, it is powered by two nuclear-powered engines and can reach a depth of about 900 meters. It can remain submerged for an unlimited time depending only on the provisions and food it can carry. It carries a specialized crew of 9, made up entirely of US Navy personnel, plus two scientists. It is capable of moving at an average speed of 2 knots (maximum 4 knots). Some features, unique for a nuclear-powered submarine, are the retractable depth wheels that allow it to move on the bottom, three portholes for direct observation of the seabed (thickness of the portholes 10 cm), external projectors, and 17 cameras as well as divers and cameras for depth studies, a mechanical arm for retrieving objects weighing over 400 kilos, a manipulator that can be used to grab and cut materials. NR-1 is also equipped with very sophisticated sonars and electronic computers useful for navigation, communication, location and identification of objects. Sonars can operate in 11 different ways, detecting a huge area around the submarine and building the shape of structures buried under the mud of the seabed. As already mentioned, an ROV (remote controlled vehicle) and a nuclear submarine were used, with the support of a research vessel, among the most sophisticated in existence today. The scenery is the depths of the Mediterranean Sea. The team is made up of oceanographers, geologists, engineers and archaeologists, led by Robert Ballard, and it is they who have discovered the largest concentration of ancient shipwrecks ever found in the depths of the sea, one of them dated before the birth of Christ. The group of 8 ships, with thousands of artifacts, spanning a time span of about 2,000 years of human history, lie about 800 meters along an ancient trade route. These include 5 ships from the ancient Roman period, sunk between 100 BC. and 400 AD, an Islamic ship from the late 1700s, early 1800s and two modern ships sunk at the end of the 1800s, early 1900s. The discovery that includes the recovery of totaling 115 artifacts (about 15 for each ship), was announced on July 30, 1997 in Washington at the headquarters of the National Geographic Society. Many wrecks sunk in shallow water are torn apart by impact against rocky areas, or are encrusted with coral, or are looted by divers or trawler fishermen. These deep sea sites are covered with only the finest sediment dust and have never been touched by humans to date.

THE WRECKS

Researchers used the US Navy's NR-1 nuclear submarine, commanded by Lt. Commander Charles Richard, to locate the wreck sites. Capable of mapping large areas of the ocean depth and over a very long period of time, the NR-1 uses a sophisticated long-range sonar that can locate wrecks at a much greater distance than the sonars normally used by oceanographers. It was also equipped with a hanging arm capable of retrieving very heavy lead anchors, (300-400 kilos). The remote-controlled vehicle Jason, from the Woods Hole Oceanographic Institution, was used to explore and bring up the 115 artifacts, carefully selected by archaeologists to help date the ancient wrecks. In the different sites Jason was automatically placed on a spot and it was able to do the topographical survey of the site with a precision never before obtained in the depths of the sea. The Jason's pilot was also capable of maneuvering and retrieving artifacts smaller than an inch, such as coins, including glass objects, and delicately picking them up and transporting them on an elevator that carried them to the surface without damaging them. What presented itself was an incredible scenario, which made you take your breath away. The oldest wreck is of particular importance as it is one of the few and oldest wrecks of Roman ships ever discovered, dated from the late 2nd century. B.C. at the beginning of the first century. B.C. It lies undisturbed, with most of the artifacts intact. The visible remains suggest a ship of about 30 meters in length, with two holds loaded both in the bow and stern area. The exceptional and varied collection of artifacts includes an assortment of kitchen utensils and other household artifacts, precious bronzes of the ship, two heavy lead anchors, and at least 8 different types of amphorae used for wine, olive oil, fish sauce and for preserve fruit. Another 3 wrecks were found, probably dating from the 1st century. A.D. One of them wore a heavy load of high quality marble, made up of irregularly cut granite blocks perhaps taken from a quarry to be finished in place on arrival. They were carefully stacked in at least two layers in a central square section of the hold, also included 2 monolithic columns and large irregular blocks, and a large assortment of kitchen items. Sampling the splendid kitchen items preserved in the wreck was like going shopping in a Roman kitchen utensils store. The researchers believe that the ships, scattered over an area of 20 square miles, sank as a result of sudden storms that frequently occur, during certain times of the year, in the Mediterranean, turning this part of the region into a "Bermuda triangle" of lost ships. Prior to this discovery, no shipwreck sites greater than this have ever been discovered and explored by archaeologists in water deeper than 60 meters; an area that represents less than 5 percent of the world's oceans. The technologies used by the team can reach 6,000 meters, the depth of 98 percent of the oceans. The team of explorers consisted of a collection of scientists from different fields of research, geologists, oceanographers, engineers, archaeologists, who were working together for the first time to establish the new research field of deep sea archaeology, and they represent a unique collaboration between government, high technology and classical disciplines. Oceanographers and engineers were headed by Dana Yoerger of the Woods Hole Oceanographic Institution. The team of archaeologists was led by Anna Mac Cann of Boston University; the Conservation team was led by Demis Piechota of Object and Textile Conservation, Arlington, Massachusetts. The "Skerki Bank Project" was funded by the United States Navy, Office of Naval Research and the Navy's Office of Deep Submergence Systems; by National Geographic Television, by the National Geographic Society's Committee for Research and Exploration; from the Kaplan Fund, a New York foundation that funds only high-tech projects. Until now it had only funded NASA projects. And then again Sun-Star Electric Inc. Private foundations and private donors. Support for the team of archaeologists came from the University of Boston, University of Victoria, British Columbia, Joukowsky Foundation and private professors who are part of the academic staff of various American universities.

Fig. 1 - Oceanographic Ship Carolyn Chouest

Fig. 2 - Submarine NR-1

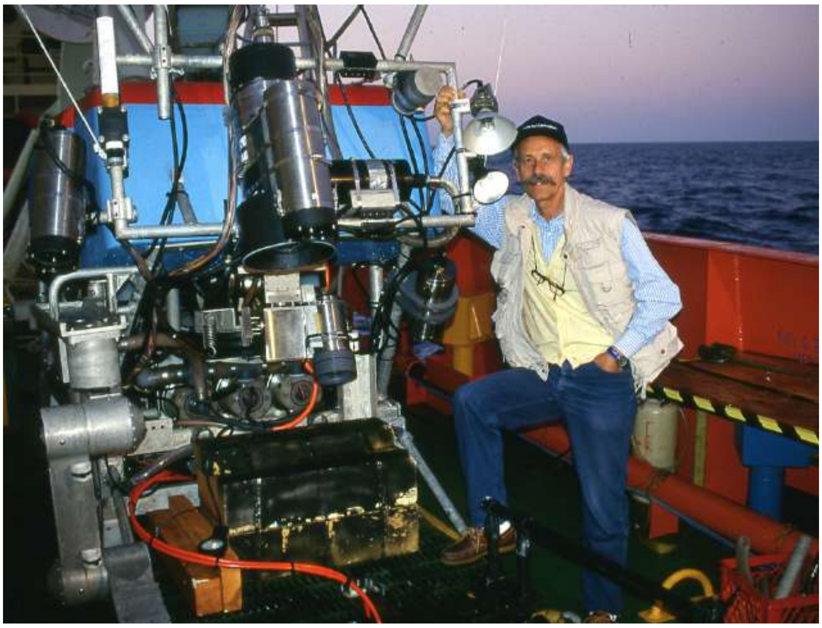


Fig. 3 - Prof. Torre and the ROV Jason.

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Deepwater Archaeology of the Black Sea: The 2000 Season at Sinop, Turkey

Abstract

In 2000, a major expedition for deep water archaeology was conducted by the Institute for Exploration in the Black Sea along the north western coast of Turkey from the Bosporus to the Turkish seaport of Sinop. A complementary land-based expedition will be reported upon elsewhere. The 2000 underwater expedition had three research objectives: to search for evidence of human habitation prior to major flooding of the Black Sea that researchers predicted occurred some 7,500 years ago; to investigate a deep water shipping route; and to search for ancient wooden ships in the sea's anoxic bottom waters. Research methods included the use of a phased-array side-scan sonar, a towed imaging sled, and a small remotely operated vehicle (ROV) to collect deep-sea survey data. Three shipwrecks and a probable site reflecting human habitation prior to the proposed flooding event were located at depths around 100 m. One additional shipwreck was found within the anoxic layer at a depth of 324 m. The ship found within the anoxic layer was intact, in a high state of preservation, and dated to the Byzantine period of 450 A.D.

The Black Sea became a major crossroads of the ancient world with the advent of Greek colonization in the period 800-700 B.C. Seafaring economies participated in trade from the central southern Black Sea coast to the Crimea, taking advantage of strong winds and currents. This north-south commerce is documented by finds of significant quantities of amphorae and tiles manufactured at Sinop, Turkey at settlements along the north central coast of the Black Sea. (Fig. 1) Sinop is the best natural harbor along the Turkish Black Sea coast, and its fertile and gentle coastal plain has evidence of occupation from prior to the flooding to modern times. The 2000 underwater season reported here was the first systematic survey in waters deeper than 85 m; this deepwater research complements the previous systematic shallow water survey near the Sinop peninsula and the ongoing land survey of the hinterland behind the port of Sinop.

The Black Sea has significant potential for archaeological and oceanographic research as a result of its history of fluctuating sea level over the last several thousand years and its non-oxygenated (anoxic) water below 200 m. An ancient coastline, which appears to have been abruptly flooded, is preserved in many places with a minimum of sedimentation at 150 m below the present-day surface. The abrupt flooding of this landscape appears to have caused the lowest layer of water to be deprived of oxygen, allowing a high degree of organic preservation in deep water, of particular importance in the study of shipwrecks. Willard Bascom first suggested, however, that the unique anoxic bottom water conditions of the Black Sea should result in the preservation of ancient wooden ships in a fashion unlike any other deep- water region. This prediction could not be tested with the technology available at that time, but since 1996, a deepwater archaeological expedition has been developed by the Institute for Exploration to search for ancient shipwrecks in the anoxic bottom waters of the Black Sea. Recently, marine geologists William Ryan and Walter Pitman challenged the conventional sequence of events leading to the conversion of the Black Sea in the Holocene from a lacustrine environment prior to postglacial melting to its present marine conditions. Ryan et al. based their 1997 findings upon a survey conducted in 1993, during which a high frequency sub-bottom profiling system was used to survey two areas on the Black Sea's northern continental shelf, to the east and west of the Crimea peninsula.

Their seismic survey revealed an erosional angular unconformity throughout the survey areas everywhere above the present 150 m contour of the sea's shelf. Draping the erosional surface is a thin uniform layer of sediments that Jack any internal structure or evidence of transgressive features that might be associated with a slow rise in sea level.

Cores taken during the survey penetrated the uniform layer as well as the underlying erosional surface. The upper draping layer proved to be sapropel mud, further suggesting a sudden transition from a well-oxygenated environment to one now lying in a macerating and putrefying anaerobic environment. Mollusks extracted from the cores at the base of the uniform draping layer and resting on the unconformity had identical radiocarbon ages of 7150 ± 100 years B.P.

Ryan et al. went on to conclude that the flooding of the Black Sea at 7150 B.P. was virtually instantaneous, resulting in the submergence of 150,000 km^2 of previously exposed land that now makes up the Black Sea's continental shelf. They also asserted that this sudden flooding "may possibly have accelerated the dispersal of early Neolithic foragers and farmers into the interior of Europe at that time."

In the summer of 1999, the Institute for Exploration carried out a survey of the continental shelf off the north central Turkish seaport of Sinop to determine if such a flood had occurred there and at what time. Using a side-scan sonar, small remotely operated vehicles, and a series of dredge lowerings, an ancient exposed high energy shoreline at a depth of 155 m. was located, inspected, and sampled. Analysis of mollusks collected from this ancient beach revealed a sudden flooding of the Black Sea in this area around 7,500 B.P. changing it from a lacustrine to marine environment. This ancient surface remained in contact with the bottom waters of the Black Sea for a long period of time before being draped by a thin layer of sapropel mud characteristic of today's anaerobic conditions.

Based upon the results of this 1999 study, the operational plans of the 2000 expedition were modified to include an effort to search landward of the 155 m contour for evidence of human habitation prior to this flooding event.

RESEARCH METHODS

Three major mapping systems were utilized during the 2000 survey. These included the DSL-120 side-scan sonar system, the Argus imaging vehicle, and the Little Hercules remotely operated vehicle (ROV) system.

The DSL-120 is a phased-array 120 kHz side-scan sonar developed by the Woods Hole Oceanographic Institution and capable of working in over 6,000 m of water. Owing to the small targets (i.e., less than 10 m on a side) being sought, the effective total swath width of the sonar was 600 m from one side to the other while the sonar was being towed at an average altitude of 40-50 m. Tuning the sonar to detect these small targets, however, resulted in the inability to measure the phase of the returning signal and therefore the loss of topographic information within the acoustic swath of the returning signal.

The Argus imaging vehicle, developed by the Institute for Exploration, is towed at the end of 0.68 inc. fiber-optic cable. It has an operating depth of 3,000 m and carries multiple cameras (a low-light level video camera, three color video cameras, and a 35 mm still camera) mounted on a train- able platform. At the back end of the vehicle are two 400 watt and one 1,200 watt lights that illuminate the ocean floor. It also carries a 675 kHz obstacle avoidance sector scanning sonar, an electronic still camera (ESC), magnetic compass, altimeter, and depth sensor. Thrusters are mounted on either end of the 4-m long stainless steel frame perpendicular to the long axis of the vehicle capable of spinning the vehicle on its vertical axis while being towed. The Argus vehicle system can be deployed alone or used in conjunction with the Little Hercules ROV.

The Little Hercules remotely operated vehicle.

It was developed by the Institute for Exploration and also is capable of working to 3,000 m. It has four thrusters, a 330 kHz obstacle avoidance sector scanning sonar, altimeter, magnetic compass, depth sensor, two 400 watt HMI lights, and either can carry a 1 chip color video camera and 35 mm camera or a 3 chip color video camera. Little Hercules operates from the end of a 30 m long neutrally buoyant tether that is connected to the Argus vehicle. THE 2000 SURVEY: METHODOLOGY

Survey using all three vehicle systems in 2000 was conducted in three separate areas. Research in deep water began by surveying the geography of the underwater region to the east of the Sinop peninsula. The central area, in deeper waters, was investigated specifically for the purpose of identifying ancient shipwrecks in anoxic water. The westernmost area, with its gently sloping submerged topography, was surveyed for evidence of both human habitation prior to flooding 7,500 years ago and ancient shipwrecks in oxygenated water. We initially identified the ancient Black Sea shoreline off of the Turkish coast in the eastern search area in the 1999 season. Because of stream piracy farther inshore in today's Turkish landscape, no major rivers flow into this area. Thus, while we were able to pinpoint the location of the submerged coastline, the probability of finding a human modified landscape landward of the shoreline to the east of the Sinop peninsula was low. In contrast, the western coast of the peninsula, where there are clear indications of pre-flood occupation, appeared to be a particularly good region to begin systematic survey for evidence of occupation along the submerged coast.

The 2000 study therefore concentrated on the area at west of Sinop, where more than 400 km2 of underwater terrain lies between the 155 and 90 m contours. This region lies between the shoreline of the ancient freshwater lake and the near shore area where archaeological survey evidence indicated there would have been abundant opportunities to hunt and gather in lacustrine, and upland regions. That said, the submerged landscape in the western search area was poorly defined based upon previous bathymetric data. To compensate for this, during the 2000 expedition, we generated local bathymetry by combining data from two sonar systems. This was made possible by combining the vehicle's DSL-120 side-scan sonar altitude data with its depth to determine total depth beneath the tow fish. This data, combined with a series of separate lines using the ship's echo sounder, was used to construct a bathymetric map of the study area. An area approximately 50 km along the coast was mapped. More than 200 sonar targets (bottom surface anomalies identified by sonar) were detected during the survey of this area. Of these, 52 targets were visually checked with video and ESC mounted on Argus and Little Hercules. Most sonar targets were evident rock outcrops, but three targets were identified as ship- wreck targets and two potential submerged terrestrial sites were inspected by the ROV. Of the possible submerged sites, the 7lst target proved to be uninterpretable based upon video and remote photographic inspection from the Argus and Little Hercules vehicles. The other potential submerged site, Site 82 (the 82nd target identified), however, appeared uniquely rectangular in its sonar image and was examined as thoroughly as possible within the limits of our technology and research permits.

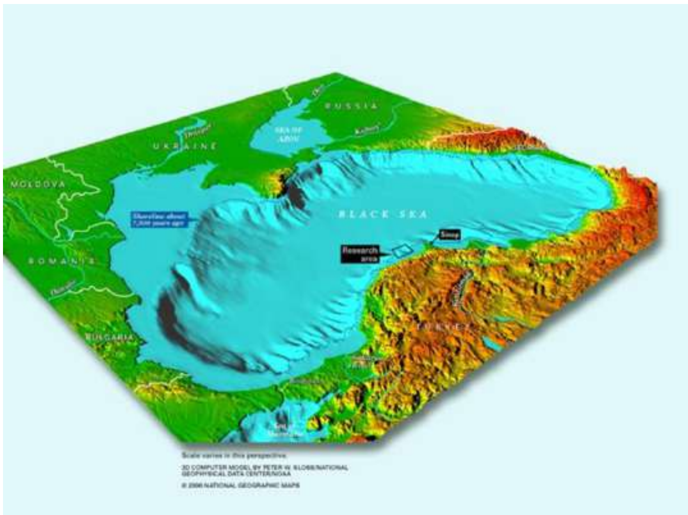

Fig.1 -Black Sea and the research area.

Fig. 2 - Torre and Ballard in the Black Sea.

Fig. 3 - Ancient Bridge near Sinop - Turkey

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Problematiche e prospettive per una migliore gestione, tutela, conservazione e valorizzazione dei reperti provenienti dal mare

Vincenzo Ruvolo

Direttore Area Mare di Arpa Sicilia

Stimolare ed intensificare il dialogo tra gli archeologi del mondo sommerso che operano in un settore affascinante come è quello dell'archeologia subacquea e chi si occupa di problematiche ambientali che riguardano il mare trova elementi di reciproca utilità e crescita professionale.

L'Archeologia Subacquea non è solo recupero di antichi oggetti sommersi, ma è l'insieme di tantissime specifiche fasi preliminari e successive al recupero che rendono il processo estremamente ricco di spunti di collaborazione con chi opera nel contesto complessivo del monitoraggio ambientale marino.

L'*Area Mare* di Arpa Sicilia ha sede a Palermo ma svolge la propria attività relativa al monitoraggio ambientale dell'ecosistema marino costiero, anche in attuazione delle principali Direttive Europee (2000/60CE – e Strategia Marina), lungo tutte le coste e le isole minori del territorio regionale e, tramite accordi di collaborazione, anche in altre regioni come la Sardegna e la Calabria, nonché partecipando a progetti nazionali ed internazionali sempre in ambito "mare" con paesi europei ed extra europei ricadenti nel bacino del mediterraneo
La Struttura comprende tre laboratori a valenza regionale: Biologia marina, Ecotossicologia e Geochimico-fisica del mare e gestisce in conto proprio 3 imbarcazioni:

la Calypso South di circa 23 m
la Teti di circa 12 metri
ed una imbarcazione minore

Ha una dotazione organica di circa 40 unità di personale tra: biologi, chimici, geologi e naturalisti nonché personale addetto specificatamente alla gestione e conduzione delle tre imbarcazioni in conto proprio.

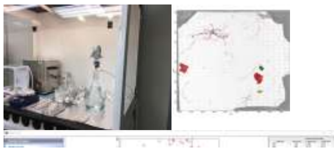
Avvalendosi del supporto operativo delle tre imbarcazioni nonché del Laboratorio specialistico acque marino costiere per le attività biologiche, chimiche e geologiche, la struttura studia le acque, i sedimenti marini, gli indicatori biologici quali le praterie di Posidonia oceanica, i popolamenti macroalgali delle coste rocciose, il macrozoobenthos dei fondi mobili, al fine di arrivare ad una classificazione di qualità dei tratti in cui è stata divisa la costa, nonché, fino alle 12 miglia nautiche, monitora i contaminanti chimici nell'acqua, nei sedimenti e nel biota, misura tutti i parametri chimico-fisici (pH, temperatura, ossigeno disciolto ecc.) e valuta l'abbondanza delle specie fitoplanctoniche e zooplanctoniche.
Con indagini oceanografiche sui fondali marini determina l'estensione e lo stato di salute dell'Habitat Coralligeno e dell'Habitat di fondi a Maerl e verifica gli habitat sottoposti a danno fisico per abrasione da pesca.

Inoltre svolge attività laboratoristica inerente all'analisi dei nutrienti, della clorofilla e dei feopigmenti e la determinazione della specie Ostreopsis ovata e delle altre dinoflagellate bentoniche potenzialmente tossiche mediante epifluorescenza. Svolge anche analisi della comunità macrozoobentonica di fondi molli e di altri parametri correlati.
Esegue saggi ecotossicologici sulle diverse matrici ambientali. Partecipa a studi di sperimentazione e validazione di metodi alternativi ai saggi ecotossicologici su vertebrati.
Identifica e determina svariate tossine algali ed inoltre svolge attività di monitoraggio relativamente all'impatto delle microplastiche nell'ambiente marino anche attraverso la loro caratterizzazione chimica sia nelle acque che nel biota.

La struttura laboratoristica dispone di moderna strumentazione scientifica ed in particolare:

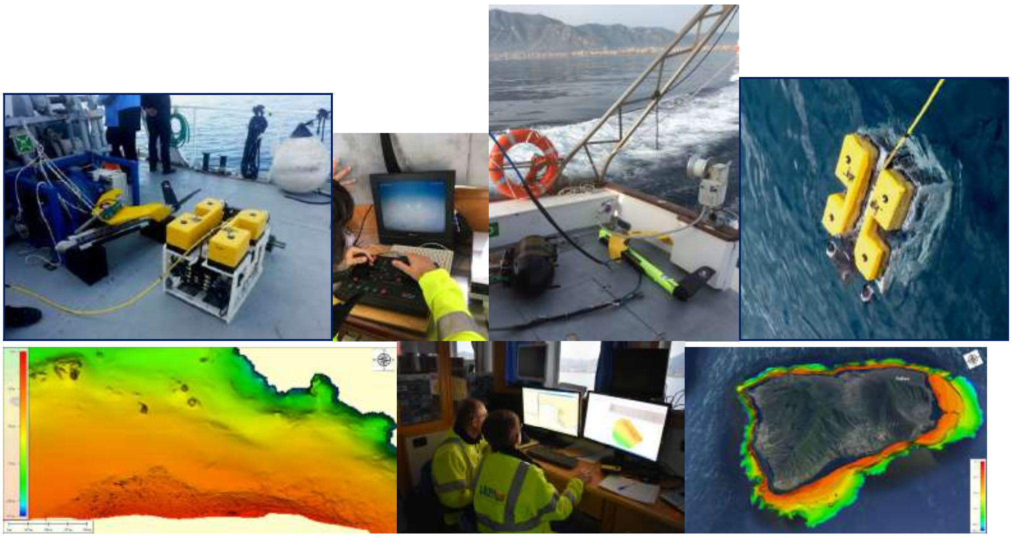
Thermo Scientific U-HPLC- Q Exactive™ Hybrid Quadrupole-Orbitrap™ Mass Spectrometer

Thermo Scientific In10 Ftir Microscope Ultrafast Packa per microplastiche Sistema di criofocalizzazione Entech per analisi gassose interfacciato con GC-MS Agilent



GC-MS Agilent con sistema GERSTEL MPS munito di Termodesorbimento e Pirolisi
AxFlow Spa Sistema QuAAtro per analisi di nutrienti
Granulometro Laser Analysette 22 Nano Tech e Setacciatore Elettromagnetico Tridimensionale 3 Pro Fritsch per la caratterizzazione geo-fisica dei sedimenti marini.

L'imbarcazione oceanografica Calypso South è equipaggiata con strumentazione per eseguire survey con acquisizione di dati morfobatimetrici e di tessitura mediante l'ausilio di sistemi MultiBeam e Side Scan Sonar e osservazioni dirette mediante veicolo ROV per la raccolta di immagini e video georeferenziati ad alta risoluzione per la realizzazione di attività di mappatura e monitoraggio di habitat di pregio ambientale.



La strumentazione di cui è equipaggiata consiste in:
Multibeam R2Sonic, multibeam di quinta generazione con frequenza variabile 200 kHz - 700 kHz (Ultra High Definition) e Profondità di impiego: da 1 m a 500 m.
Le caratteristiche dello strumento consentono di ottenere una risoluzione inferiore al metro a profondità di circa 100 m, con una copertura continua. Lo strumento è interfacciato con sistemi ausiliari con compensazione tridimensionale Applanix e sistema di posizionamento di precisione.

Le attività di rilievo batimetrico tridimensionale effettuate mediante il sistema Multibeam R2sonic 2024 sono supportate dal *Side Scan Sonar Klein 3000. Tale sistema, trainato mediante apposito cavo fino a 500m, opera in prossimità del fondale garantendo una risoluzione centimetrica dei dati acquisiti con Profondità di impiego: da 1 m a 300 m.*

*ROV di classe observer superiore per indagini fino a 400 m. munito di propulsori capaci di operare anche in aree interessate da correnti marine che consente di acquisire immagini (FHD 1920*1080 a 25 fps) e video ad alta risoluzione. Tali informazioni vengono georeferenziate in tempo reale mediante un sistema di posizionamento subacqueo USBL (ultra short baseline).*

Preso atto che la propensione di acquisire dati scientificamente attendibili rappresenta una fase imprescindibile soprattutto operando in un contesto ampio e diversificato rappresentato dal mondo sottomarino che necessita della possibilità di accedere a strumentazioni e laboratori altamente specializzati nel settore ambientale, le potenzialità di convergenze e di sinergie sono veramente molteplici:

lo studio dei processi e meccanismi di degrado di materiali sommersi che implica la vasta conoscenza dell'habitat marino e ritrae un vero contesto di vita naturale, in cui i materiali stessi trovano un nuovo e peculiare sito di giacitura;

lo studio e la sperimentazione di metodi preventivi e di controllo del degrado, con l'obiettivo di limitare il danno e mettere a punto strategie conservative;

la valutazione dell'ambiente e delle sue interazioni con le proprietà costitutive del bene, operazione necessaria nella pianificazione di un progetto di diagnosi e conservazione rivolto a manufatti di provenienza subacquea che può essere realizzato attraverso lo studio dei processi/meccanismi di degrado, valutando l'interazione tra agenti di danno e materiali costitutivi dei beni;

la valutazione dello stato di conservazione attraverso una corretta indagine diagnostica indispensabile per la pianificazione di qualsiasi intervento conservativo e, più in generale, per una corretta gestione, valorizzazione e fruizione del bene.

Infine, i diversi tratti costieri lungo la nostra isola, in cui la concentrazione di relitti e aree archeologiche sommerse risulta particolarmente elevata, manifestano stati conservativi e forme di deterioramento variabili, che si diversificano in relazione alle diverse e mutuabili condizioni di esposizione ambientali in cui il monitoraggio "in situ" ed in tempo reale di parametri ambientali rappresenterebbe un fattore importantissimo per la loro migliore conservazione

Indagare su tutti questi aspetti e condurre quindi uno studio sistematico-ecologico di un dato habitat, rappresenta un approccio metodologico multidisciplinare che consente vasti ambiti di collaborazione.

Archaeology

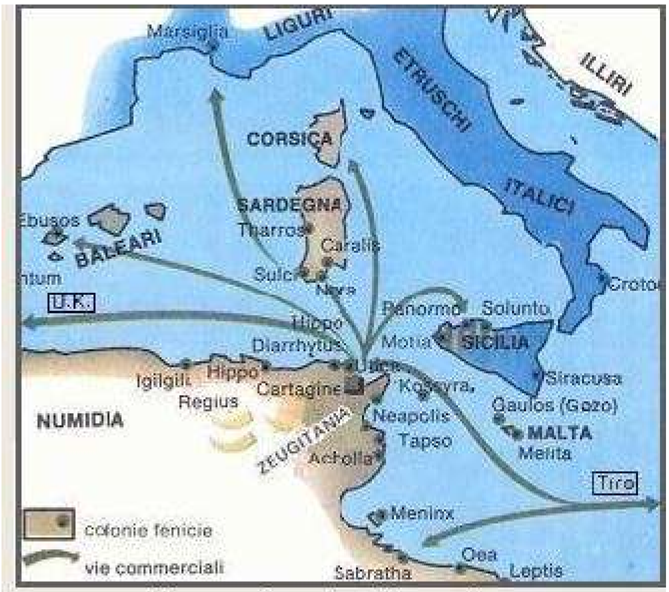
From material culture to marine myths

Francesca Oliveri

Archeologa, Soprintendenza del Mare

francescaoliveri25@gmail.com

Exposure to the dangers of navigation stimulated a strong religious sentiment among sailors in antiquity. Archaeological, iconographic and literary sources testify to a persistent and complex devotional apparatus, generically designated in the Roman world with the term *tutela navis*. It included ceremonies and rituals, officiated both on board and ashore, and the decorative-votive setting of the ships: marks of divinities were affixed on the boats or on their equipment, perhaps to impetrate their protection. Ships indeed, in ancient seafaring societies, were often considered to possess divine spirits which protected mariners from the unpredictability of the sea. Numerous ancient cultures followed various practices which seem to be aimed at gaining the protection of a deity or deities for a vessel, whether it was a river barge, merchant vessel or warship. For the Phoenicians of the first millennium BC maritime and religious concerns were often closely entwined: since Phoenicians' relied on the sea for their economic and political vigour, this is not a surprise, but of very great significance. Phoenicians perceived their vessels as more than simply pieces of timber nailed together to form a platform on which men could conduct their daily lives whilst at sea[1]. [Fig. 1]



L'espansione fenicio-punica

1 Basch 1987

Phoenicians regarded them as sacred entities imbued with a living spirit that needed the protection of a number of gods and goddesses. Two types of divinity were important to ancient mariners: firstly, those whose attributes were somehow seen to facilitate safe travel (such as the goddess Asherah[2] whose association with the moon, a vital navigational aid when travelling at night, made her indispensable to sailors), and, secondly, those who controlled the winds and storms (such as Baal-Haddu/Sapon). While a variety of maritime deities, including 'Semitic Poseidon', Astarte, Tanit and Melqart, had significance for Phoenician sailors, it is the storm deity Baal-Haddu/Sapon, whose totem was a bull and whose cult gave prominence to sacred horns[3]. [Fig.2 - 3]

Baal Saphon is an Ugaritc manifestation of Baal that deals with the control of the atmospheric phenomena such as storms, thunders and lightening. It's not in strict senses a marine divinity but a god that bears a protective and favoring nature for navigators and their maritime wanderings. Archaeological evidence suggests that cults dedicated to Baal-Haddu first came to prominence in the late-16th early 15th centuries BC and quickly spread along the Syrio-Palestinian coast[4]

In religious texts he is recorded as the lord of the sky who governed the rains essential for fertilising the earth and enabling the growth of crops; moreover, as controller of the winds

2 Olyann 1988; Culican 1976; Maier 1986

3 Woolmer 2012; Obbink 1937 ; Yadin 1970

4 Schwemer 2001, 505-511; 2008, 8-9; Herrmann 1999, 132-139; Pettinato 1980, 203-209.

he could aid or hinder maritime voyages [5] Moreover, Mt. Sapon, which is identified with modern Jebel el'Aqra' located forty km north of Ras Shamra on the Syrian coast, rises to a peak of over 1700m. Its great height renders the mountain visible from a considerable distance, and it is accordingly a useful navigational aid for mariners[6] ; some scholars believe in the existence of a lighthouse, turning to the seal stone found at Tell Dab'a to support their conclusion. Although it is far from clear that the seal stone does depict any kind of lighthouse, the imagery certainly strengthens the impression of an intimate link between Baal-Sapon and mariners. The seal stone presents the deity striding out from his mountain fortress atop Mt. Sapon: behind him is his totem animal, a bull, beneath him are a snake and lion, both totems of the goddess Asherah, whilst in front of him is a small sailed vessel[7] and it is assumed that the boat should be under the god's protection. In Ptolemaic Egypt Baal Saphon was related with *Zeus Kasios*, an oriental manifestation of Zeus which worship spread all over the oriental Mediterranean, not only in Ugarit and Egypt but also into the islands of Corcyra and Delos[8]. This Oriental form of the Greek god Zeus, was worshipped in Mountain Kasios,between Egypt and Syria, located it in the Mediterranean coastline[9] and was also found in the Egyptian Mount Kasios which points out to a cultural and religious diffusion movement, due to geographical proximity of both centers of cult and also due to the establishment of syropalestinian populations in Egypt since the times of the Hyksos invasion, which made easy the religious acculturation and syncretism between divinities[10].
Zeus Kasios's avatar is often depicted under the form of a young man's image showing clear affinities with another Greek god, the young Apollo and to Harpocrates, the Hellenized designation of the Egyptian god Horus. [Fig. 4A]

5 Fantar 1977, 43-94.

6 Oliveira 2016 ; Day 2002, 107-16

7 Porada 1984, 485-486

8 Oliveira 2016

9 Semple 1927

10 Perea Yébenes 2004

All the region of the Delta was deeply Hellenized since the 3rd century B.C. onwards and for centuries it was a crossroad for Semitic and Near Eastern contacts thus facilitating the introduction and diffusion of Asiatic divinities that assume similar functions within the Egyptian pantheon.
This manifestation of Zeus is found in Egypt, mainly in locations where Baal Saphon was worshipped, most of them located in emplacements related to sea harbours or in the proximity of the Mediterranean Sea. This fact may be a lead to determine that Zeus Kasios in spite of not being a sea god was indeed a protective deity of the seafarers of the Mediterranean. This cult extended itself through the Mediterranean basin until the Roman era under the name of Jupiter Cassius.
Anchors frequently appear among the vectors of magical-religious symbologies, as shown by the numerous stocks inscribed with the names of divinities, expressed both explicitly and symbolically, through particular decorative devices.
Among the deities most frequently attested are *Zeus-Iuppiter* and *Aphrodite Euploia* or *Sozousa*. And among the anchor stocks found by the Soprintendenza del Mare one, coming from the waters of San Vito Lo Capo, shows inscribed the name *Zeus Kasios*[11].

In the autumn of 2004, the Carabinieri of the Nucleo Tutela Patrimonio Culturale, with the help of the colleagues of the Nucleo Subacqueo di Messina, have recovered, at a depth of -150 m from Cala Tonda, off the island of Favignana (Trapani), a lead anchor with inscription in Greek engraved on one of the arms [12]. [Fig. 5]

Cala Tonda, located in the direction of Marettimo, is a natural landing place being, thanks to its shape, one of the most protected coves of Favignana, even when the wind blows strong, but also indicative of the presence of a Greek ship of the fourth century BC, in transit in the waters of Favignana, on the route between Mozia and mainland Italy. The presence of inscriptions and/or symbols with an apotropaic or decorative value on lead anchors is a widespread custom in the ancient world[13]. These elements can often constitute a link with the divinity to which the object was consecrated. Euploia identifies Aphrodite in its auspicious marine connotation[14]: in fact, as a goddess of the sea and the sky, who provided

11 Sara' 2008, p.22, n. 16

12 Oliveri 2015

13 Gianfrotta-Pomey 1981

14 Musti 2002, p. 34-40; see E. Mainardi , *Osservazioni sul culto di Euploia*, MGR, 14, 1989, 123-124, part. 128-137 on the cult of Aphrodite Cnidia and her characters as Euploia, 137 s. on the cult of Isis Euploia in Delos at the

aid during navigation, Aphrodite was invoked with the epithet of Euploia (Lady of Good Navigation), Epilimenia (Lady of the Port), and Pontia (Lady of the Sea) and sanctuaries dedicated to her rose in the most important port cities[15]. The oldest was that of Naukratis, a large commercial emporium on the Nile delta, founded around 600 BC, frequented by Greeks and Phoenicians, disseminators of the cult dedicated to her. Other sanctuaries to the goddess in marine connotation, such as Euploia, stood in Paphos (about which an anecdote reported by Athenaeum (15.675f - 76a) tells us the adventure of the merchant Herostratos) and in Knidos, famous for the cult statue by Prassiteles, the first classical sculptor to show the nudity of the goddess [Fig. 4B]. Reknown are the verses with which Getulico, in the first century A.D. asked marine Aphrodite for benevolence[16] or from the same period come inscriptions with dedications to Euploia to ensure good fortune and a good journey, on the walls of Pompei. In Sicily at present there are no comparisons with other anchors bearing the term *Euploia*, but there are testimonies with the names of Venus: a lead anchor stump of fixed type from Isola delle Femmine, can be found at the Archaeological Museum of Palermo with inscriptions with the names of two gods *Veneri/Iovi*[17] and recently from Panarea, one of the Aeolian Islands, a leaden anchor stock that bears in Latin the letters *SALVTEM* (salvation)[18][Fig. 6].

From Sardinia comes instead the stock with the inscription *SOTIRA* (savioures), recovered in 1965 at Isola dei Cavoli, Villasimius, Cagliari. In Spain is known a strain from Cartagena with the inscription *Aphrodite Sozousa* (Aphrodite Saviouress)[19].

Also some decorative motifs such as dolphins and shells can refer to the same cult of the goddess; above all the great diffusion on the anchors of the astragals motif is to be linked to the "Venus's blow" that gave the highest score in the most popular gambling of antiquity [20],

end of the second century BC and on the assimilation with Aphrodite Euploia, goddess who moves between the connotations of the auspicious sea, good navigation and those that favor productivity and abundance.

15 Larson 2007, 123.

16 Getulicus, *To Afrodite Euploia*, XXV : *Guardian of the coast, I offer you these sweets, gifts of a poor sacrifice; for tomorrow I will cross the wide wave of the Ionian Sea, hurrying into the arms of our Eidothea. Shine with favor on my love as on my main tree, O Cypride, Lady of the alcove and the beach.*

17 Sarà 2008

18 La Rocca 2016

19 Gianfrotta 1981.

20 Queyrel 1987, pp. 207-12

similar to the game of dice: the games were played with four astragals, each of which had only four useful faces. The jet in which four faces, all different from each other, were obtained was called the "Venus shot". and whoever did it took away the entire plate. It can be hypothesized that in addition to her saving benevolence towards ships and ports, the sailors turned in a particular way to Aphrodite Euploia while performing anchor maneuvers or kept the anchors dedicated to the goddess as "saving anchors" to be used in moments of extreme danger.

On July 2020, from the seabed of San Vito Lo Capo, in the Trapani area, the Soprintendenza del Mare, in collaboration with the Guardia di Finanza and the BCSicilia Association, has carried out an operation to recover an anchor from the Hellenistic-Roman period which presents a dolphin relief decoration on one of the two arms.[Fig. 7B; Fig. 8]



This animal is considered among the marine symbols related to Aphrodite Euploia, one of the most auspicious for navigation.

Among the creatures of the sea, extraordinary resource and way of communication for economic-cultural exchange from the earliest antiquity, the dolphin is believed to be, perhaps also for its marked intelligence, close to the humans; to it has always been attributed a symbolic character, so as to become the protagonist on floor mosaics, wall frescoes, vases and even coins and personal ornamental objects [21]. Numerous are the myths and legends among the populations of the Mediterranean civilizations that see it as the protagonist.

Herodotus, Pausanias, Claudio Eliano, Pliny the Old are the sources that hand down to us the news about aspects and characters of the dolphin, friendly to children and sailors. One of the most famous is the legend of Arione, reported both by Herodotus, and in the Dialogues of Lucian and in the Book of animals by Elianus. The musician of Lesvos, lived between the VII and VI centuries B.C., had reached fame by operating at the court of Periander of Corinth. Wishing to travel, he visited for some time Magna Graecia and Sicily, but at the moment of return, the crew of the ship that transported him home, to take possession of the of its riches, forced him to throw himself into the sea. Only thanks to his melodious singing, a dolphin approached him and on his back led him back to shore[22]. The myth of the

21 Oliveri 2009, pp. 335-36

22 Donati- Pasini 1997, pp. 156-57.

foundation of Delphi is also linked to the intervention of a dolphin; dolphins appears often with good function against disaster also on the anchors. It was a widespread belief among sailors, that the souls of the drowned returned to live in form of dolphin, regaining possession of that vital force that the sea had stolen them. Throughout the Mediterranean basin, from the Palace of Knossos to the Hypogeum of Hal Saflieni of Malta, spiral decorations, rosettes or dolphins are the attributes of the Great Goddess in her benevolent appearance as a bearer of life.[23].

Another anchor, part of the Soprintendenza del Mare collection, probably coming from the waters near Palermo shows a caduceus relief decoration on one of its arms[24]. The caduceus symbol is a rod with two symmetrically intertwined snakes towards the extremity, and at the end two spread wings; in ancient Greco-Roman it was the attribute of heralds and messengers, especially Hermes [Fig.7A].

The origin of the symbol seems to be oriental, then transmitted to the Phoenicians, where it is connected to the cult of Tanit and its shape was different from the one we know today, which dates back to the fifth century BC. In ancient times it was depicted ending in two juxtaposed circles, the first closed, the second open at the top. In Carthage as with the Phoenicians, the Hittites, the Jews, the Egyptians, there are emblems of similar shape to its primitive, and even the representation of the snake or the two intertwined snakes is notoriously common in the ancient Orient.

Symbol of prosperity and peace, the hermetic caduceus is called "golden" in the Homeric Hymns (III, 529) and has the virtue of fascinating the eyes of mortals and putting them to sleep, attracting the dead from the underworld, changing the objects touched into gold, etc.. To it, moreover, many other meanings were given. Fundamental is that, already mentioned, of the attribute of the messengers. In the Romans the word *caduceator* is used to designate the messenger of peace (Liv., XXXII, 32)[25].

Other naval objects of strong cultic value are the leaden horns, which refer to the Mycenaean origins of Mediterranean navigation [Fig. 9A - B].

23 Gimbutas 1999.

24 Gianfrotta 1981, P. 110, fig. 21

25 Donadoni 1966

In the spring of 2008 the local Maritime Office of the Coast Guard, during a patrol, discovered traces of probable archaeological interest at a short distance from the coastline, about 150 m, from the beach near Punta Biscione and at a maximum depth of 2.50 m.

The location of Punta Biscione is already a well-known area of archaeological interest, as an anchorage place in case of difficult sea and adverse conditions, having returned in the past several stocks of anchor of Hellenistic-Roman[26], some in lead and other lithic anchors, now preserved in the Regional Archaeological Museum Baglio Anselmi in Marsala , and was the subject in the eighties of careful reconnaissance campaign by the University of Oxford and the University of Palermo [27]. In fact, one of the young sailors during a dive noticed some wooden remains and in the middle of them a gold coin, which turned out to be a Carthaginian coin with pony and head of Tanit, among the most known and widespread.

The Superintendence of the Sea immediately made a wider survey of the area, but the poor visibility of the day, due to the suspension created by the seabed moved by the sea conditions, did not allow to find the wooden remains; on the contrary, leaden objects appeared, promptly recovered: a sounder, of the type often found on ancient ships and an horn shaped object. The most singular horn-shaped lead object can instead fall into the category of objects with apotropaic function. In fact, the many mortal dangers that navigation entailed for sailors and the constant need to resort to divine help have given rise to a deep religiousness in the seafaring environment, sometimes very close to superstition. It is known that certain practices to ensure the success of navigation and the benevolence of the gods of the sea already began in the shipyard before the ship was launched. The vessel was given the name of the god under whose protection it was entrusted; images of gods were placed both at bow and stern, both painted and carved in relief on metal plates placed presumably on the bow. On the occasion of the housing of the foot of the main mast, one or more coins with auspicious function were introduced inside the hull [28].

26 Falsone, Bound, 1983 , pp. 169-170

27 Falsone, Bound, 1983, p. 161

28 Hornell 1943 ; Kahanoz 2005

Apotropaic meaning also had the custom, still in use today among Mediterranean fishermen, of fixing horns in the bow area. An interesting comparison is given by the image of a ship on the face of Phoenician and Roman coins and various findings of naval horns in lead both on wrecks (Albenga and Punta Scaletta) and sporadic [29].

These are ox horns or other large lead-lined animals presumably in order to be more easily nailed to the ship's deck structure [30]. On the wreck A of Mateille a boar tusk was found that could have had the same purpose [31] ; similar function must have had the goat horn found in the wreck IV of Cala Culip and the one found in the wreck of Guernsey. Prophylactic character could also have had the one carved in the wood of the wreck of Madrague de Giens [32]. A closer comparison comes from a spontaneous delivery of another similar horn from the waters of Mazara del Vallo: this find (h. cm 13) has an internal bone part (bovine?), covered by a bronze foil. Another naval horn comes from Filicudi's seabed and was recovered by Santi Romagnolo, passionate diver, in 2013 and promptly deposited at the Museum of Lipari. The lead horn is broken into two parts, its length 30 cm and its weight 1,3 kg.

Considering that ships and navigation techniques throughout the ancient world are basically those described in Homeric poems and that for centuries that seafaring has not undergone major changes, it is necessary to remember an epithet that Homer often uses to describe an obvious characteristic of ships: orthòkrairos, that is "with erect horns"[33] [Fig. 10].

It has been said about Baal Saphons figurative representations with horns and his inclination to favor mariners: Woolmer notes that the horns adorning the prows of Phoenician ships should be understood as emphasising the ship’s bull-like ferociousness in order to avert the gaze of evil spirits[34]. Near Eastern bulls were so much renowned for their ferociousness, that even a metaphorical representation of their form could ward off evil. The strength and

29 Mas, 1985; fig 116

30 Mouchot 1972, 315-18; figg.8-10

31 Kapitan 1985

32 Gianfrotta 1997, 112

33 Mark 2005

34 Woolmer 2012

ferocious temperament of the ancient near eastern bull is attested by the frequency with which bull hunts are recorded in the chronicles detailing the great achievements of the Assyrian kings; such regular documentation indicates that the hunting of wild bulls was considered a brave and noble activity; a reputation which must have been derived from the bull’s ability to inflict significant damage upon an antagonist. Furthermore, a bull, when preparing to charge, would have lowered its head in order to bring its horns level to its antagonist: it was this aggressive stance that Phoenician shipwrights tried to reflect through the mounting of horns on the prows of their vessels.

But the presence of horns on ancient ships could have also a different and practical motivation behind their existence.

In a relief of the Torlonia Collection, of the beginning of the 3rd century A.D., two horns appear in good evidence on a ship. It is the marble relief, found in Porto representing a merchant ship in full navigation, with the veiling inflated by the wind [Fig. 11].

The ship deploys, between the top of the mast and the *antemna* (flagpole), an additional sail structured in two parts, the *siparum*, with which the wind was more exploited by increasing the speed. What is of interest now is that the two ends of the master shaft's *antemna* terminate each with a twisted horn. Horns finds an appropriate place at the ends of the *antemna*, that the Greek and Latin sources indicate with the terms *κέρας* and *cornu*. Their figurative sense is found in various fields, but in the naval one their recurrent employment, on which is explicit Tertullian, Adv. Marc. 3, 18: *"in antemna ... extremitates cornua vocantur"*, is reflected in the iconographic testimonies[35]. The presence of horn is marked, for example, at the ends of the *antemna* of the ship on the left of the mosaic of the

35 Also used to indicate the *antemna*: Ovid., *Met*. 11, 482; Lucian., *Amores* 6; Achill. Tatius, 3, 1, 1-2. For other reference to *keraiai* (pennoni), known from athenian records of 330 B.C. , see also Casson 1971, pp. 232 e 276.

navicularii Misuenses and on those of the ships of the mosaic of *statio* 46 of the Corporations Square in Ostia; in the same square location, but facing downwards, horns can also be recognized on the ship for animal transportation in the mosaic of Piazza Armerina and on one of a late-imperial bas-relief in the baptistery of Florence. There is evidence of naval horns in depictions of boats already of the beginning of the millennium B.C.[36]

Lead horns were useful for its specific electrical resistivity property which, in some circumstances, could avoid risk of serious damage, that could have been produced by the accumulation of atmospheric electricity, right at the ends of the *antemnas*. Clearly visible at night, the phenomenon, then known in the Mediterranean navigation as "fires of St. Elmo", could occur on the mast and the lines of force of the electric charge could determine a particular corona effect around to the *antemna* tips.

As the phenomenon, tends to occur at the height of violent storms its appearance was considered to be beneficial for the simple reason that the storm often calmed soon after its manifestation[37]. The Greeks regarded it as the manifestation of the Disocuri, Castor and Pollux, sons of the sky god Zeus and protectors of seamen. Homeric Hymn 33 mentions the sailors calling upon the Dioscuri from 'the forepart of the prow'. The points of 'ornamental' horns are an ideal location for the occurrence of St. Elmo's Fire and would have been clearly visible to the crew.

Pliny, who ended his life as commander-in-chief of the Miseno fleet, is demonstrates a precise knowledge of the phenomenon much feared by sailors, who obviously ignored the real causes of it[38]

In the world of ancient navigation densely pervaded by religiosity and superstition, leaden naval horns therefore appear as expressions of empirical knowledge summed up by different experiences, especially meteorological-physical, able to to meet expectations of supernatural protection and probably provide some concrete results. The great anthropological relevance of the horns, generalized and still current seasoned by other allusive meanings, against the evil, expressed with reproductions or with the skirmish gesture of the bent fingers of the hand, except the index finger and little finger, or in others forms, authorizes to think that the saving potentialities attributed to it probably had originates from distant protective applications in top positions, both in the sea that on earth, in the face of terrifying natural phenomena.

And finally, still other finds, albeit probably destined for trade, such as the *orichalcum* ingots evoke the Homeric legends and the submerged world of Atlantis. At the end of 2014 in the seas of Sicily, in the waters of C.da Bulala, in shallow waters about 300 meters off the coast of Gela, the Rhodium-Cretan colony founded in the early seventh century B.C.,were found, thanks to a report of a local enthusiast diver and to the prompt intervention of the

36 For the Ostia mosaics: Becatti 1961, tavv. 178 e 179; Basch 1987, figg. 1093-1094;

37 Mouchot 1970, pp. 316-317; Gianfrotta 2018

38 Plin., *n. h.* ii, 101; Mart., *Liber spect.* xxvi e Stat., *Silv.* iii, 2, 8-12 (v. 9 … *antemnae gemino considite cornu*).

divers and archaeologists of the Superintendence of the Sea, 90 ingots (or rods) of *orichalcum* , whose dimensions range from 23 to 30 cm., [Fig. 12A -B].

They were part of the cargo of a ship that had probably arrived in Sicily following a route from Greece or from Asia Minor. The discovery is among the most important for the rarity of findings of this precious metal known so far only through ancient sources and some, rare, ornamental small objects. For centuries, experts have discussed on the composition and origin of the metal. According to the ancient Greeks, *orichalcum* was invented by Cadmus, the mythical founder andfirst king of Thebes, whose Acropolis was originally called Cadmeia in his honor. It is an alloy of copper and zinc, similar to today's brass, produced in antiquity by cementation, obtained by the reaction of zinc, coal and copper, but considered second only to gold for beauty and economic value. This is what Plato reports in the dialogue Crizia, who describes it as one of the major productions of the legendary island of Atlantis, which the gods had assigned to Poseidon and which he had baptized with the name of his eldest son, Atlas.

The island had been blessed with all the gifts necessary for life and abundant mineral and metal deposits, including the dazzling oricalco that covered the three outer walls of the temple of Poseidon: the first was made of brass, the second of pond, and the third, which included the whole citadel, a flash of red oricalcum light". The interior walls, pillars and attics of the temple were also completely covered in oricalcum, and the roof with gold, silver, and oricalco. In the center of the temple a column of oricalcum, on which were engraved the laws of Poseidon. (Crit. 116-119) The name, which derives from from the Greek *oreichalkos* (consisting of *oros*, mount and *chalkos*, copper), already appears in the Homeric Hymn to Aphrodite (VI, 5-9): the goddess prepares for the council of the gods assisted by the Horae, daughters of Zeus, which make her wear divine garments, placing the perforated lobes *orichalcum* flowers... The term is also used by Pseudo - Esiodus, in the poem *The shield*, that narrates the fight between Heracles and Cycnus, son of Ares, describing the armor of shiny orichalcum, beautiful gift made by Hephaestus ... (120-121). In Virgil's Aeneid (XII, 21) the armor that Turno wears is in "golden and white orichalcum";

while the Jewish historian of the first century Yoseph ben Mattityahu (Joseph Flavius) narrates in his "Jewish Antiquities" (Book VIII, 88) that the vases of the temple of Solomon were of orichalcum; the artisan of Tyre, Cheiròm, particularly skilled in the working of precious metals, modelled basins, forks and every other bronze instrument that in splendour and beauty was like gold.

The 80 ingots of oricalcum from Gela have revealed through fluorescence X-ray analysis a composition for 75% of copper and 15% zinc, with traces of lead and nickel. The concomitant presence of woods belonging to the hull confirms the fact that they were part of a ship's cargo, which is possible to date thanks to the presence of some specific ceramic finds, among which a Corinthian imported *exaleiptron* or *kothon* with geometric decoration attributable to the second half of the sixth century B.C.

Figure caption
Fig. 1 - Mediterranean Sea routes in the Phoenician period
Fig. 2 - Baal Saphon (Louvre Museum)
Fig. 3 - Asherah or Anat (Louvre Museum)
Fig. 4 a -b Zeus Kasios and the Aphrodite of Cnidus
Fig. 5 - the Euploia anchor
Fig. 6 - the Salutem anchor
Fig. 7a -b Anchor stocks with caduceus symbol and dolphin decoration
Fig. 8 - Recovery of the dolphin anchor
Fig. 9a - b - Naval horns from Petrosino and Filicudi
Fig. 10 - Sidonian coins with horned ships
Fig. 11 - Torlonia collection relief with naval horns
Fig. 12 a - b - Orichalcum ingots from the archaic Gela shipwreck

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The Punic ship of Lilybaeum: new data and hypotheses for the archaeological research

Maria Grazia Griffo
Parco archeologico di Lilibeo-Marsala
mariagraziagriffo@gmail.com

On the occasion of the new exhibition layout of the Lilibeo Museum (2016/17) which entailed the finds reordering based on the contexts of discovery and their integration through the recovery of many unpublished and never before exhibited finds, different genres of materials pertinent to both the on-board equipment and the structure of the Punic ship were "rediscovered" (figg. 1, 2 a-b).

Furthermore, important structural elements of the so-called Sister Ship, and a selection and separation of the Punic Ship finds from those materials recognized as cargo or endowment of other wrecks found off Punta Scario (Isola Grande, Stagnone di Marsala) was made, around the site of the wreck itself, defined in a picturesque way "the ship cemetery" (fig. 3).

The selection and integration of the finds to be exhibited, according to new strictly stratigraphic criteria, involved study and research and, at the same time, opened many questions, not all resolved, concerning: the chronology of the wreck; the method of ship manufacturing; the life on board the ship; the type of boat to which the *Lilybaeum* Ship would have belonged, as an extraordinary testimony of the ancient seafaring in the Mediterranean.

Moreover, the emerged problems in recent years regarding the conservation conditions of the hull woods, with halos around the nail heads, signs of distortion of some structural elements and, lastly, the crumbling of organic materials, such as esparto rope tops and twigs of *Phillyrea,* subjected to preliminary conservation interventions for the exhibition "*Carthago. Il mito immortale*" (Colosseum Archaeological Park, September 2019-March 2020), have constituted important opportunities to always keep attention on the Punic Shipwreck.

In this regard it is worth mentioning the scientific activities in progress, carried out in collaboration with some researchers of STEBICEF Department of the University of Palermo in the archaeometric sector, of Fermi Center in Rome for the 3D scans of a garboard, and also the diagnostic analyzes on the degradation of woods and metals, conducted by the Camille Jullian Center, CNRS Aix-Marseille University, in collaboration with the ARC Nucléart Center of Grenoble, for the purpose of planning restoration interventions.

Maintenance and cleaning of the wreck were also carried out in 2016, under the supervision of the CRPR thanks to the sponsorship of Cantine Pellegrino, whose owner, Pietro Romano Alagna, was one of the main patrons of H. Frost's mission (fig. 4).

The discovery

The discovery of the Punic Ship, like any adventure of this kind, begins with a casual discovery, which occurred during the sand dredging operations off the Isola Grande in the "Stagnone" Lagoon of Marsala. Miss Honor, with typically British irony, used to say that the wrecks had been discovered by the crew of a sand dredger. Captain Diego Bonini, dredging the sandy bottoms just off the Stagnone (Punta Scario, Isola Grande), came across some woods and tiles and showed them to Edoardo Lipari, administrator of the island of Mozia for the Whitaker Foundation.

In 1969, while Honor Frost was by chance in Mozia with Gerhard Kapitän, E. Lipari and D. Bonini showed her the site of the wrecks, one of which, marked by the presence of tiles, must have belonged to a cargo ship.[1]

When Frost and Kapitän returned in 1970 to conduct the first underwater investigations, they found no the "tile wreck", submerged by the sand dunes due to the movements of the currents, but, on the other hand, they identified many other wrecks, without commercial cargo, perhaps to relate to war events. For this reason, the stretch of shallow and sandy bottom was called "the cemetery of ships" (fig. 5).

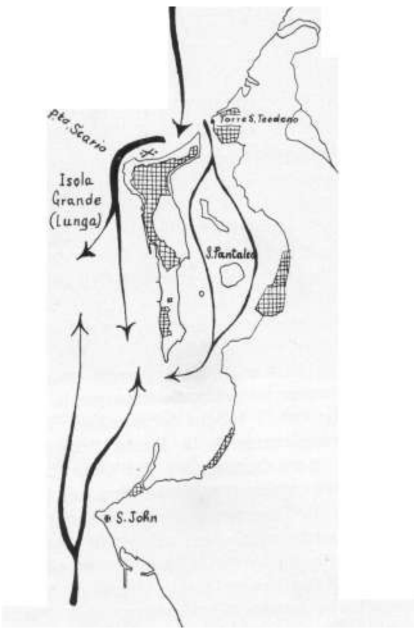
Thus began the venture of Honor Frost, commissioned by the British School at Rome to lead the mission for the excavation and recovery of the wrecks in collaboration with the Department of Antiquities of Western Sicily.

The Punic ship was discovered by chance almost at the end of the first campaign, on the 7th August 1971, by the photographer of the mission, David Singmaster, who saw a large piece of wood emerge between two heaps of ballast stones, in which later was recognized the stern of the ship (fig. 6). Three excavations followed, completed in 1974 with the recovery of some parts of the so-called Sister Ship, discovered 70 m south of the Punic Ship.[2]

The context

From the sources (Polyb. I, 46-47) we know that, due to the shallow and sandy bottoms that surrounded the ancient *Lilybaeum* and the sea currents present between the Egadi Islands and the coast of Sicily (fig. 7), the ships were obliged to follow a very specific route to enter the port outside the city, today called “Punta d'Alga”, due to the narrow strip of land covered with algae that borders it.

The route, starting from Favignana, the ancient *Aigussa*, skirted the Isola Grande externally, to head inside the lagoon, whose mouth was well protected by a pier that extended the island towards the promontory of Punta d'Alga.

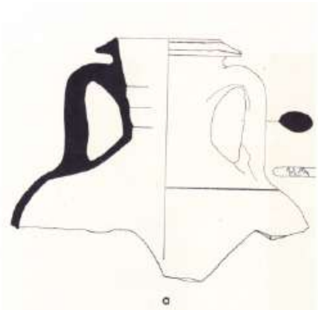


As it is well known, the sinking of the Punic Ship was related to the events of the First Punic War: the siege of *Lilybaeum* (250 BC), which involved the blockade of the port by the Romans (repeatedly forced by Hannibal Rodio's fast *liburnian*), or the Battle of the Egadi, which on 10 March 241 BC ended the conflict. It is in fact presumed that, after the defeat, some Carthaginian ships sought shelter in the *Lilybaeum* harbour and were sunk by the Romans, who launched in pursuit of them.[3]

The hypothesis, certainly fascinating, is based on the assumption that the wreck is dated around the middle of the 3rd Century BC, but the question is complex and the British mission already approached the problem critically and expounded it in the report of the excavations, published in 1981.

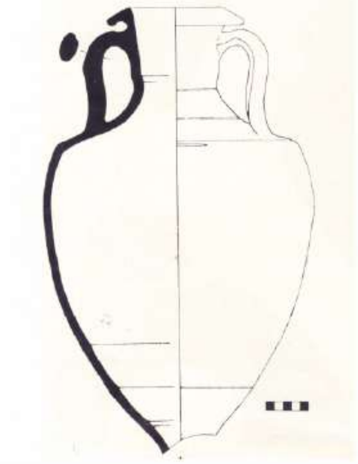
The dating

The main elements on which the dating of the wreck was based are the following: the radiocarbon tests, the paleography of alphabetic signs, the study of the materials that made up the ship's cargo and the equipment on board.

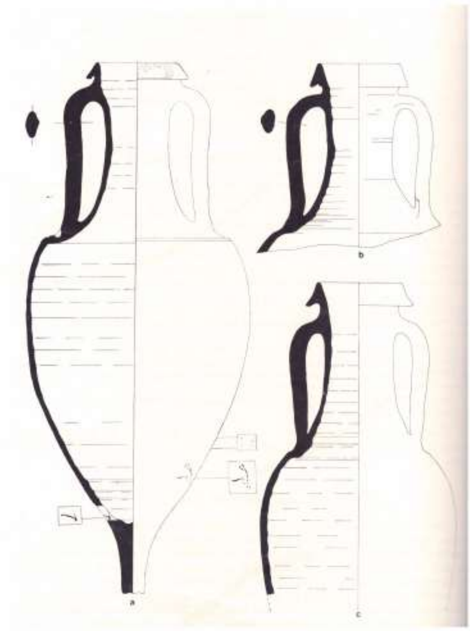


The C14 investigations were carried out on three twigs of the dunnage and on wooden fragments of the ship's structure (keel and planking); the analyzes were crossed and repeated in two laboratories, the Harwell Division of Nuclear Energy Atomic Energy and the Research Laboratory of the British Museum in London and reported the same result: 235 ± 65 BC.

The paleographic study of the letters of the Phoenician Punic alphabet, conducted by W. Johnstone, traced the chronological range to 300/250 BC.[4]



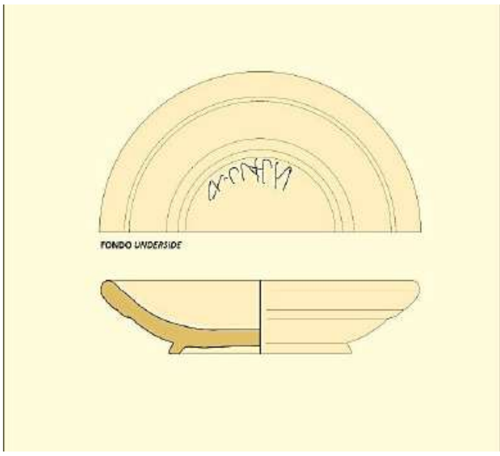
More problematic are the data that emerged from the study of tableware and amphorae, conducted by W. Culicun and J. Curtis, who reached conclusions that are still valid today: even if the oldest materials date back to the third century BC, the most recent can be attributed to 200-120 BC, it follows that the most reliable dating of the wreck goes back to the late 3rd-first half of the 2nd Century BC.[5]



Going into detail, it is noted that the amphorae found in close association with the hull are attributable to two distinct groups from a chronological point of view.[6] One, datable to the last decades of the 3rd century, consists of amphorae of the Greek Italic type VC, comparable to the wreck of Cala Rossa-Terrasini (type MGS VI Vandermersch / Will 1B), produced in Campania-Latial area and Bruttium and characterized by Latin stamps, like our M.VAL. (MARCI VALERI) (fig. 8).

The other, dating from around the second half of the 2nd century, is composed of late Greco-Italic amphorae/Will D (fig. 9)

and Punic amphorae Ramon T-7.4.2.1, T-7.4.3.1, T-7.3.2.1.[7] Also the typological and archaeometric studies carried out by Gloria Olcese distinguish the Greco-Italic amphorae of the Punic Ship into two very different groups, one dated to the first half of the 3rd, the other to the 3rd-2nd century BC.[8]



The kitchen and table ceramics, that presumably constituted the on-board equipment, have the same wide chronological range: alongside black glazed productions Campana A or Petites Estampilles, datable to the 3rd century BC, there are thin-walled cups of 2nd century BC, coarse ware cooking pots and tableware, especially beakers, datable to the Republican age (2nd-1st century BC), a mortar with inscribed inscription in Osco-Campanian characters attributed to the mid-2nd century BC (fig. 10), and also a moulded lamp, the dating of which cannot go back beyond the last quarter of the 2nd century (fig. 11).

It is interesting to underline that Honor Frost had already reached the same conclusions elaborated in the later studies
"*The pottery is of little help because in William's Culican view based on all the sherds we lifted, even those from the surface of the seabed, the consensus dating sholud be late (rather than mid-) 3rd to late 2nd century BC...once again, we are left with the choice of either accepting the date of 241 BC or awaiting the evidence of further comparable excavations*".[9]
One wonders if it is possible that an overlapping of wrecks has occurred, or an intrusion of residual materials due to the frequentation of the area, as suggested by the comparison between the Greek-Italic transition amphorae founded in the Punic shipwreck and those found nearby, eg. near the Tile Wreck. H. Frost excludes it, explaining the strictly stratigraphic method adopted to distinguish the materials strictly pertinent to the wreck from the intrusive ones.[10]

The architecture of the ship

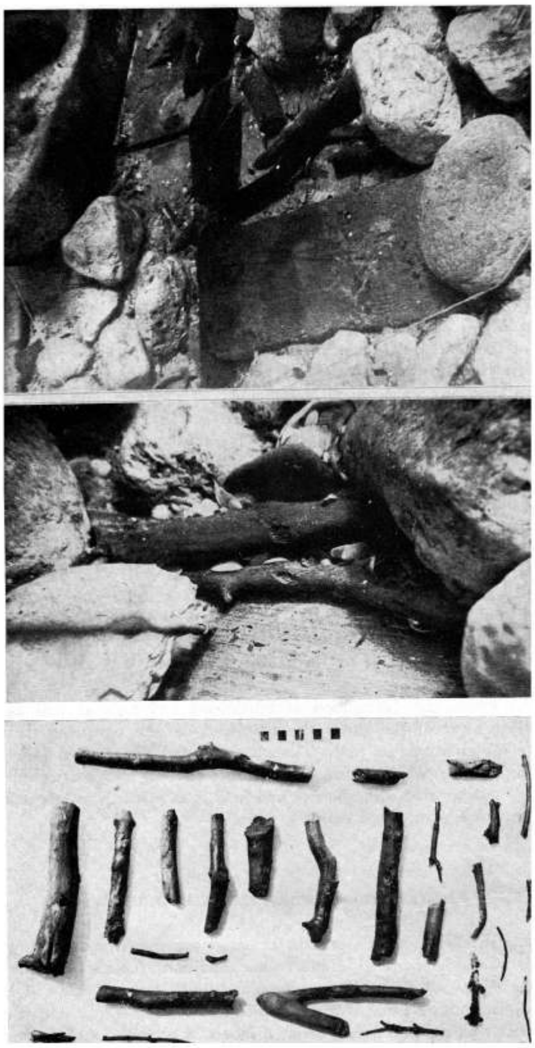
As it is known, the wreck is of an extraordinary importance as it documents the manufacturing method of ancient ships and in particular the skill of Punic naval carpenters. The stern part and the port side of the ship have been preserved, for about ten meters in length and three in width.

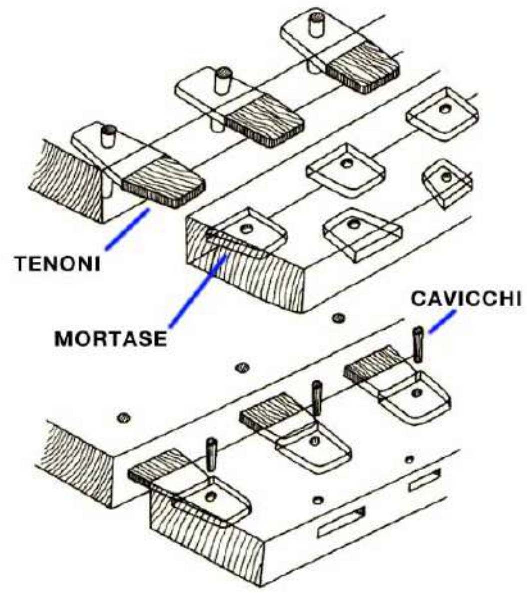
At the time of discovery, the hull was cluttered with ballast stones, consisting largely of pebbles and a small percentage of volcanic rocks, most likely coming as a whole from the campanian-latial coasts and not from Pantelleria, as it was assumed first. The presence of ballast, normally used to stabilize the weight of the boat, together with the smallness of the load, consisting of transport amphorae and fragments of tableware, allowed at first to exclude the hypothesis that it was a merchantship. The stones were placed in the hold on top of a layer of cut branches that served to protect the hull, like a kind of dunnage (fig. 12).

It was noted that part of the resinous putty, which was used as an adhesive and to close the cracks between the woods, remained attached to the ballast stones and the branches on the bottom of the ship: undoubted evidence of the haste with which the ship was launched. The fact that these branches were still green at the time of the discovery was alleged as proof that the boat sank shortly after the launch.

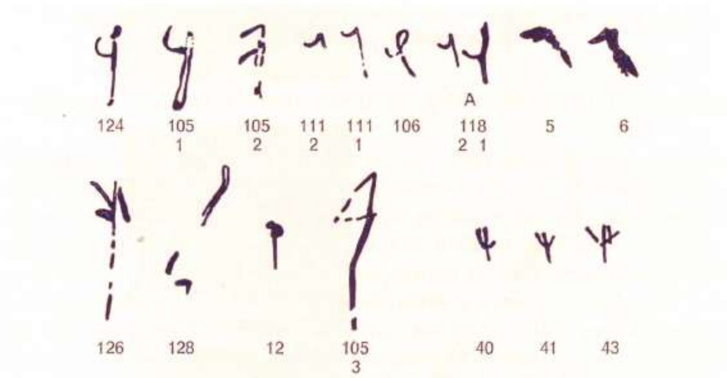
The hull was built according to the technique, typical of the ancient world, called "shell first", based on the partial construction of the planking and the subsequent insertion of the internal structure.

To the main beam, known as the keel, the planking courses were hooked with the "tenon and mortise" system, consisting of interlocking elements: the tenons, hardwood (oak) tabs inserted in special joints, the mortises, made in the thickness of the planks. The tenons were then blocked by wooden dowels into which the nails were inserted (fig. 13).



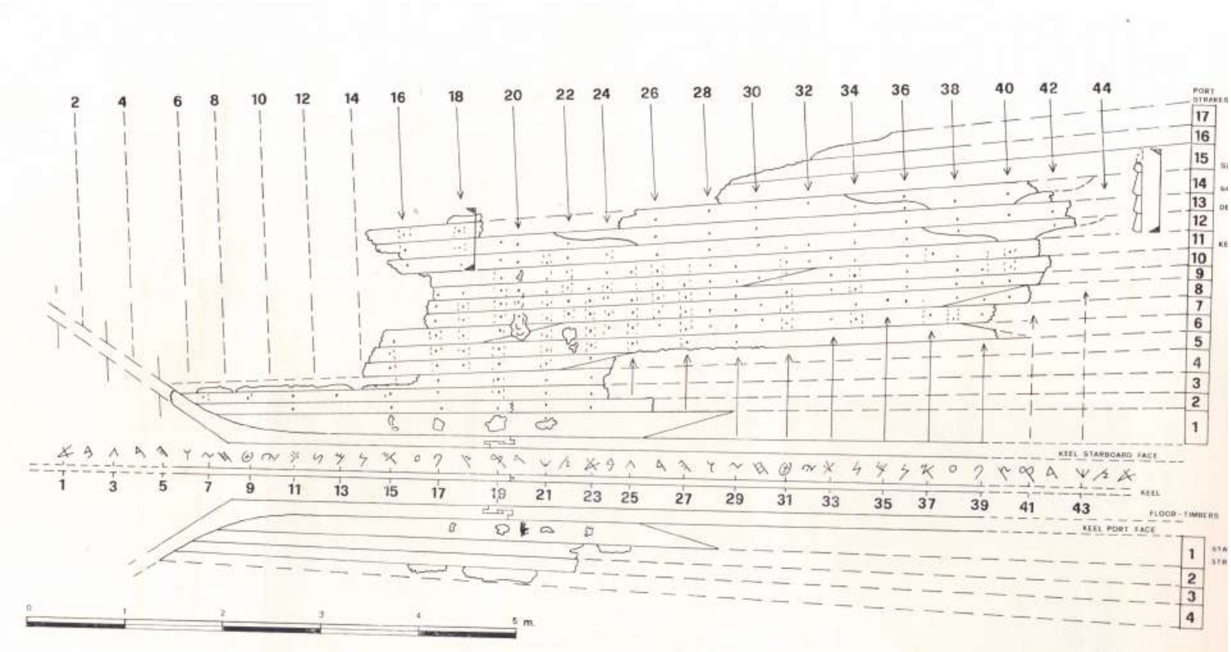


One of the most interesting features of this ship are the geometric signs and guidelines painted or engraved and the letters of the Phoenician-Punic alphabet painted, to guide the construction phases. They are distinguished: geometric signs and letters that identified the position of the floors; alphabetic signs in different combinations, of one, two or three letters, which most likely identified the different manufacturing phases of the ship.



Out of 200 signs, about 30-40 seem to be relevant to the Phoenician-Punic alphabet, visible in whole or in part. Only seven are used with certainty: bet (2), he, waw (7), kap, lamed, qop, and res (fig. 14). Thanks to this study, 2 new words have

been added to the Phoenician lexicon known up to now: bhr (keel) and waw (nail). Infact both the letter waw and the double waw occur in the points where a nail appears, proving that with that letter was intended to indicate its position.
The paleography of the letters indicates a dating between 300 and 250 BC. As the place of origin in the Phoenicio-Punic world, the balance of possibilities points to the central Mediterranean, Sicily itself being a probable candidate.
The construction phases of the ship was possible thanks to the study of the signs and letters: first of all the alphabetic signs were traced in sequence on the left side of the keel to mark the position of the frames from the beginning (fig. 15).



Then they proceeded with the insertion of the garboards, first the starboard, then the port garboard. In the next phase eleven parallel sided planks were attached, some of which as a prefabricated unit. When the construction of the hull reached the eleventh course, the alphabetic signs were reproduced inside in order to allow the carpenters to insert the internal skeleton of the ship, consisting of floor-timbers and ribs, respectively the lowest and the highest part of the ordinates, placed alternately. These were fixed with putty, used both as a filler and an adhesive, and also with wooden dowels that functioned as a sort of plugs with nails inside, riveted from the outside inwards and folded. The six courses of planking above the eleventh were characterized by the deflector edge, which was used to divert the water that broke on the hull outwards to increase its speed and the ability to slide into the sea.
The partial prefabrication of the planking is also documented by the circular imprints left by the bottom of a pot soiled with paint between two courses of planking in different points of the hull, pertinent to the curved area: it is evident that the paint pot must have been placed when the boards were joined on a horizontal plane.[11]

The Punic Ship is therefore an extraordinary archaeological testimony of what is reported by ancient sources regarding the skill of Punic naval carpenters and the speed of ship building during the First Punic War (Pliny NH, XVI, 192; Polybius I, 20 and 59, 8).

As for the materials used, the planking was made with *Pinus nigra* and *silvestris*, the floor-timbers with oak and maple wood, the stems and the keel with pine and maple, in the keel used in a different way, being made of maple the lateral parts, the central part in pine.

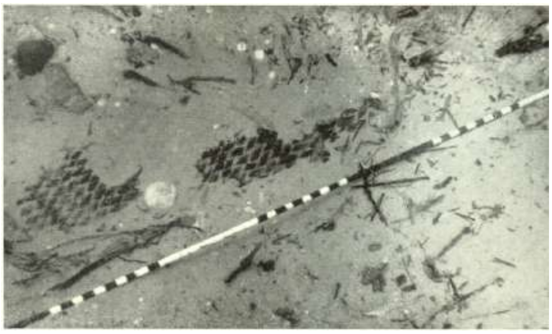
The tenons and dowels, that had to be particularly sturdy, were made of oak. It seems that the combination of soft and malleable woods for the planking and the central part of the keel and hard and robust woods for the structural parts was common in ancient naval carpentry. Beech, Turkey oak, pistachio, walnut and cedar were also used in the superstructure. The external part of the hull was covered with lead sheets (fig. 16), fixed with bronze nails, to prevent the woods from being attacked underwater by the seaworm, the feared *teredo navalis*, while a waterproofing fabric, impregnated with a resinous substance, was between the planking and the metallic coating, as evidenced by the finding of thick layers of fabric soaked in resin in the Sister Ship. In reality, the lead sheating is a characteristic of cargo ships, as documented by the wrecks of Kyrenia, Madrague de Giens, Mahdia, rather than the combat ones, considering that the latter would have been weighed down and made less fast by the leaden plates, moreover the cargo ships were more exposed to *teredo navalis* due to long stays at sea.[12]

The plant material

We can get an idea about the life on board, the eating habits and activities of the sailors, and also about the ship's equipment, through the organic materials found in huge quantities in the wreck. Among these, a small esparto broom, a vegetable fiber still used today for the manufacture of baskets (fig. 17). Ropes and hawsers of various thicknesses were made of the same material, which could be used for anchoring, or to reinforce parts of the hull (fig. 18).

The cordage was spliced, that is braided and reinforced, thanks to a wooden instrument ending in a point, found on board, still used today and called marlin spike (fig. 19).

There has been much discussion on the presence in the Marsala vessel of *Cannabis*, found in the form of yellow stems, both in the cavity of the keel together with food remains, and inside two baskets in woven vegetable fiber, very similar to the Tunisian "coffe" (fig. 20).



In reality, the doubt remains that it was actually *Cannabis sativa*, a variety of *Cannabinaceae* rich in beneficial and medicinal properties, given that some organic characteristics of the plant are no longer recognizable due to the long stay in an anaerobic marine environment (fig. 21).

Honor Frost hypothesized that *Cannabis* leaves were used to make an infusion, an invigorating drink that gave courage and strength to men who were about to fight, or to face complicated and exhausting maneuvers with the oars.

The diet on board the ship

From the bones of animals recovered (fig. 22), cut into pieces as they have already been slaughtered, we deduce that the diet of the sailors was based on meat from sheep, beef, pigs, sheep goats and venison, grilled or pre-cooked with the salting method, because no pans suitable for cooking meat, but rather small pots were found. On the other hand, logs of firewood and coals document the presence of a hearth that could be used to cook on the grill.

H. Frost thinks it probable that the head of a cow and the head of a pig were pre-cooked with the method of salting and smoking. However, the same data could mean the presence of live animals on board, both in the aforementioned case of cattle and pig, and in the case of a horse, of which one premolar and the right metacarpus are preserved. Signs of slaughter are instead evident on a rib of sus-scrofa and on a lumbar vertebra of ovis-goat, cut across its length like a slaughtered carcass.

Faced with a diet based mainly on the consumption of meat, the vertebrae of a sea bream and a raia were found which testify that fish had also arrived in the ship's kitchen.

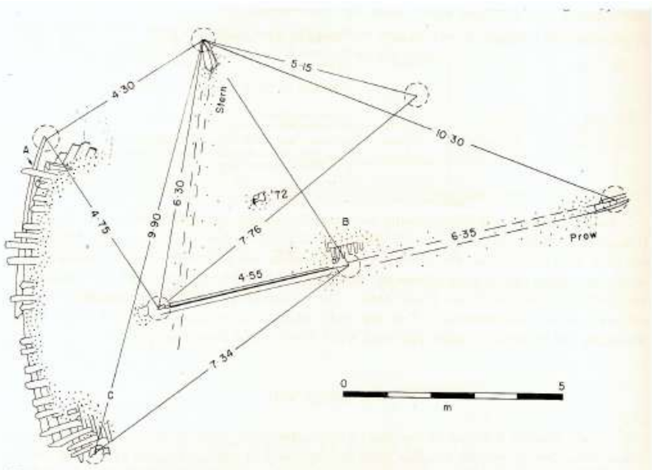
Wine certainly accompanied meals, judging by the presence of resin-coated wine amphorae, sealed in two cases with corks (fig. 23).

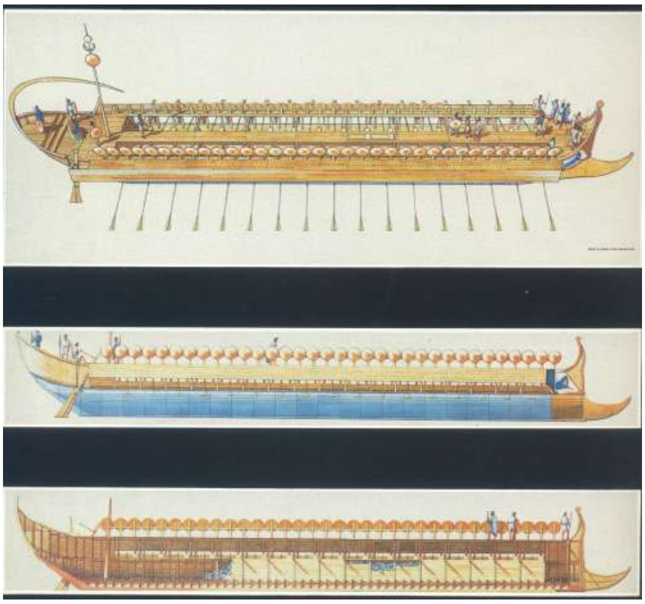
The absence of fresh fruit pits and the presence instead of olive pits and walnut shells in the middle of the branches that protected the hull from the ballast, probable hasty meal of naval carpenters, could mean that the ship was launched during the autumn months or winter.[13]

The galley had to be located in the center of the hull, and not in the aft part as in all known commercial boats, because in this sector of the wreck the cordage, the remains of meal, fire logs and the onboard pottery, consisting of the typical equipment of the crew, were concentrated: mugs, plates, bowls. The impact that caused the sinking of the ship caused organic light materials such as baskets with Cannabis stems and onboard tools to slide along the keel towards the stern (kitchen area I), while throwing heavier materials overboard, such as tiles and transport amphorae (kitchen area II).[14]

The bow of the "Sister Ship"

A ship so similar to the first that it was defined as a "Sister ship", was found about 70 m from the first, with the keel broken into two parts, thrown at two diametrically opposite angles, so much so as to suggest that this wreck was also sunk violently (fig. 24). While the Punic ship has returned the stern part, the "Sister ship" has preserved the remains of the prow, so thanks to the union of the data, the British Mission tried to reconstruct a single model of ship (fig. 25).





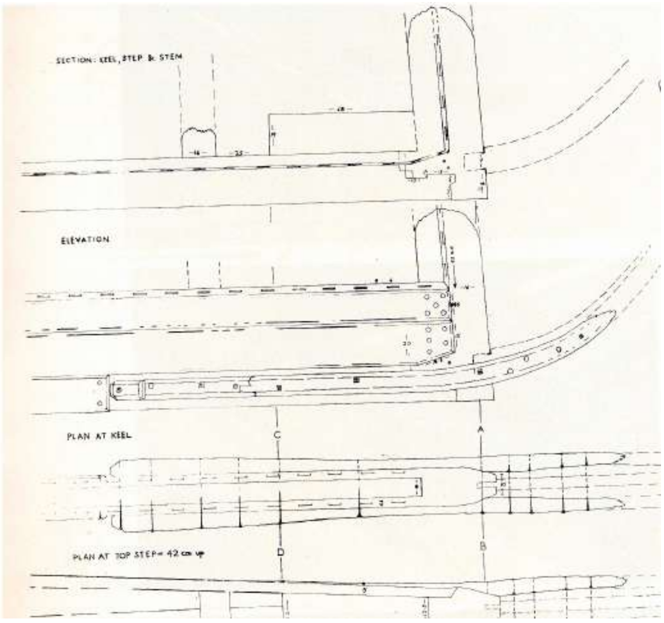
The Punic Ship, in the reconstructive design of the English mission, looks like a typical long and fast warship: the hull is about 35 m long and 4.80 m wide, with a ratio of 1:7 between the two dimensions; the tonnage of 120 tons; propelled by 17 oars on each side, operated by 68 sailors in all, arranged two by two for each oar. The number of oars was calculated on the basis of the total length of the ship and the measure of the interval of 1.50 m.

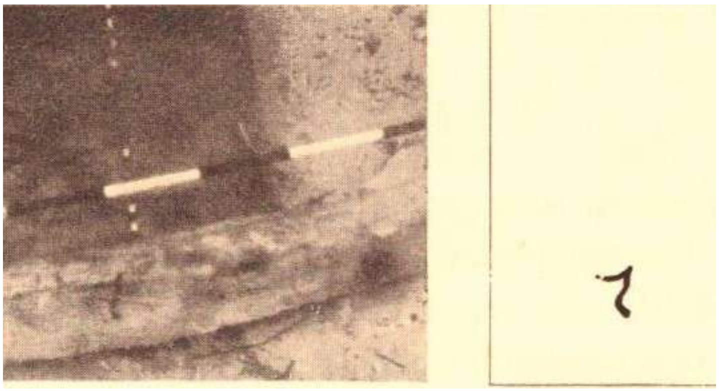
If the Punic "nationality" of the ships has been proven by the presence of letters of the Phoenician-Punic alphabet on the planking courses, on the other hand the supposed origin of the ballast stones, considered as a whole, from the coasts of Rome or Naples could mean that it was a Roman ship built by Punic carpenters, prisoners of war, or that ballast stones from ships, possibly sunk, were reused in Carthaginian shipyards.[15]

Warships? A question still open

Judging by the inclination of the keel of the Punic Ship underwater and also by the position of Sister Ship prow and stern broken in two parts, it would seem that both ships suffered a violent impact. H. Frost supposed that ramming would explain both sinking.

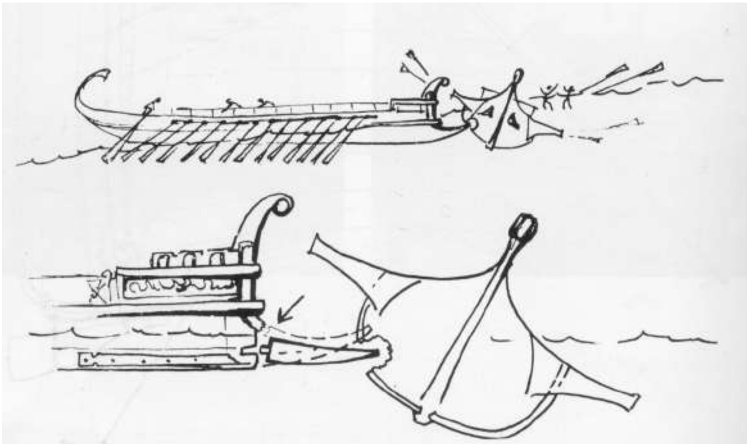
In addition to the circumstances of the shipwrecks, the tapered lines, typical of "long ships", and the supposed absence of a cargo, the ships of *Lilybaeum* have been interpreted as warships above all on the basis of a *rostrum* identified on the Sister Ship. This element looks like an appendage of the stempost, consisting of two timbers curved upwards, nailed to the sides of the keel, like "boar’s tusks", as defined by H. Frost, and a third central element, no longer existing, which was originally connected to the stempost by a tenon inside a mortise and secured to the tusks with nails (fig. 26). The word nail (*waw*) was traced on the starboard tusk, perhaps to remind the carpenter to reinforce the element with a nail (fig. 27).



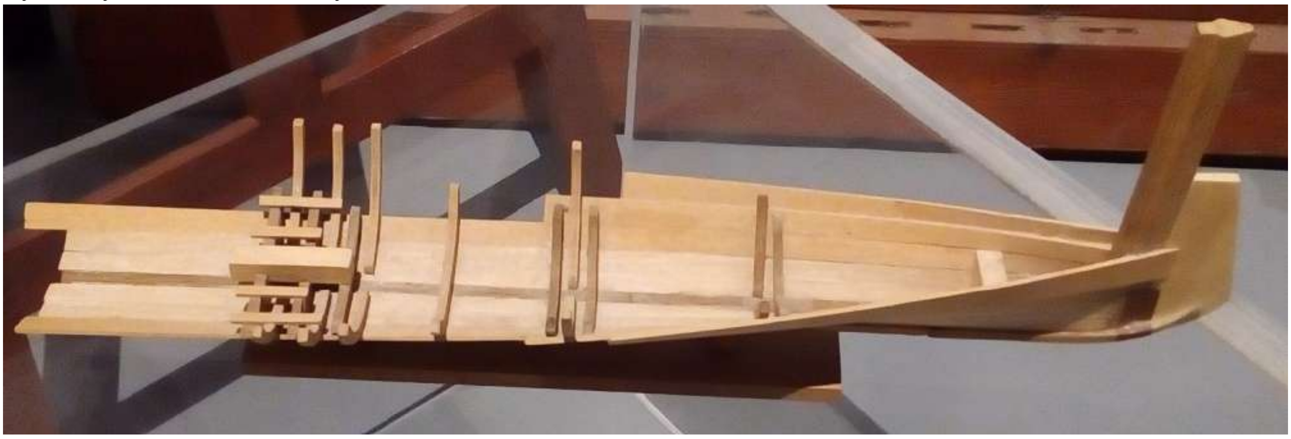


Around these curved timbers thick layers of woven fabric smeared with resin and also a small sheet with this resin still attached between the stempost and the starboard tusk were found, so it is believed that the entire element of bow, interpreted as *rostrum*, was coated with metal to obtain greater resistance.[16]

It has been hypothesized that the function of the central tusk was like a "sting", destined to break after penetrating the hull of the enemy ship, so that with a retreat maneuver the attacking ship could detach itself from the opposing ship, that was sinking due to the hole made by the *rostrum* (fig. 28).



Against this reconstruction, certainly very fascinating, of the wrecks of Marsala as Punic warships, various criticisms and observations have been advanced which essentially lead back to two hypotheses: 1) the appendix had the function of a cutwater, that is an extension of the hull intended to improve navigation speed and protect the bow from the low and sandy bottoms of the *Lilybaeum* coast and the Stagnone lagoon (fig. 29); 2) it could have a nautical function that anticipates bulbous bow in modern ships, which facilitate the penetration of the hull into the water, improving the hydrodynamic efficiency of the boat.



The first thesis was supported by P.G. Dell'Orco, M. Ascani, E.M. Penso, M. Bonino,[17] and lastly by D. Averdung and R.K. Pedersen,[18] who, through the realization of an experimental model, have tried to demonstrate the functionality of this forward element for landing on sandy bottoms and for navigation in the lagoon; the second thesis was proposed by P. Dell'Amico,[19] while Stefano Medas in his book on the Carthaginian navy summarizes the two theses, believing that the prow had both the function of cutting and that of an *antelitteram* "bulb".[20]

The interpretation of the bow element as a combat ram appears really weak, also due to the "single-use" mode proposed by Honor Frost and also supported by Lucien Basch on the basis of the iconographic sources: in fact, once the ship had lost it, after having launched the attack, would have found it impossible to continue fighting. Furthermore, continuous repairs and renovations would have been necessary which would have involved wearing down the end of the keel and the forefoot (the part of the bow directly connected to the keel).[21]

However, the weakness of the spur in the shape of "boar's tusks" emerges above all from the comparison with the robust structure of the trident rams, known through the Athlit rostrum (Israel)[22] and the conspicuous series of finds in the Egadi sea:[23] a powerful tool offensive in bronze, firmly grafted onto a wedge-shaped element placed, as a continuation of the keel, on the extremity of the keel itself, on the low lateral wales and on the forefoot. In this way, the impact force of the ramming was absorbed by the lateral wales and keel, the strongest elements of the hull.

Another element that contrasts with the interpretation of our ships as a combat unit is inherent in the line of the hull, characterized by the V-shaped floor timbers and the prominent keel, elements that increase the hull drift angle, as is usual in the sailing ships.[24]

The combination of these elements implies that the *Lilybaeum* ships, although probably part of a military fleet, were not combat units, but auxiliary boats, propelled both by sail and rowing, which served as support for warships, both for the supply of foodstuffs, and as a reinforcement in the actions of boarding or disturbing the enemy fleet. We know from the sources that in the military fleets there were ships of different types and functions, eg. the *Naves actuariae*, fast and light, built on the model of pirate boats, used for the transport of troops, or the *Naves speculatoriae*, which were used for preliminary patrols to naval battles.

The debate remains open in view of the forthcoming detailed analyzes of the hull remains of both ships still not studied, of the study by XRF and Raman spectroscopy of the letters and signs of the carpenters still visible on the hull, of the three-dimensional reconstruction of the hypothetical Punic ship in its entirety, which will have to be the final outcome of the research project started with the Center Camille Jullian.

Because the history of the Punic *Lilybaeum* ship is still to be written …

Figure caption

fig. 1.a-b. The new layout of the Punic ship (Park Archive)

fig. 2. The materials on board the Punic ship (Park Archive)

fig. 3. Wrecks and sporadic finds from the surrounding areas of the Punic Ship (Park Archive)

fig. 4. Cleaning and maintenance of the shipwreck (Cantine Pellegrino Archive)

fig. 5. The site of the wrecks (Google photo)

fig. 6. The sternpost of the Punic Ship on discovery (Frost 1981, fig. 3)

fig. 7. Sea currents around the harbours of *Lilybaeum*

fig. 8. Greek-Italic amphorae, second half 3rd century BC (Frost 1981, fig. 80 a-b)

fig. 9. Late Greek-Italic amphorae, second half 2nd century BC (Frost 1981, fig. 82)

fig. 10. Mortar with the name of the owner, mid-2nd century BC (Frost 1981, fig. 107.a)

fig. 11. Oil lamp, last quarter 2nd century BC (Park Archive)

fig. 12. Dunnage *in situ* and samples of different variety of plants (Frost 1981, fig. 31)

fig. 13. Tenon and mortise system with wooden dowels

fig. 14. Letters of the Phoenicio-Punic alphabet occurring among the shipwrights marks (Frost 1981, fig. 149)

fig. 15. Plan of the Punic ship with ipothetical sequence of letters on the keel (Frost 1981, fig. 113)

fig. 16. Lead sheating of the hull (Park Archive)

fig. 17. Little esparto besom (Park Archive)

fig. 18. Esparto ropes (Park Archive)

fig. 19. Marlin spike (Park Archive)

fig. 20. Remains of basket underwater (Frost 1981, fig. 24)

fig. 21. Yellowish stems similar to *Cannabis sativa* (Park Archive)

fig. 22. Faunal finds (ph. E. Brai)

fig. 23. Wine amphorae with corks (Park Archive)

fig. 24. Plan of the Sister Ship (Frost 1981, fig. 167)

fig. 25. Punic Ship: reconstructive drawings by M.L. Leek-H. Frost (Marsala Lions Club, 1977-1981)

fig. 26. Sister Ship: the ram structure (Frost 1981, fig. 168)

fig. 27. The word nail (*waw*) on the Sister Ship ram (Frost 1981, fig. 150)

fig. 28. Function of the ram (Frost 1981, fig. 172)

fig. 29. Reconstructive model of the Sister Ship (prof. Marco Bonino, University of Bologna, 2007)

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Wreck "A" of Lido Signorino (Marsala).

Archaeometric analysis and archaeological research on the ship's cargo

Filippo Pisciotta

PhD student Université Aix-Marseille e Università di Palermo.
filippo.pisciotta78@gmail.com

As part of the reorganization of Baglio Anselmi Museum in Marsala (Fig 1) and *the Marsala' Shipwrecks Project,* a project directed by Prof. Fabiola Ardizzone and funded by the Honor Frost Foundation[39], a systematic study has been carried out of all the findings recovered during the underwater excavation campaigns, conductedby Gianfranco Purpura in the years between 1983 and 1986, of the two wrecks "A" and "B" in the Berbaro district (Lido Signorino) with the aim of making a contribution to our knowledge on trade, which affected Sicily during the Islamic and Norman ages[40]. The study provided for an interdisciplinary approach based mainly on the archaeometric aspect, more precisely the mineralogical-petrographic analyses[41] were used to identify the clayey components of the finds and therefore to make hypotheses about the production centres, and a chemical analysis of the amphorae contents were used to identify, as far as possible, the product transported (Gas chromatography- mass spectrometry GS-MS)[42]. The first news about the discovery of the wrecks was published first by Gianfranco Purpura in 1985[43] and later by Angela Maria Ferrone and Costantino Meucci in an article of 1995-1996 in the bulletin of Underwater Archaeology[44]. In this last article there is a wide preliminary panorama on

[39] I would like to thank Dr. M. Luisa Famà, Director of the Regional Archaeological Museum Lilibeo/Baglio Anselmi di Marsala, for having granted us the authorizations for the study and for the access to the appropriate warehouses; Dr. M. G. Griffo, archaeologist management officer of the Marsala museum, for the availability given to us. Honor Frost Foundation for funding the project.

[40] The project was born from an idea realized by Professor Fabiola Ardizzone who had shown her interest in thetwo wrecks for a long time, and in particular in the loading of the two small boats, today mostly exhibited in the new museum set-up in Marsala. I thankDr. M. G. Griffo, the director of the Lilibeo Museum A. M. Parrinello and the architect and current director of the archaeological park of Selinunte Enrico Caruso (direction of the works and design variations of the new museum set-up in Marsala) who allowed me to follow with them the new set-up of the two medieval wrecks of Lido Signorino.

[41] Archaeometric analysesconducted by C. Capelli of the University of Genoa, are still ongoing, it has not been possible to present them here.

[42] The chemical analyses were carried out by Nicolas Garnier

[43] Purpura 1985, pp. 129-136.

[44] Ferroni-Meucci 1995–1996, pp. 283–350.

excavation, graphic documentation, reconstructions of the two boats and a study of the materials found in both wrecks. Scholars, on that occasion, hypothesized a probable contemporaneity of the two boats dating from the 11th to the 12th centuries.

In the following pages you will have a part dedicated to the discovery and recovery of the two wrecks and thenpresent the data so far emerged on ceramics, thanks to a morpho-typological study of containers based on the latest studies of medieval ceramics in Sicily and Ifrīqiya, addressing the different problems both on the chronology, on the trade and on the product transported, proposing new hypotheses on the wreck A of Marsala[45].

Fig. 1: detail of the new exhibition areas of the wreck a and its cargo

[45] Preliminary data of the material of both wrecks have already been subject of a publication during the XI conference of theAIECM3 (Ardizzone, Pisciotta, Sacco 2018) and in the days published in honor of Fabiola Ardizzone (Pisciotta, Garnier 2018)

In 1983 along the south coast of Marsala (TP) in the "Berbaro" district, near Lido Signorino (fig. 2.1), some remains of the hull of a wreck called "Arab-Norman"[46] were identified.

The importance of this discovery was immediately understood, after the first emergency interventions, a fairly articulated project was elaborated in the following year; it included: the excavation of the affected area, a set-up of a restoration laboratory for the finds recovered during the excavation inside the Baglio Anselmi Museum in Marsala, the restoration and recovery of the wrecks and the materials contained in them.

1

2a-b

Fig. 2: 1. topography of the site; 2a-b. phases of recovery of the amphorae

From 1983 to 1986 several systematic underwater prospecting and excavation campaigns were carried out in difficult conditions, in an area affected by strong currents

[46] We have decided to abandon the use of this expression because in the first place it generates a chronological problem, and then betrays a unified approach to the Islamic and Norman age that fortunately has been largely overtaken in recent years.

and sea storms that caused continuous phenomena of cover-up and uncovering.

In addition, the proximity of the two wrecks made recovery work particularly difficult, and in the more superficial layers it was difficult to isolate the materials of wreck A from those of wreck B[47]. In 1983 the excavation of wreck A began, which involved the recovery of much of the material contained in it (Fig. 2.2a-b). In fact, on the occasion of a strong sea storm, which brought back the wreck, the amphorae were recovered and an initial graphic documentation was carried out, unfortunately missing from the exact location of the ceramic finds, of which, judging by the photos, some of them seem to lie in the original position; although the conditions were favorable it was not possible to take all the cargo of the ship. In the following year a second excavation campaign was carried out to document and recover the rest of the amphorae but, the particular situation of the site, very close to the coast and at a shallow depth always subject to strong currents, did not allow to document, by photo and relief, their position and only recovery was carried out. However, the relief of the ship was conducted,allowing to rebuilt the part of the hull under the waterline[48]. The difficulties continued in the subsequent excavation campaigns of 1985 and 1986.

However, the underwater excavation, despite the difficulties, highlighted additional elements of great importance. It was in1985that wood en structures were unearthed and were initially mistaken for the side of the so-called wreck "A", but it was only later that it was realized it was another boat, a few kilometers away from the first, smaller in size and called "B". In 1986, in order to better analyze wreck B, excavations were planned, this time using the stratigraphic method, during which five stratigraphic units were recognized. The oldest is US 4, which relates to a time before the shipwreck. To the layer comprising the wooden elements of the craft was assigned US 3, while the US 2 is the cover layer of the wreck that contains the bulk of the materials. US 1 covers the latter, which preserves wreck B materials shuffled with fragments of the cargo amphorae of wreck A. This layer appears

[47] Ferroni, Meucci 1995-1996: 285-286.

[48] The construction modes are a backbone; to build the boat you first set the profile (grain, aft and bow straight) on which the ordinates were nailed (madieri and staminali) and then the skeleton was backed with the bandage. This technique in shipbuilding is typicalbyzantine and medieval dating from the 7th to the 14th century (Yassi Ada, SerçeLimani, Contarina). Literary sources mention the name of this type of ship: *karabion* in the Byzantine context, *qarib* in arabic. It is a small ship with Latin sail mast and side rudders sheltered by two "wings" aft. At the top of the mast there was a pulley for the halyard of sail. The anchor is the typical Byzantine one, in iron in the shape of an inverted T, with a strain of fixed circularsection.

to have formed due to currents, immediately after the cover-up of the two vessels. Finally, the most superficial stratigraphic unit is US 0 which has returned finds related to wrecks but also from differenteras.

The type of amphorae of the load of the wreck "A" by Lido Signorino ("Faccenna A"[49]or "Ardizzone N"[50], fig. 3) belongs to a family of small/medium containers quite heterogeneous, with dimensions ranging from 35, for the smallest module, to 47 cm in height for the largest module and a capacity ranging from 2.5 to 3 liters. As far the production area is concerned the hypothesis already put forwardwas these amphorae were produced in the territory of Palermo, a hypothesis that today is completely confirmed by the archaeometric analyses carried out by Claudio Capelli[51]. In fact, the type of dough is typical of Palermo productions of dark orange/red color and with the presence of many including small and medium-sized white limestone already visible through an autopsy analysis. In addition to the ship's cargo, other objects were found during the underwater excavation which were probably part of the personal on-board equipment and therefore used during navigation within the ship (Fig 3).

[49] Faccenna 2006, pp. 40-41.

[50] Ardizzone Lo Bue, 1 2012, pp. 121-122,149-150, fig. 47.

[51] I warmly thank Claudio Capelli who gave us the preliminary results on archaeometric analyses of the analyzed samples of the pottery found in the wrecks A e B of lido Signorino.

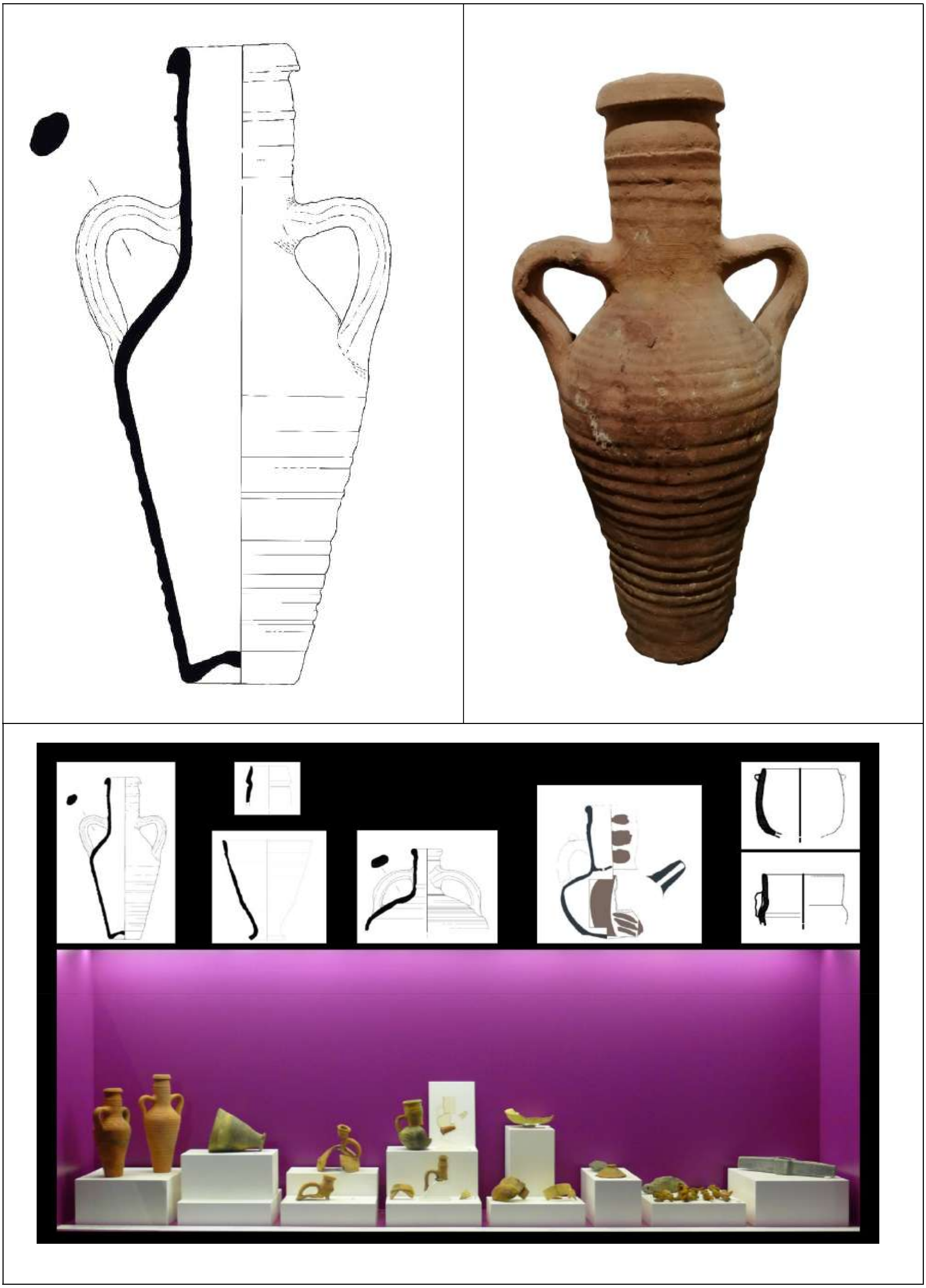

Fig. 3: Amphorae Faccenna A/Ardizzone N and personal on-board equipment and therefore used during navigation

Among these, two amphorae hems of Palermo production should be mentioned (Fig. 4.2), relating to the same specimen and comparable with some amphorae recovered at the San Nicola in Carini district dated between the second half of the10 thand 11th centuries[52]; two amphorae (Fig.4.4a-b) which can be dated from these cond half of the 10th century thanks to the comparison with the finds of Ṣabra al-Manṣūriyya and in this regard it is evident that the most accurate comparison must be made with the small jars of the Sabra 4 type[53]. In fact, like the latter, those found in wreck A have the same morpho-typological characteristics and from a decorative point of view they have the same wavy decoration engraved on the neck[54]. In addition to amphorae, inside the wreck, canteen ceramics have also been identified, probably also intended for on-board life, represented by some specimens of cups (Fig. 4.5), a fragment of a carinated bowl with a bifurcated hem, a bottle painted with red bands[55] (Fig. 4.7) and, finally, a vase with filter **(N. I. 4855)** decorated with vertical bands alternating with parallel oblique streches and a horizontal wavy band on the neck, all of the same thickness (Fig. 4.3) similar to other specimens found in X-XI century contexts[56]. In addition, there was also a pot (Fig. 4.6) and a handle of a canal-beak lamp, all typical materials of contexts dating back to Sicily between the middle of the 10th and 11th centuries[57]. To conclude, among the finds of the wreck, mention should be made of an amphora (**MBA130**) of Islamic age painted in bands of the type Faccenna B[58] or Ardizzone L[59] (Fig. 5.1-2), which is compared with a fragment

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[52] This type of amphora, according to the classification by FabiolaArdizzone made for the finds of Carini, belongs to

group V; moreover, it was considered the prototype of the amphorae of XII-early 13th century type A of Zisa Ardizzone Lo Bue 2012, p. 103, fig. 31; Ardizzone 1997-1998, p. 675.

[53] Gragueb Chatti *and alii* 2011, p. 202.

[54] The archaeometric analyses carried out by Claudio Capelli, despite the samples seem contaminated and difficult to read, they are probably attributable to the Area of North Africa.

[55] *Cfr*. Ardizzone Lo Bue 2012, p. 176, fig. 39L; Pezzini 2004, p. 359 n. 215.

[56] For the shape and decoration *Cfr*.Nef, Pezzini, Sacco 2015, p. 60; it should also be noted that the decoration is very similar to that found in the amphora Faccenna type B found in the load of the same wreck A of Lido Signorino. Chemical analysis of the content carried out by Nicolas Garnier highlighted that the vase with filter contained red wine confirming that not always these small containers were used to filter water but also wine.

[57] I thank Dr. Viva Sacco for the preliminary data on commonly used ceramics. Being part of the project, she studied all the canteen ceramics of the two wrecks of Marsala,

[58] Faccenna 2006, p. 42.

[59] Ardizzone 2012, p. 115, 120.

found in Piazza Dante in Pisa, dating from the 11th to the 12th century[60], but according to the latest studies on transport containers and decorative warp probably the chronology of this amphora goes from the end of the 10th to the first half of the 11th century[61]. This specimen aroused particular interest because you notice on the shoulder the Arabic word, scratched post cooking, 1 *mudd*. In other *words, the mudd* specifies a unit of measurement for arid used in the Islamic world and corresponding to half state, in this case to indicate the weight of the contents of the amphora.

[60] Ardizzone 2012, 120; Menchelli 1993, pp. 521-522.

[61] For the new chronologies of transport containers *Cfr*. Ardizzone, Pezzini, Sacco 2014, pp. 209-211.

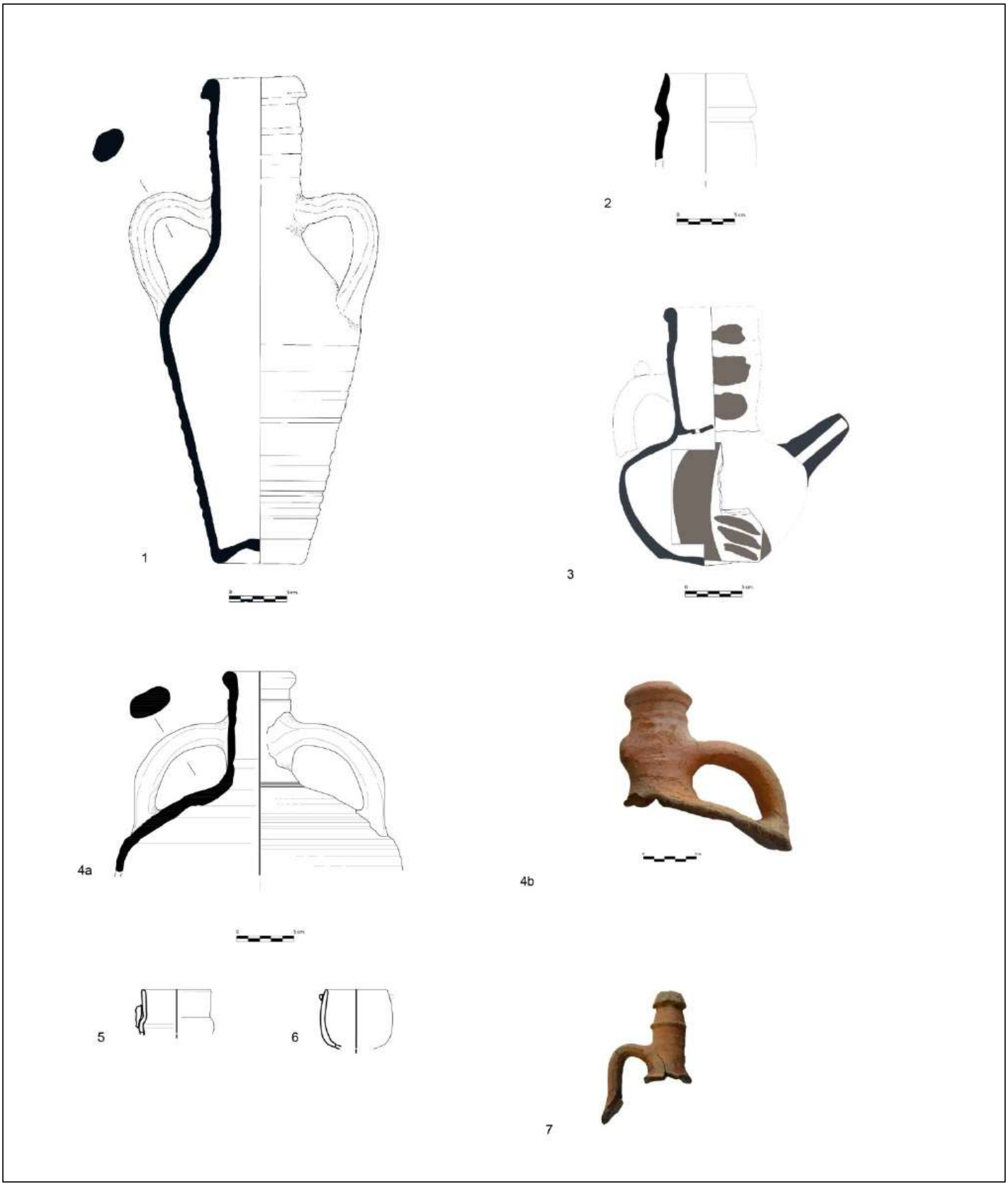

Fig. 4: 1-2, amphora of Palermo production; 3 vase with filter; 4a-b, amphora of African production; 5, cup; 6, pot; 7, bottle.

In this respect, however, it must be made clear that the amphora in question has had more reuse, at different times; the analyses have found the presence of more content, including wine. Of particular interest were the chemical analyses of the contents of the amphorae of the entire load or the Facenna A, which have always created many problems precisely with regard to the content they carry.Today we can say with certainty that these amphorae were used for the transport of wine, at least as far as those of wreck A of Marsala.

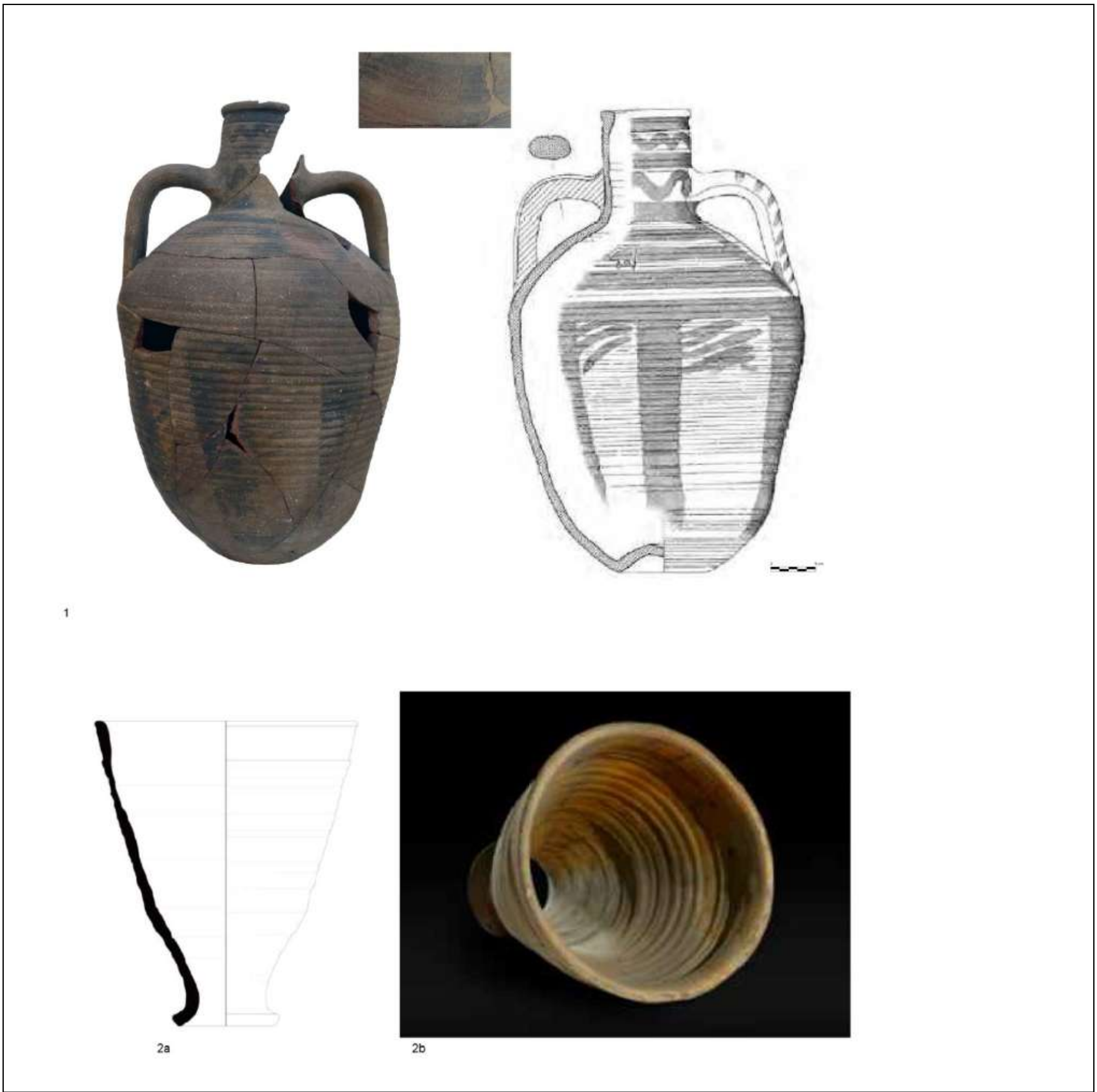

Fig. 5: 1, Amphora Faccenna B/Ardizzone L; 2a-b, funnel.

Chemical analysis of the content, carried out by Nicolas Garnier, showed that there are traces of natural resins to waterproof the container, while tartaric acid and syringe acid found in most of the samples analyzed are markers for the presence of grapes and in particular of red wine. Angela Maria Ferroni and Costantino Meucci in their article had already reported that probably these amphorae were closed with a cork; in fact, during the excavation campaigns of 1983 an intact amphora was recovered with its original cork. Furthermore, it is clear from their study, that these amphorae contained a yellow substance deposited on the inner surfaces of the walls and analyses carried out on some samples confirmed that Faccenna A were coated with a natural resin and in particular a pine resin or its derivatives, but nothing had yet been said with certainty about their content as it is still being studied. However, despite this, the author had validated the hypothesis, already put forward by Purpura, that the content of amphorae could be sugar. Purpura pointed out that there is a lack of a sealant product for caps in amphorae, and therefore he claimed that there was a solid or viscous content, such as sugar, the production of which was introduced in Sicily, in the 9th century by the Aghlabidae. To confirm this hypothesis, according to Purpura, it was the discovery among the woods of wreck A of a sort of terracotta funnel for sugar cane processing (Fig. 5.2a-b). These hypotheses have currently given rise to some doubts, first of all if it was necessary to coat the amphorae and then to waterproof them with natural resins for the transport of sugar, which is quite logical for the transport of liquid and in particular for that of wine; moreover, with regard to funnel **(N. I. 4853),** also of Palermo production, the analyses carried out on the occasion of *the Marsala' Shipwrecks Project* clearly showed, as well as amphorae, that there are residues of acids related to the fermentation of wine and in particular of the red one for which its use inside the ship was probably for the transfer of wine from one container toanother.

From the current state of the study of wreck A of Marsala emerge some details that help us to define aspects that were unclear until now, at the same time others arise that we hope to be able to outline with the continuation of the study but, above all with the publication of new excavations and the discovery of new wrecks in the western Mediterranean and beyond. In fact, the archaeological data can more comprehensively complete the information that is already given tous for the Islamic period from the few historical sources and clarify the data on the trade and circulation of ceramic products and artifacts both Sicilian and imported. Among the first historical sources are the *letters of the Cairo Geniza* that inform us, from the 10th to the 12th century, about Sicily's intense long-range trade with Ifrīqiya and Egypt in particular; these correspondences once again confirm the economic relations of Sicily and in particular of Palermo with Mahdia in ifrīqiya and Fustât the oldest and most commercial district in Cairo[62]. The letters of the Cairo Geniza also inform us about both agricultural and pastoral products that were transported such as cereals, rice, fruits and vegetables, including citrus fruits and in particular lemon juice, but also dried fruits and various types of nuts (almonds, hazelnuts, chestnuts), skins and cheeses.And it still witnessed how in Islamic Sicily the vine continues to be cultivated and therefore to produce wine and export it, a production that will increase more during the Norman period[63]. In the Islamic age, despite its prohibitions, wine continued to be produced and consumed[64]; it was often sung or mentioned in the poems of the various Muslim poets using numerous names that in most cases were either adjectives indicating color, strength gradation or aroma or better still nouns such as "limpid", "clear", "matured". The preferred wine was red or rosé wine which was often mixed with water or honey and sometimes scented with moss[65]. Little is known about the transport containers for liquids and /or solids and in particular about the shapes and types that were used for transport or pantry although in recent years we are trying to understand and outline the morphological and decorative evolutions of these containers[66].

That said, returning to the amphorae of Wreck A of Marsala and the cross-comparison with some contexts, in particular with the context of Sabra where the amphorae such as "Faccenna A" or "Ardizzone N" were found as well as, in the on-board material of the Marsala boat, the discovery of two amphorae, most likely from North Africa production(?) and which find comparison with some specimens found in Sabra, nothing detracts from the fact that there can be a direct carrier from Palermo towards Ifrīqiya[67]. The ship's own cargo, not composite, but consist in mainly of a single type of small amphorae could

[62] Bresc 2001, pp. 13-35; Nef 2007, pp. 273-291.

[63] Bramoullé 2015, 271; Nef, Pezzini, Sacco 2015, p. 56; Nef 2007, pp. 289-291.

[64] There is nothing to show that the production of wine was not necessarily intended for the Islamic people but for those Christian communities still present in the territories during Islamic rule.

[65] White 2003, pp. 172-175

[66] Normally the containers with small mouthpieces were used for the transport of liquids while those with a larger mouthpiece were for the transport of cereals, and fish; *Cfr*. Ardizzone 2014, pp. 130–131; Sack in this volume.

[67] Moreover, the documents of Geniza of Cairo already mension the Palermo-Mazara-Sousse-Mahdia stage (Nef 2007, p. 285).

support the hypothesis that there was a specific demand for that product, which in our case is red wine, transported from Palermo to North Africa[68].

As for the contexts of discovery of the "Faccenna A" currently there are really few and often wefind them only in underwater finds such as those of Mondello[69], San Vito lo Capo[70] and Marsala[71]; other underwater findouts are those coming from the Castellamare del Golfo[72] area, an amphora currently exhibited in the satirical museum of Mazara del Vallo and some exhibited in Baglio Florio in Favignana[73];while they are not currently present in Sicilian contexts and this confirms that perhaps they were containers intended only for extra-island transport. Other discoveries are as we have already seen those of Ṣabra al-Manṣūriyya[74] that of Naples[75] and those recently identified on the southern coast of France (Arles and Marseille)[76] although they have painted decorations that are missing in the amphorae of the wreck of Lido Signorino.

One of the key objectives we set ourselves at the beginning of our research, in addition to the problem of circulation and that of the products transported, was the chronology of the vessel. Today, thanks also to the latest studies on Palermo's productions and some new published contexts such as that of Sabra, we can advance the hypothesis that wreck A of Marsala can be cautiously framed in a chronological arc that does not go beyond the first half of 11th century.

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68 Recently a summary by Molinari on the circulation of transport amphorae and not in the western Mediterranean,also considering the amphorae of Marsala and San Vito, it testifiesa wide economic and commercial spread in Sicily during the 10th-11th century and states that the strong presence of Palermo amphorae, in different contexts outside the Sicilian territory, are linked to a medium-large-scale trade in products other than wheat but also other good quality Sicilian products destined for precisely to elitist groups (*Cfr*. Molinari 2010, pp.162-165).

69 Sacco 2018, p. 224, fig. 1.d.

70 Faccenna 1993, p. 186; Ead. 2006, p. 39 fig. 30-35.

71 Ferroni, Meucci 1995-1996.

72 Now kept in the warehouses of the Marsala museum

73 Currently, it has not been possible to verify the origin of theseamphorae

74 Gragueb Chatti *and alii* 2011, p. 202.

75 The amphora found in Naples looks like a variant (Arthur 1986, p. 549 fig. 4).

76 Tréglia *et alii* 2012, pp.205-207 fig. 1.6-9.

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Scienza e Archeologia: esperienze di ricerca congiunta

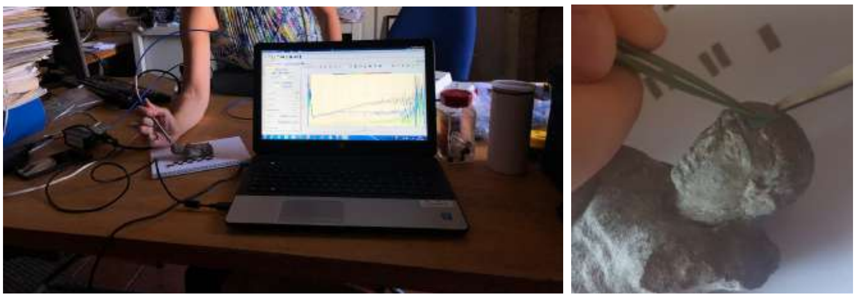
Monica de Cesare

UniPa - Culture e Società
monica.decesare@unipa.it

Abstract

L'intervento mira a evidenziare l'apporto delle indagini scientifiche (chimico-fisiche e petrografiche) alla lettura di reperti di varia natura e dei contesti che li hanno prodotti e nei quali sono stati impiegati. Sono prese in considerazioni, in particolare, alcune esperienze di ricerca congiunta tra scienziati e archeologi, condotte in prima persona o portate avanti da collaboratori e colleghi, che hanno consentito di ampliare l'orizzonte di conoscenza di contesti archeologici sui quali la scrivente conduce ricerche da diversi anni, nel sito di Segesta. L'interazione disciplinare non solo ha permesso di acquisire dati tecnici relativi a specifici manufatti provenienti da questo sito (ceramiche 'indigene', anfore da trasporto greche e puniche, sculture in pietra e in marmo), ma ha anche fornito gli strumenti per affinare la ricostruzione storico-culturale dei contesti di produzione e d'uso di tali oggetti.

The report aims at highlighting the contribution of scientifc analysis (chemical-physical and petrographic) to the reading of finds of various nature and the contexts that produced them and in which they were used. In particular, some experiences of joint research between scientists and archaeologists, carried out by me in person or by collaborators and colleagues, are taken into account. This research allowed to broaden the knowledge of archaeological contexts on which I have been conducting research for several years, at Segesta. In fact, not only did the interaction between experts provide the acquisition of technical data related to different artefacts from this site ('indigenous' ceramics, Greek and Punic amphorae, stone and marble sculptures),, but it also allowed to refine the historical-cultural reconstruction of the contexts of production and use of such objects.



Indagini spettroscopiche effettuate sulle tracce di colore individuate su una statuina di fabbrica greca rinvenuta nel santuario di contrada Mango a Segesta

Archeoecologia: al di la dei confini

Franco Andaloro

Stazione Zoologica Anton Dohrn

franco.andaloro@szn.it

La ricerca scientifica si nutre della curiosità degli studiosi. Le discipline non hanno i confini rigidi a cui le obblighiamo ma si incontrano e scontrano e lo fanno nei momenti meno aspettati, spesso ciò avviene tra due amici di fronte a un caffè. Così l'archeoecologia è nata mentre parlavo con Sebastiano Tusa in un luogo davanti al mare dove i confini dell'ecologia e dell'archeologia sono scomparsi

Una vertebra di pesce in un'anfora da garum o un murice in una da porpora hanno l'età del naufragio e possono parlarci del mare antico, del suo clima e della sua pesca; un balano sull'orecchio di un reperto sottratto al mare ci racconta molto di lui di quanto tempo sia stato in acqua; una tessitura diversa del sedimento o la composizione del benthos che ricoprono il fondale ci possono fare immaginare che li sotto si nasconda qualcosa; di pesca antica ci parlano i reperti di ami in osso e di arpioni in selce così come i dipinti apotropaici nella grotta del Genovese a Levanzo; l'ecologia e il trofismo di un'area possono dirci se dei reperti trovati possono rimanere in acqua nel luogo dello scavo senza essere aggrediti dall'ambiente e cosa fare per preservarli; ancora i relitti moderni scoperti insieme parlano di storia all'uno e di rischio ambientale all'altro. Sono molti i luoghi e i modi dove ecologia e archeologia si incontrano e si incontreranno se saremo ancora capaci di sognare insieme.

Archaeometry

Electrochemical techniques in cultural heritage diagnostic

Mario Berrettoni ([a]), Paolo Conti ([a]), Silvia Zamponi([a]), Rosalinda Sciacca([b])

(a) School of science and technology, University of Camerino, ITALY
(b) Dpt. Of Industrial Chemistry "Toso Montanari", University of Bologna

mario.berrettoni@unicam.it

Introduction

In the last decade the interest on electrochemical techniques applied to archaeometry, and in general to the cultural heritage matter grown up. Several reviews recently reported the state of the art on this field pointing out the relative potentiality as well as the intrinsic limits of the electrochemical approach (1-3). The electrochemical techniques have been applied to all branches of the cultural heritage, hereafter named with the acronym **ChemCultHerit**, ranging from diagnostic, dating, preservation, restoration, and conservation and to different materials: metal, pottery, painting, and paper.

In this contribution we are going to explore the use of the voltammetry of immobilized particles (VIMP) in Archaeometry. The voltammetry is an electrochemical technique that probes the existence, in the sample under test, of atoms and/or molecular species that can undergo a redox process. The experimental setup is very simple and consist of an electrochemical workstation coupled with a classical three electrodes cell: working, reference, and counter. The electrochemical workstation varies the potential applied to the working electrode (WE) vs reference electrode (RE) and records the current flowing between the WE and the counter electrode (CE); the resulting output, called voltammogram, is he plot of current vs potential. The way of varying the potential characterizes the different voltammetric techniques. Despite the simplicity of the experimental setup the interpretation of the results can be complex due to the great amount of chemical information hidden in the voltammogram. A more detailed explanation of Voltammetric techniques is out of the scope of this contribution (4).

The VIMP technique is based on the mechanical stick of some micro particles of the material under investigation on the surface of the WE, usually graphite. In principle this seems to be a destructive technique, but actually the very small amount of material needed, in the order of nano/micro grams, permits to classify the VIMP investigation in the class of non-destructive techniques. Practically the electrode is pressed on the surface of the artefacts (i.e. bronze) and used to record the voltammogram related to the small particles of patina retained on the electrode surface.

This technique was firstly developed for electrochemical studies on solid particles, i.e. metal oxides, mixed hexacyanometallates. It find application on ChemCultHerit by the innovative work of A. Doménech-Carbó and co-workers. Recently appears a very informative review by A. Doménech-Carbó and F. Shultz stated the state of art of the use of VIMP technique on dating metal artefacts of archaeological interest. The response of VIMP has been also used in PCA analysis to discriminate the origin of commercial paper.

Dating applications

The technique was applied to dating lead and copper bronze artefacts (2). In principle the dating process is based to the different amount of corrosion products, and hence to the different intensity of the redox peaks observed in the voltammogram, that can be related to the age of the specimen. The chosen peaks in the voltammogram become the age markers of the sample.

The VIMP on artefacts based on copper alloy shows the reduction peaks of the copper corrosion products: cuprite (Cu_2O) and tenorite (CuO). The corrosion process in these materials start with the formation of cuprite follows by the oxidation to tenorite. The relative amount of this oxides can be used as marker for the age of the sample.

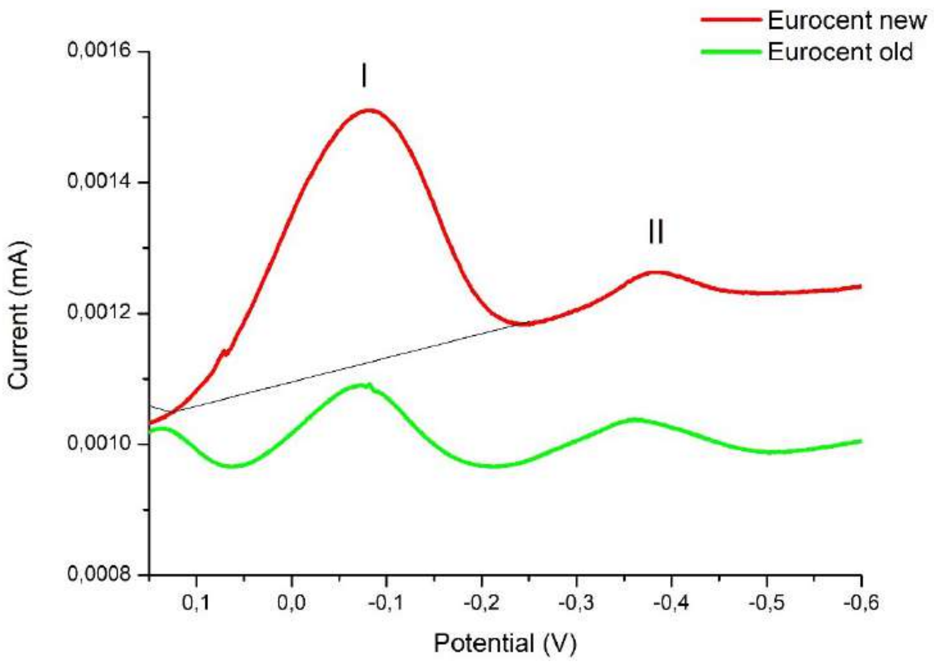


Fig.1 VIMP on eurocent coins using Square Wave Voltammetry (SWV), scan rate 0.001 V/s, frequency 25 Hz, amplitude 50 mV. Electrolyte acetate buffer 0.1M. pH=4.5. The black line indicates the background used to calculate the peak hight.

The reductio peaks A and B can be assigned to the following reactions:

I $$\mathrm{Cu_2O_{(solid)} + 2\,H^+{}_{(aq)} + 2\,e^- \rightarrow 2\,Cu_{(solid)} + H_2O}$$

II $$\mathrm{CuO_{(solid)} + 2\,H^+{}_{(aq)} + 2\,e^- \rightarrow Cu_{(solid)} + H_2O}$$

And hence the ratio of peak intensity of I and II can be considered an age marker of the sample.

Actually, the peak II in Fig. 1 increases respect peak I with the age of the coin.

Further we must consider that the relative intensity of the peaks is depending also on the sampling deepness in the corrosion film. This problem is overcome by normalizing the intensity to the hight of peak I(2). The resulting ratio intensity $i_{(II)}/i_{(I)}$ can be expressed by:

$$\frac{i_{(II)}}{i_{(I)}} = G + \frac{A t^a}{B + t^b} \qquad (1)$$

In literature are reported several examples of calibration curve based on VIMP for cupper artefacts. In general, some constrains are required to apply this techniques. An essential condition is that all objects have a similar corrosion history.

The fig. 2 show the calibration curve for cupper in bronze alloy and for gold artefacts.

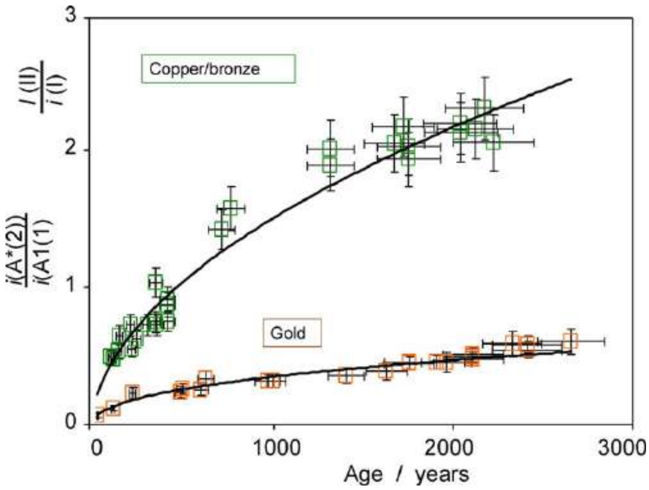


Fig. 2. Calibration graphs of [i(II)/i(I)] vs time applicable for age determinations of copper/bronze objects and [i(A*(2))/ i(A1(1))] (for Au case see below). The continuous lines correspond to the theoretical variations predicted by eq. 1 (copper/bronze) and eq 2 (gold). Figure from REF [2]

In the case of gold artefacts the corrosion is quite absent, nevertheless the VIMP can be use in dating process. In solution of HCl Au can be oxidised following the reaction (peak A_1in Fig. 3)

$$Au + 3H_2O \rightarrow Au(OH)_3 + 3H^+(aq) + 3e^-$$

The other peak A_* Is due to the oxidation of a more reactive Au that become available for the redox process after a cathodic scan. In the second anodic sweep peak A1 decrease and peak A* increases. The ratio $i(A_*(2))/i(A_1\ (1))$, where (2) and (1) denotes the first and second anodic sweep, is the age marker for gold artefacts described by the equation 2.

$$\frac{i(A_*(2))}{i(A_1(1))} = H - Q e^{-kt}$$

(2)

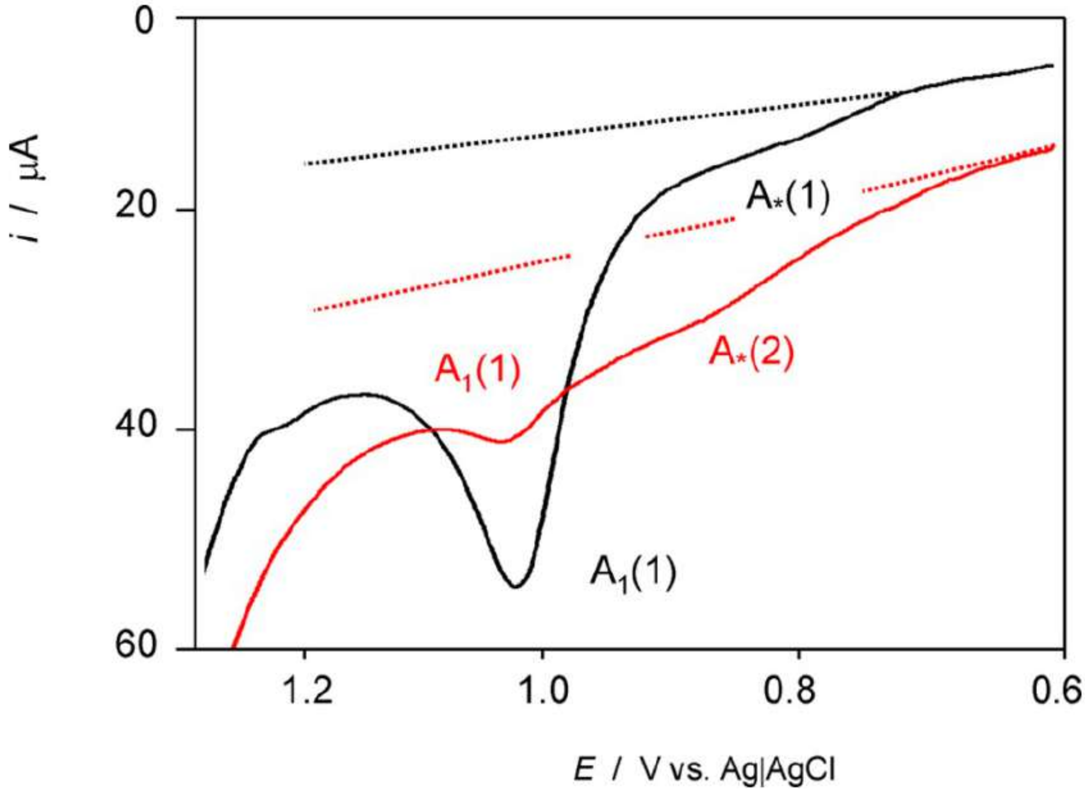


Fig. 3 VIMP linear sweep potential for a Aurum coin, Cartago 310-290 BCE, HCl 0.10M, sca rate 50 mV s-1. Black: first anodic scan; Red: secondo anodic scan after a cathodic one. Figure from REF [2]

Similar results have been obtained also for lead artefacts. The VIMP response can be also used as raw data in classification techniques. The voltammogram features of several lead ingots correlate very well with the available data of isotopic ratio.(5)

Classification

The electroanalytical technique has bene applied also in materials other than metals. Features of the Voltammograms recorded on different paper samples coming from Japan, China, and Korea elaborated with principal component analysis (PCA) permits to discriminate the origin of the paper. (6) In this case the paper was firstly macerated in Acetone and the obtained suspension dropped on a Glassy Carbon Electrode (GCE). He SWV results are shown Fig.4. The voltammograms presents a serie of peaks due to the lignin and its degradation products oxidations. The voltammograms reproducibility is better for potential scan limited between 0—1.6 V. In order to highlight the peak features the CV semi-derivative convolution has been applied the region of the A-peaks Fig. 5.

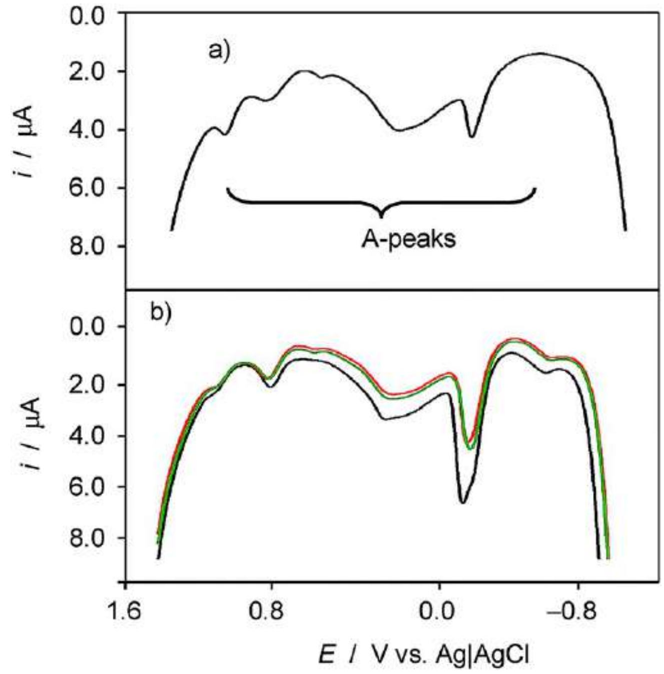


Fig. 4 SWV for VIMP of microparticles of paper macerated in acetone on GCE in 1.0M H2SO4. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.. :(a) P01; and (b) P08 , see ref. [6] for details. Three replicate experiments on freshly conditioned electrodes are superimposed in (b). Figure from ref. [6]

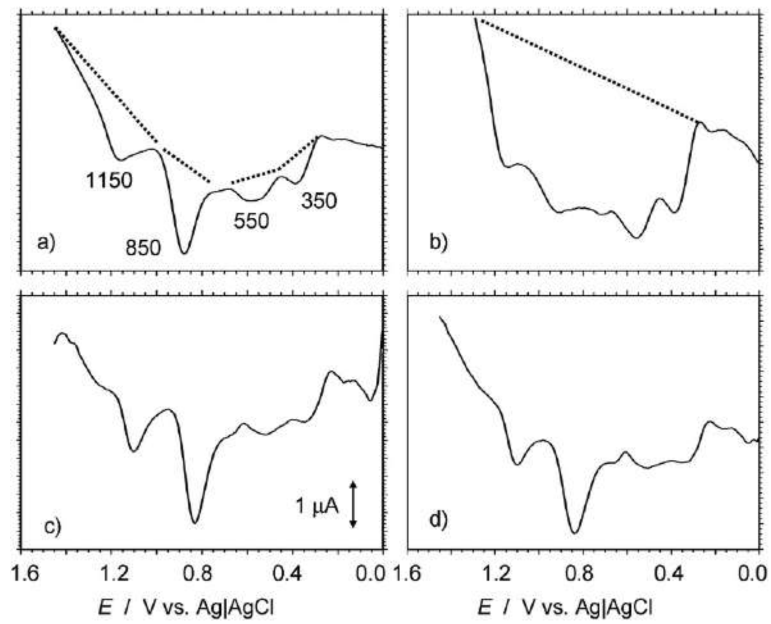


Fig. 5 CV results, after semi-derivative convolution, of microparticulate deposits on GCE of the acetone extracts, 1.0 M H2SO4 1, Potential scan initiated at 0.0 V in the positive direction; potential scan rate 50 mV s1. (a) P04 (pulp type); (b) P01 (kozo type); (c) P07 (Manila type); and (d) P08 (mitsumata type). For details see ref(6). Figure from ref. (6)

The CV of different paper show different peak features. The peaks hight values became the variables input in a chemometric classification analysis. Fig. 6 report hierarchical cluster analysis of voltametric data.

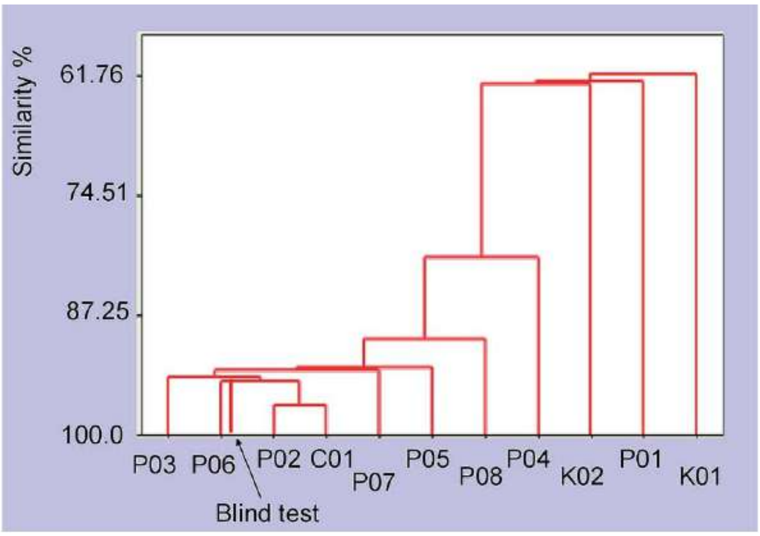


Fig. 6 Hierarchical cluster analysis of voltammetric data for a selection of the studied papers. The problem sample used for the blind test is marked.

This example shows a potential use of VIMP techniques in classification methods.

The related info can be used in the archaeometric studies of ancient paper to assess and/or distinguish the manufacturing methods of ancient papers.

Conclusions

In conclusion the VIMP techniques is a powerful tool to obtain useful information from an artefact of **ChemCultHerit** interest. The main advantages are the cost-effectiveness, the execution time and, practically, to be non-invasive for the sample. When used in the dating process, some very restrictive conditions must be met. The main is that the sample must have a corrosion history very similar to the ones used for the calibration curve.

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Nanoscale investigations of the degradation of metallic artefacts from underwater archaeology

Maria Pia Casaletto

Consiglio Nazionale delle Ricerche – Istituto per lo Studio dei Materiali Nanostrutturati (CNR-ISMN)
Area della Ricerca di Palermo, via Ugo La Malfa 153, 90146 Palermo (Italy)

mariapia.casaletto@cnr.it

Abstract

Metallic artworks recovered from underwater archaeology represent an extremely valuable section of Cultural Heritage. Remarkable examples are archaeological Bronzes found in the Mediterranean Sea, such as the Riace's Bronzes and The Dancing Satyr. Archaeological metallic artefacts from marine sites presents some of the most difficult problems encountered by conservators. The evaluation of the conservation state and the identification of degradation phenomena of archaeological copper-based artefacts will be addressed in this work, since they may suffer from a pronounced and very dangerous electrochemical corrosion (also known as "*bronze disease").* This post-burial degradation phenomenon is due to the ubiquitous presence of chlorine in seawater or in coastal marine environments that could induce the active cyclic copper corrosion and finally lead to the total consumption of the original alloy. Different analytical techniques can be fruitfully used in the investigation of metallic artworks. Among these, X-Ray photoemission spectroscopy (XPS) that probes the surface reactivity at the nanometric scale, is a very powerful tool for understanding the chemical processes that lead to the deterioration of the artwork in different aggressive environments.

Keywords: Metal degradation phenomena; Underwater corrosion; X-ray Photoemission Spectroscopy; Cultural Heritage.

Introduction

Archaeometric studies of metallic artefacts provide very useful information to archaeologists, art historians and conservators about the artistry, craftsmanship, conservation and restoration treatments.

A limited number of metals (copper, iron, tin, lead, silver and gold) were intentionally used in the past with regularity to manufacture tools, weapons, ornaments, monumental items and architectonical insertions. Each of these metals was used individually and in combination with others (zinc or tin) to produce more serviceable alloys, such as bronze, brass and pewter. Depending on the nature of the original discovery site (terrestrial or underwater archaeology) and on that of conservation and fruition conditions (aerial atmosphere or microclimate in museums and deposits), metal artworks may suffer from severe corrosion and degradation processes that should be adequately investigated and cured, if possible. Lead anchors and plumb lines, gold and silver-based coins and jewels, and, above all, copper-based artefacts (bronzes, orichalcum, brass etc.) are commonly recovered from underwater archaeology (Figure 1). The corrosion of metals in sea water can be discussed as a function of the temperature, pH and the presence of aggressive anions like chloride. Furthermore, the presence of oxygen and moisture resulting from the post-burial exposure to the atmosphere may dramatically affect the long-term stability of the metallic artwork. Copper-based artefacts deterioration results from natural processes of decay and from the interactions between the artefact and the environmental conditions that can produce a variety of deposits and/or surface *"patinas",* surface and/or bulk alteration layers. In order to improve the treatments of conservation and restoration of archaeological bronzes a deep understanding of surface phenomena, such as *"patinas"* formation and surface corrosion mechanisms, is requested**.**

Figure 1. Different metallic (gold, lead and copper-based alloys) artefacts recovered from underwater archaeology.

X-ray Photoemission Spectroscopy (XPS) is a very surface-sensitive analytical technique, commonly used in the field of materials science in the nanoscale range, and also successfully applied to Cultural Heritage, both for diagnostics and for conservation purposes (1). It provides information on the nature and the state of conservation of metallic artefacts by determining the presence of efflorescences, patinas, degradation and/or corrosion products, and also the presence of coatings and protective layers applied in restoration treatments. Furthermore, the validation of innovative eco-compatible corrosion inhibitors, the choice of the most suitable conservation and restoration protocols and the monitoring actions following the restoration treatments can take advantage from the application of XPS as a powerful diagnostic tool (2, 3).

Materials and Methods

Small fragments of copper-based artefacts recovered from different underwater archaeological sites in Sicily were submitted to XPS analysis in order to define their nature and their state of conservation (4). A metallic bulkhead of an ancient ship sunk in the Mediterranean Sea (Figure 2) was investigated by using X-ray based analytical techniques, such as X-ray Photoemission Spectroscopy (XPS) and X-ray Diffattrometry (XRD), and Optical Microscopy (OM). After observation with a digital optical microscope, metal findings were sampled in different state of conservation: some heavily degraded, others in relatively acceptable conditions. It was also possible to mechanically clean some metal fragments, in order to obtain the dust of the corrosion products and the pure alloy substrate for further analysis.

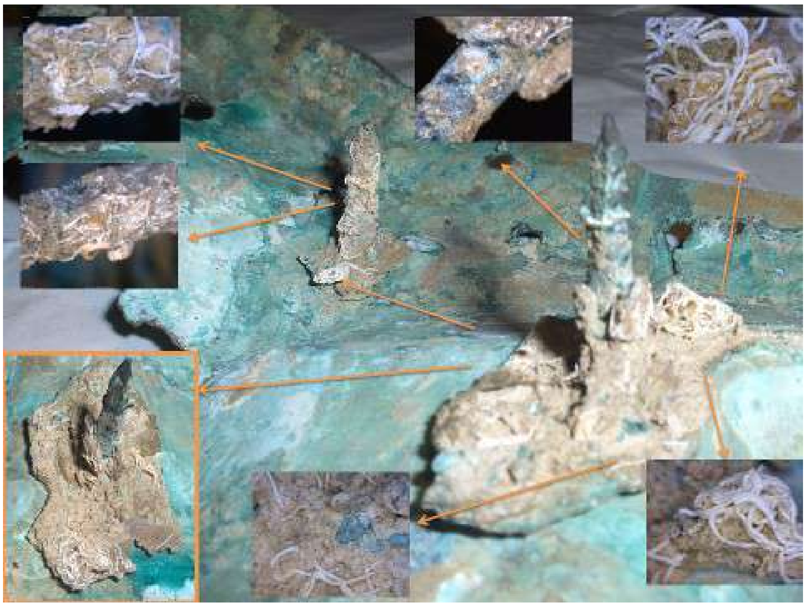

Figure 2. Copper-based bulkhead of an ancient ship covered with fossil encrustations (Magnification 50x and 200x).

XPS is a powerful analytical tool capable of identifying the presence of chemical elements on a surface and determining their quantitative composition. It also allows to discriminate the oxidation state of an element present at the nanoscale and, therefore, to study the reactivity of the surface. The advantages related to the use of XPS concern: i) the possibility of carrying out a non-destructive multi-elementary analysis (all the elements of the periodic table are detected, except H and He); ii) the use of an extremely small amount of sample (a few mg), due to the very low sensitivity limit (0.1 a.%); iii) the determination of a chemical analysis relatively only to the surface of a sample (sampled thickness of 1-5 nm); iv) the possibility of making depth profiles in the case of multilayer structures. Additionally, surface element distribution maps (XPS imaging) can also be provided. The constraints related to the XPS technique concern the need to use Ultra-high vacuum (UHV) conditions to be able to analyze the electrons during the experiment; to carry out an adequate sampling and to dispose of a sophisticated and expensive equipment that, unfortunately, is immovable and, therefore, cannot be used *'in situ'*.

XPS surface investigations of the corrosion of archaeological copper-based artefacts artworks.

The chemical composition of the surface revealed by XPS analysis, shown in the following Table 1, indicates that the artefact was made of a copper-based alloy, containing zinc and lead. After interaction with the marine environment, it resulted heavily degraded. On the surface of the analyzed fragment, a quite high concentration of chloride was detected, in addition to the presence of alkaline-earth elements (Ca, K, Mg), silicon and nitrogen which correspond to the interaction with sea water and to the action of the microorganisms dissolved in it. The degradation of the fragment alloy is evidenced by the low copper content present on the surface and the total disappearance of zinc and lead from the surface of the fragment.

SAMPLE	Cu	Zn	Pb	Cl	C	K	Ca	N	O	Na	Mg	Si
ALLOY	12.6	25.2	1.6	-	23.0	-	-	-	37.7	-	-	-
FRAGMENT	4.7	-	-	2.1	24.1	1.1	2.4	2.6	44.6	4.5	4.0	9.8
POWDER	10.5	5.7	0.2	4.9	29.3		6.9		38.6	-	3.9	-

Table 1. XPS relative surface chemical composition of the coatings, expressed as atomic percentage (at. %)

The analysis of the line shape of the XPS Cu 2p signal provides further information on the copper species present on the surface. XPS spectra of Cu 2p evidenced that the metallic Cu^0 species in the alloy turned into Cu^{2+} ions, as indicated by the appearance of the diagnostic satellite peak located at a binding energy (BE) around 942 eV. The extent of this oxidation is different in the different samples analyzed and varies according to the degree of corrosion suffered by the metal fragments. Figure 3 shows the results of the curve-fitting of the Cu $2p_{3/2}$ signal in some investigated samples.

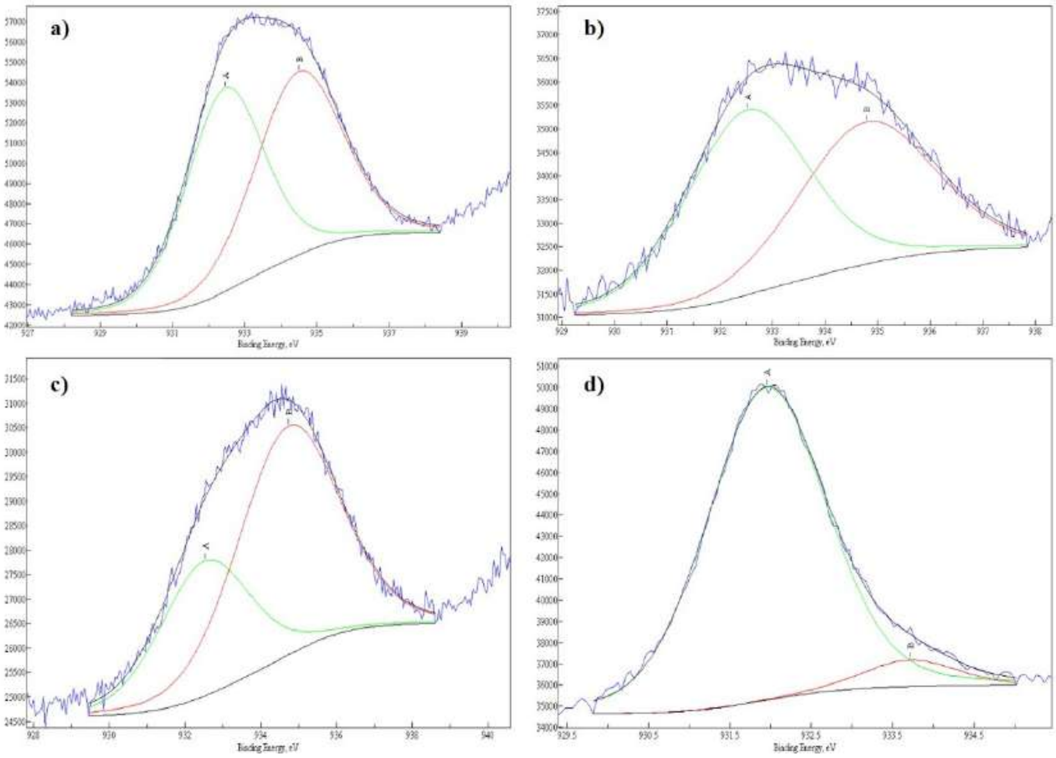

Figure 3. XPS curve-fitting of Cu $2p_{3/2}$ spectra in the investigated samples: a) fragment from the internal part of the sample; b) fragment from the external part; c) powder of corrosion products; d) metallic alloy

As a result of the corrosion of the copper-based alloy, XPS evidenced the presence of two localized components of the Cu $2p_{3/2}$ photoemission peak, located at BE = 932.5 eV and BE = 934.5 eV, shown in Fig. 3 a-c. They can be assigned to the presence of Cu^{2+} species in the form of oxide and of basic oxychloride (atacamite/paratamite), respectively (5). The Cu $2p_{3/2}$ spectrum of the pure alloy, reported in Fig. 3d, consisted in a major component located at BE = 931.5 eV that is attributed to Cu^{0}/Cu^{1+} species on the surface.

The XRD analysis of the fragment and that of its corrosion products (powder) is shown in Figure 4. In addition to the crystalline phases of calcium and magnesium carbonates, i.e. aragonite and magnesite, the diffraction of X-rays revealed the presence of paratacamite, the trigonal phase of basic copper chloride, which is the product of the active corrosion of copper-based alloys, also known as “*bronze disease*".

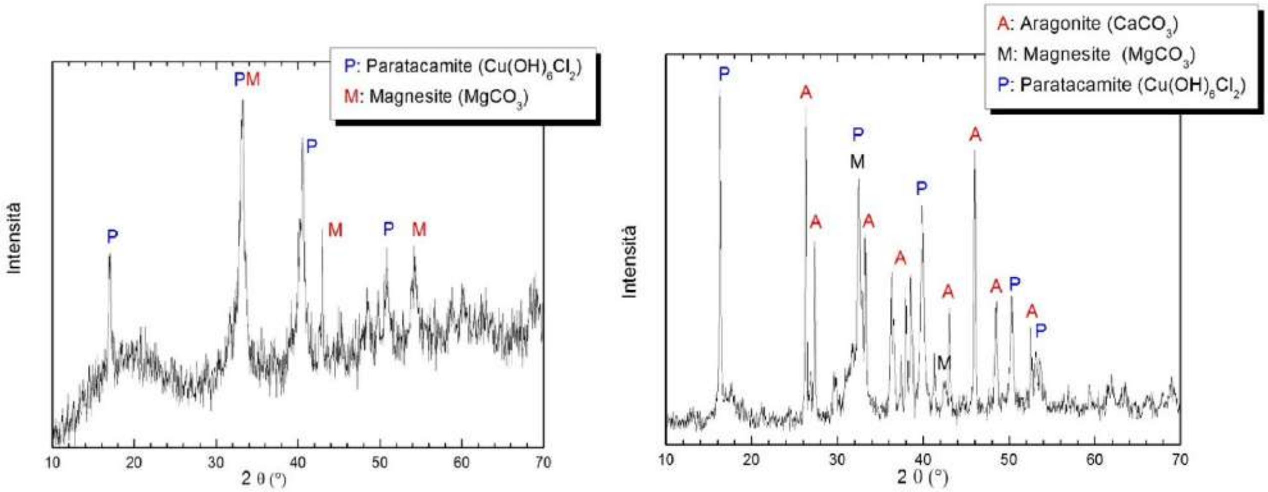

Figure 4. XRD patterns of the metallic fragment (left) and the powder of corrosion products (right).

In a marine environment, the two most commonly encountered copper corrosion products are cuprous chloride and cuprous sulphide. The first step in the electrochemical corrosion of copper and copper alloys is the production of cuprous ions. These, in turn, combine with the chloride in the sea water to form cuprous chloride as a major component of the corrosion layer:

$$Cu + Cl^- = CuCl + e^-$$

Cuprous chlorides are very unstable mineral compounds. When cupreous objects that contain cuprous chlorides are recovered and exposed to air, they continue to corrode chemically by a process in which cuprous chlorides are hydrolyzed in the presence of moisture and oxygen to form hydrochloric acid and basic cupric chloride (6):

$$4\ CuCl + O_2 + 4\ H_2O = 2\ Cu_2(OH)_3Cl + 2\ H^+ + 2\ Cl^-$$

The hydrochloric acid in turn attacks the uncorroded metal to form again cuprous chloride:

$$2\ HCl + 2\ Cu = 2\ CuCl + H_2$$

The reactions continue until no metallic copper remains in the alloy. This chemical corrosion process is commonly referred to as '*bronze disease*.' The process is self-catalytic and the difficulty in countering this mechanism also lies in the fact that the active species is located at the interface between the metal substrate and the corrosion products and continues to carry out its harmful action from the inside. Therefore, it is not sufficient to remove it by a mechanical or chemical cleaning of the surface. The corrosion mechanism must be blocked by inhibiting one or more reactions that determine it if the stability of the specimen must be guaranteed.

'*Bronze disease'* represents one of the most dangerous post-burial form of corrosion that may affect ancient copper-based artefacts derived from underwater archaeology or from

excavations of coastal archaeological sites. If this active corrosion is not properly treated, the total consumption of copper from the alloy will be the result and, consequently, this will lead to the irreparable loss of the artworks.
Any conservation of chloride-contaminated cupreous objects requires that the chemical action of the chlorides should be inhibited either by removing the cuprous chlorides or by converting them. Following any necessary preliminary treatment, the conservation of chloride-contaminated cupreous objects requires that the adverse chemical action of the chloride be prevented. This can be accomplished by removing the cuprous chloride, or by converting the cuprous chloride to harmless cuprous oxide, or by sealing the cuprous chloride in the specimen from the atmosphere. 1H-Benzotriazole (BTA) has been intensively used in the conservation of copper-based alloys, since it has proved to be a good copper corrosion inhibitor. BTA followed any stabilization process and preceded any final sealant. Unfortunately, BTA is toxic and suspected carcinogenic and the efforts of the chemical research in this field are focused towards possible eco-compatible alternatives to BTA, either by using a new product realized by chemical synthesis or by using new formulation of natural derivative from plants (7, 8).

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New Perspectives for Metallographic Investigations in the Field of Underwater Cultural Heritage

Justine Vernet ([a,b])

([a]) Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia del Consiglio Nazionale delle Ricerche (ICMATE-CNR), Genova
([b]) Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova (DCCI-UNIGE), Genova

justine.vernet@protonmail.com

Archaeometric investigations aim at answering—or gathering clues to answer well-defined archaeological or conservation issues: "How were artifacts produced?"; "Where?"; "When?"; "By whom?"; "How are they degrading?"; "How do we protect them?" and so on. Therefore, multi-disciplinary and multi-technical methodologies are required to respect the specificities of materials which are part of a cultural heritage: rarity, fragility, alteration, and high value, for they are often the unique witnesses left over from periods and/or regions of the human evolutionary journey.

The last few decades, rich with numerous technological advances, have seen the development of both non-invasive and non-destructive protocols for analytical techniques. At present, these methodologies are routinely carried out to characterize the **constitutive materials and layers of artifacts**, to understand the **alteration state,** and to provide guidelines for their future **conservation**. The concept of gain and loss, which considers sampling procedures as a compromise between the information gained by the material which may be lost during its examination, is now well accepted (1), but still has to be carefully evaluated for each case study.

Metallography is a scientific discipline of materials that allows us to go back in time through the direct observation of the crystalline organization of metals at the microscopic scale, i.e., the metal's microstructure, allowing us to (re)discover the history of these objects' fabrication. In fact, metallic artifacts, whether they are tools, ornaments, weapons, or elements of architecture, carry the **imprint** within their microstructure **left by the craftsman**, or artist, during their production, and thus act as real solid memories. The metallographic investigation of the remains of **tangible culture** then gives us access to the **intangible culture of the metallurgical art** of ancient civilizations (2).

The technique: definitions and implementation

In most cases, metals are crystals that solidify in ordered lattices in which atoms are regularly positioned in space. When two or more metals are alloyed, i.e., mixed at the atomic scale, different kinds of spatial organization can be formed. The most common alloying structures are the so-called solid solutions in case of solubility at the solid state between the two alloying chemical elements or a multiphasic microstructure in case of insolubility.

By definition, metallography consists of the **examination and determination of the constitution and of the underlying structures of the constituents in metals and alloys** (3). This technique is frequently used in the industrial field for the quality control of metallurgical products, and the metallographic procedures have been standardized (4) and are well described in ASM Handbooks (5). This procedure is schematically illustrated in Fig.1.

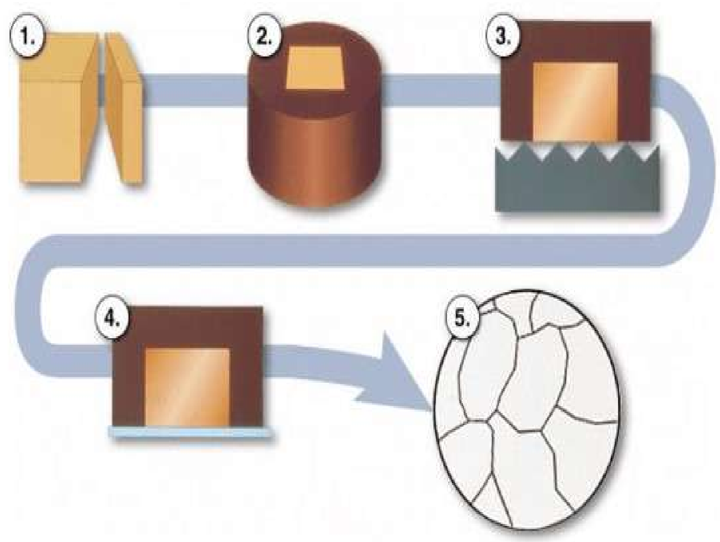


Figure 1: Sample preparation for metallographic examination. 1) Cutting, 2) Mounting, 3) Grinding on SiC disks, 4) Polishing with diamond paste, 5) Microscopic observation of the as-polished section

However, the metallographic study of materials from cultural heritage has to follow specific additional guidelines. Archaeometrical protocols for metallographic investigation have been extensively described elsewhere (6, 7, 8, 9), so only the main steps will be presented here. When a sample of material is necessary for microscopic observation, the technique is said to be micro-invasive. Only millimetric-sized samples should be taken from artifacts following the rules of the representativeness of the selected specimen within the larger corpus, the representativeness of the selected area of sampling within the whole object, and the non-alteration of the readability of the artifact. The sample removal is then performed with a precision saw which does not thermally or mechanically alter the sample, thus leaving the original microstructure intact; otherwise the archaeological information of interest would not be visible anymore. After the complete photographic documentation of the artifact and the sample location, the sample surface has to be prepared "mirror-like". This way, the observation of every microstructural detail is possible, avoiding false interpretations due to improper polishing. First, the millimetric-sized fragment is mounted in polymeric resin, which allows for easy handling, and then the double grinding and polishing steps on abrasive SiC cards or with diamond pastes of decreased granulometry follow. Finally, chemical etching of the surface is possible, to highlight some features like grain join or grain orientations. Further information can be found on polishing materials and protocol in metallurgical practice handbooks (4).

The metallographic survey is made of macroscopic observation with the naked eye or a stereological microscope, and by microscopic observation with the Light-Optical Microscope (LOM) or Scanning Electron Microscope (SEM). On the one hand, LOM examination can be carried out in two different modes: Bright Field (BF) and Dark Field (DF), which allows the observation of metallic phases and non-metallic, e.g., corrosion layers, respectively (10, 11). On the other hand, SEM today is systematically coupled with a system of Energy Dispersive X-Ray Spectroscopy (EDXS) for the chemical composition measurements of areas or local points of the studied cross-section. The investigation is considered non-destructive, as the analyzed matter is not altered or destroyed. This way the mounted sample may be reused for complementary analyses, as will be detailed later.

Gathering complete and detailed archaeological information

During the last few decades, several case studies worldwide have demonstrated how metallography enables us to gather unedited information about the manufacturing and/or corrosion processes of a large panel of metallic artifacts, from semi-finished products or metallurgical wastes to finished objects of small or high value. Indeed, the production of cross-sections, either longitudinal or transversal, in respect to the main orientation of the object, allows for the discrimination and identification of microstructural elements millimeter-deep under the surface that no other technique has easily been able to gather yet. The observation and analysis can then be carried out by identifying each element (e.g., alloy matrix, secondary components or phases, metallic and non-metallic inclusions, etc.) and not only on the whole surface volume, the way superficial methods like XRF do it.

It is worth emphasizing that the interpretation of micrographs is only possible with accurate knowledge in physical metallurgy and chemistry in order to correctly understand both state changes and phenomena occurring during solidification, solid-state transformations, and alteration processes. Some useful tools for the metallographer and the corrosionist are, for example, equilibrium phase diagrams (13), as well as non-equilibrium curves (14) and Pourbaix diagrams (15). Specific literature on these subjects can be found in metallurgical books (16, 17).

Issues associated with metallic artifacts or metallurgical sites that could be investigated using metallography are related to the whole life cycle of artifacts:

a. *The typology of raw metallic and/or non-metallic materials used for the artifact's fabrication and their geographic provenance,* which is related to the field of extractive metallurgy. These studies aim at gathering information about processes of smelting and alloying elements melting. In particular, it is worth citing the question of the circulation of raw materials in ancient times at both long and short scales with, for instance, the tin problem in prehistory (18) or the issue of metal recycling (19). The analysis of the chemical composition of the metallic matrix and inclusions have demonstrated to give precious information about early manufacturing processes (20).

b. *The* chaîne opératoire*, i.e., the succession of technical processes applied during an artifact's manufacture (e.g., casting techniques, annealing, hammering),* can be investigated by the observation of the morphology and size of grains, inclusions, and crystalline defects such as twins, as well as the chemical composition of the metallic matrix, the secondary phases or compounds, and metallic or non-metallic inclusions (20). Fig. 2 highlights how grains are modified by the various fabrication steps. Correlations between manufacturing processes, alloy chemical composition, and microstructure have been widely investigated for both ancient and modern metallic materials, with particular attention to sulfur inclusions as markers of mechanical deformation (6, 21, 22).

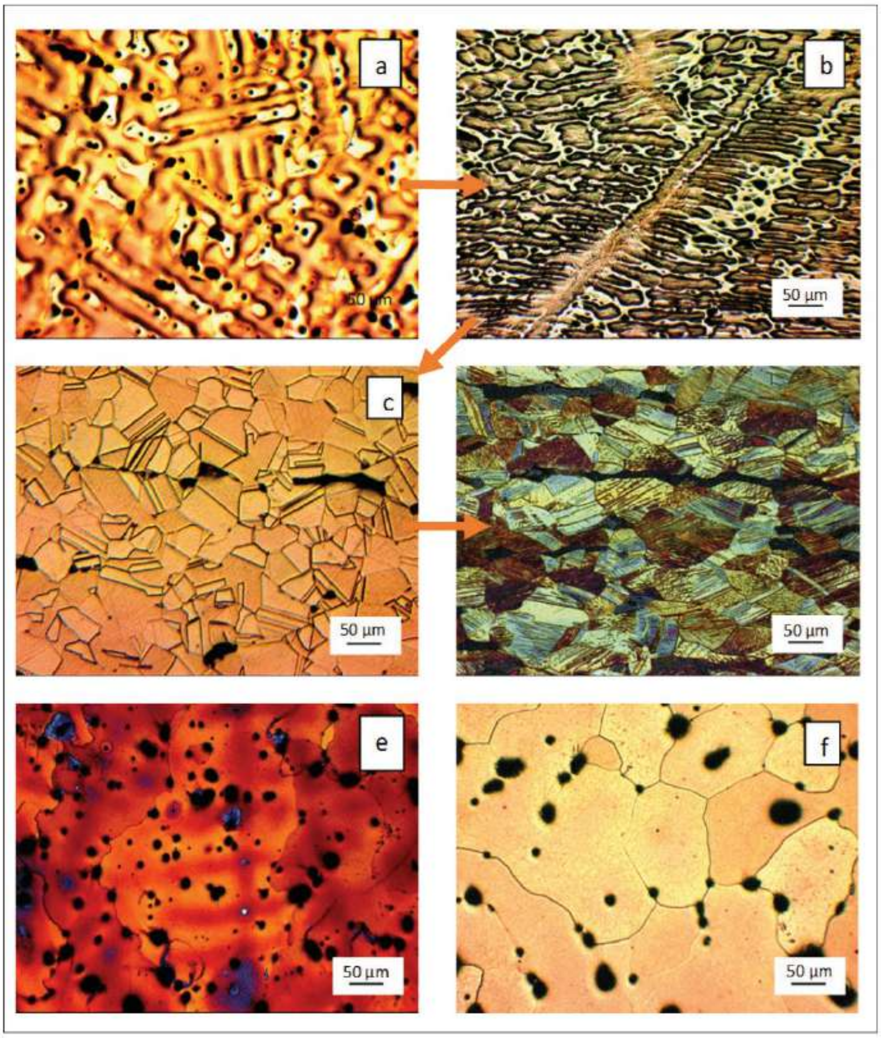
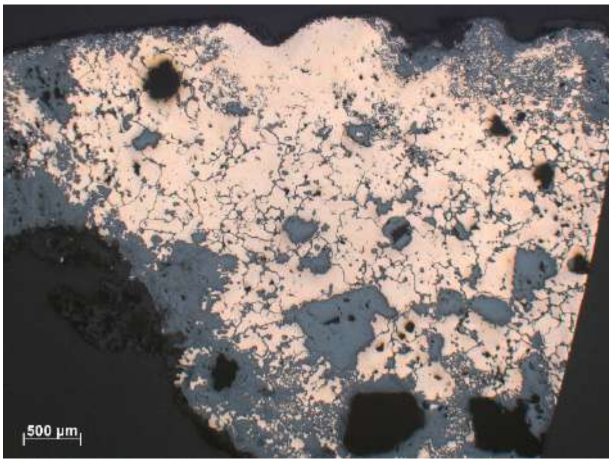


Figure 2: Microstructures associated with different metallurgical states of the same bronze (Sn10, Pb2) (6).
a) As-foundry condition; b) Mechanically cold-deformed from state (a); c) Annealing after strain hardening (30 minutes at 600 ° C) from state (b); d) Cold-deformed after annealing, from state (c); e) Low-temperature annealing (30 minutes at 600 ° C) from state (a); f) High-temperature annealing (30 minutes at 800 ° C) from state (a).

c. *The finishing processes (e.g., gilding, silver plating, bleaching procedures, hot or cold application of chemicals)* are of great interest in understanding metallurgical practices and in the wide history of techniques, because the visual aspect of an object is highly correlated to the cultural perception of the civilization that had produced it. While some finishing aspects are still being investigated by experimental archaeologists and highly specialized artisans, other finishing aspects have been explained thanks to the observation of the object's cross-section, like the technique of adornment on bracelets from Bronze-Age hoards (23) or the technique of silver surface enrichment of ancient silver coins (22). Fig 3a displays the metallographic section of a massive bracelet in which is the superficial decoration depth is well visible.

d. *The environment-object interaction (e.g., corrosion mechanisms) and the formation of a natural patina* can be investigated by the means of metallography. Like the previous subsection c), the observation of a cross-section allows us to gather information about the layers' succession from the surface to the core of the object and the identification of each corrosion product. This way, several corrosion morphologies have been identified according to the microstructural features of the material, leading to the possibility of adapting conservation and restoration procedures (2).

e. *Date and authenticity* are arduous issues in the case of metallic artifacts. Though metallography does not have the possibility to fully explore these issues and has to be completed with specific investigation protocols, it can help by gathering some clues if used as a way of observing the core of objects (25). For example, in the case of ancient artifacts, the presence of intergranular corrosion deep below the surface can be an indicator of long-term corrosion not present in fake objects (Fig 3).



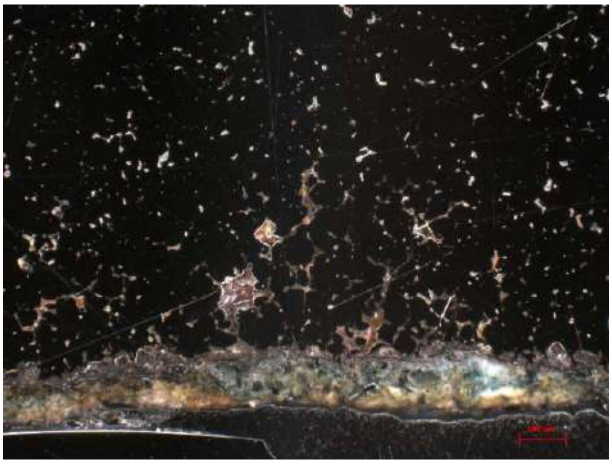


Fig. 3 Observation of different surface deformations (Photo Credit Justine Vernet) :
a) Bronze-Age bracelet manufactured with lost-wax casting and local deformation (LOM-BF, 25X) (REF),
b) Intergranular corrosion in an antique statuary from a private collection (LOM-DF, 100X)

Because observation and analyses can be carried out on the whole cross-section, the identification and discrimination of each microstructural element, e.g., the secondary phase, compound, or inclusion from the alloy matrix is possible, leading to more profound and concise metallurgical information. No superficial or non-invasive technique has been easily able to gather the same kind of information yet. Nevertheless, some techniques have been tested and developed to improve archaeometallurgical protocols of investigation towards lower invasivity. For instance, direct polishing on the object surface is possible in order to avoid the sample removal. Mounting in resolvable molding material or silicone according to the dimensions of the object is also possible (8). This methodology, however, faces some restrictions: on the one hand, some microstructural features can be easily hidden by coarse polishing and, on the other hand, the location and orientation of the observed facet cannot be adapted for the issues being investigated. Even so, this protocol can be very useful for large artifacts, like structural materials (26), or very precious small artifacts, like gold coins (27). Neutron-based analyses are another alternative to micro-invasive analyses that allow the identification of the microstructural state of archaeological objects. The Time-of-Flight Neutron Diffraction (TOF-ND), Prompt Gamma Activation Analysis (PGAA), and Neutron Tomography (NT), for example, are ideal for the investigation of chemical composition, crystalline structure, and imagery of heterogeneous artifacts that need to be analyzed in different points (28, 29). The restrictions of these techniques are the high cost of analysis as well as the low availability of the instrumentation.

However, it appears clear that multi-technical protocols for cultural heritage investigations are fundamental to increase and complete the quality of the archaeological information gathered. Metallography has the advantage of being easily combined with other analytical techniques. For instance, micro-Raman (µRS), micro X-Ray Diffraction (µXRD), or X-Ray Fluorescence (XRF) can be cited for obtaining structural data about corrosion products; trace element and isotope analyses are often used for provenance, radiocarbon analyses have been recently tested in medieval ferrous artifacts, and electrochemical analysis is of prime importance in the field of corrosion characterization.

What about the metallographic investigation of underwater metallic materials?

The rapid improvement of seabed survey technologies has lead in the last decades to an increasing number of immersed archaeological sites and artifacts being discovered. Before the UNESCO Convention in 2001, it was common to carry out the recovery of archaeological material for documentation, investigations and restoration activities the same way that archaeological artifacts are recovered from terrestrial sites. Currently, *in-situ* preservation is favored in order to maintain artifacts in their original context and limit destructive excavation procedures. This means that methodologies carried out to examine and investigate artifacts from the Underwater Cultural Heritage have to be adapted from the classical procedures already described.

Various typologies of metallic objects can be found in immersed sites and are mainly wrecks, naval items (e.g. lead or iron anchors, cannons, nails and tools), personal war items (e.g. weapons, defensive armors), coins, or commercial products (e.g. ingots). The investigation of casting techniques is only possible through metallographic cross-section which also allows a precise evaluation of the influence of micro-structural variation like microsegregation resulting from solidification and cooling conditions (30, 31, 32). While some submersed sites contain a high number of similar artifacts (battlefield objects, coins), other objects can be completely decontextualized and might result from a casual event, like the loss of an anchor, an object shifting due to a current or because of human intervention. By analyzing the constitutive matter of these objects and their specific micro-structural elements, metallography can help gather new clues to create clusters and associate isolated data to an existing data set. However, this approach requires a strong database, obtained by analysis carried out with the same experimental protocol in order to validate the results.

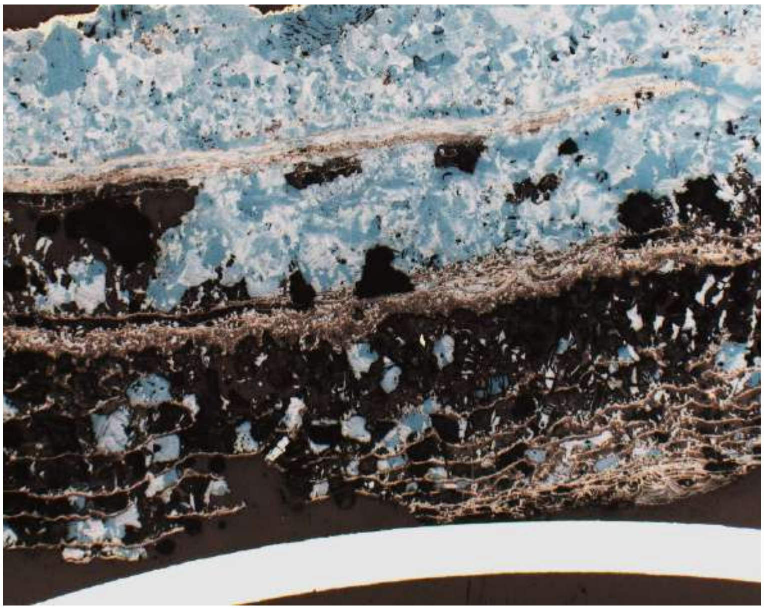


Figure 4: Cross section of a bronze helmet fragment from the Roman Shipwreck of Albenga (SA), Italy. Photo credit Justine Vernet

The seawater environment is a highly complex medium with dynamic features, either chemical or biological. Composed of pure water, mineral salts, dissolved gas, bacteria and micro or macro organisms, seawater is a particularly aggressive environment for immersed metallic materials that leads to specific issues respect of soil buried objects (33, 34). The underwater corrosion on metals and alloys has been characterized mainly on industrial materials used nowadays, e.g. aluminum alloys, copper alloys and steels, but morphology and mechanisms of long-term corrosion are definitely less known respect to long-term soil corrosion mechanisms. This difference can be explained by the obvious fact that immersed sites are less accessible than terrestrial burial sites; on the one hand, the altered surface rapidly reacts with oxygen present in the atmosphere during its recovering to surface and, on the other hand, the difficulty in performing *in-situ* examination, analyses, and monitoring, as well as regular archaeological excavation, especially in the case of high-depth sites, does not allow a complete description of the alteration mechanism. The majority of corrosion characterization has been done on recovered artifacts (35, 36, 37, 38, 39, 40) Innovative examination techniques and advanced multi-technical protocols are necessary to gather more information about these mechanisms. In this case, metallography remains in the foreground as a valid analytical technique because it is the only one able to restore to complex layers composition, from the surface to the core, as highlighted in Fig. 4: the cross section is composed by a complex alternation of copper sulfides, magnesium hydroxides and calcium compounds.

This is particularly relevant when it comes to the restoration and conservation of artifacts, either in the case of recovered artifacts, or for their *in-situ* preservation. For example, it has been highlighted how corrosion morphology of iron artifacts can influence the conservation strategy for the dechlorination process (24). Moreover, climate change phenomena that threatens the preservation of immersed artefacts highlights the importance of studying the correlation between the seawater parameters in the burial zone (salinity, conductivity, dissolved dioxygen, pH, temperature, depth, biological activity) and corrosion profiles. In this context, electrochemical tests and treatments are preponderant, but metallography presents itself as a helpful tool to characterize corrosion layers from surface to the artefact's core (chemical composition, chemical structure, width, interface, inclusions, etc.) for both archaeological and experimental samples (34, 41).

Conclusions: an "old and low-tech" method with wide perspectives

The practice of metallography is the result of centuries of experimentation. Early in the 17th century, the introduction of the first microscopes allowed scientists to study matter on a microscopic scale and to investigate natural phenomena as never before. H. Power is the first microscopist to write about pure metals and notice their specific microscopic patterns (42). Further experiments of different metallurgical states sequentially observed under a microscope allowed for the development of the first correlation between metallurgical processes like thermal treatments, mechanical deformation, or even conditions of solidification, and the microstructures of metals. With regard to optical observation only, the emergence of more sophisticated techniques of electron microscopy have enlarged the standard metallographic protocol.
Metallography is a versatile diagnostic technique which is low-invasive and non-destructive. It also has the advantage of being inexpensive and easily accessible, as well as easily combined with other techniques. In the case of underwater cultural heritage, metallography can be a great complementary tool to use with other techniques when sampling is possible or when artefact fragments are available. It allows us to observe the complex layers of composition and to expand our knowledge on long-term underwater corrosion mechanisms.

At present, metallography can be potentiated thanks to quantitative metallography. Though image analysis is often cited as part of metallographic analysis; its use still has to be developed. Microstructural patterns and spatial correlation are only quantified by simple chart comparisons with standardized microstructures. This practice highly limits the possibilities of further studies since charts only for specific alloys actually exist, e.g. ferrous materials like steel or cast-iron, and there are very few about the alloys found in Cultural Heritage.

Finally, in studies on large panels of specimens, in the field of biology for example, statistic analysis plays a fundamental role in uncovering "hidden" information. Systematic investigation based on a standardized protocol is the only way to gather the maximum amount of information possible from small or decontestualized archeological corpus, or, on the contrary, from very large datasets which would otherwise be unreadable and which require a multivariate data analysis.
In closing, the possibility of creating a link between archaeometric and archaeologic investigations from different research groups will allow for the discovery of new correlations between artefacts.

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Neutron beams to study metallic archaelogical finds

Francesco Armetta

Dipartimento STEBICEF, Università degli Studi di Palermo, Viale delle Scienze Ed. 17
90128 Palermo

francesco.armetta01@unipa.it

From ancient time sea has been place of trade routes and battlefields, with consequent presence of a huge amount of shipwreck which provide an invaluable historical treasure. The objects of this treasure can be studied both for recognize information from the past and to enable the restoration for future generations.

Metallic objects can withstand the centuries keeping original information about the metallurgy and the production, otherwise their degradation can provide useful indication about the environment parameters of the find site. The common approach to study these metal objects involve the use of metallographic analysis which reveal the structure of the metal and the distribution of corrosion products. This approach is invasive and the sampling of a piece of metal it is necessary. In recent years the growing attention to the development and the use of non-invasive investigation, drives researcher to think the use of several type of electromagnetic radiations and atomic or subatomic particles as probe to study metals.

On this view Neutrons ended up being the proper probe to get an high level of information (from surface to bulk) without “touching” the objects. Indeed, neutron beams are able to phase through metal objects providing information also from the inner part without any damaging [1]. It is also important the possibility to test the homogeneity of an object by acquiring measurement in several areas. In particular neutron diffraction investigation provide a description of the structure of the metal at atomic level, identifying the ordered phases both for metal and for corrosion products. The organization of metal atoms may be related to the metallurgy, ie. it easy to distinguish between casting and hammering production of an object. While neutron activation analysis allows to determine the elemental composition.

In this lecture the potentialities of neutron beams for the investigation on archaeological metal will be presented, and some case studio performed on objects coming from the seabed will be described. Particularly an unusual helmet recovered in Sicilian seabed and some metallic plates from Tremiti island sea have been selected. They were selected considering the differences in problematics and the possibility to answer archaeologist and restorer questions, and a proper set up of measurements was used in order to get the requested information whit respect of their integrity. The studies have been conducted be means of neutron diffraction and neutron activation analysis at the Rutherford Appleton Laboratories Neutron Spallation Source (ISIS Didcot UK).

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Fundamentals of the Neutron Tomography and its application on underwater findings

Fabrizio Lo Celso

Dipartimento di Fisica e Chimica "Stanislao Cannizzaro", Università degli Studi di Palermo

Fabrizio.locelso@unipa.it

Computer tomography is a nowadays a very well known non invasive investigation technique, which returns precious information about the inner structure of a sample. From the greek "tomos" which translates "to cut" and "graphein" which means "to write" this tool allows to digitally reconstruct not only the shape of a wide variety of objects but also to determine with a high spatial resolution its inner components both from the chemical and the structural point of view. Here in particular we will focus our attention on the Neutron Tomography (NT), a technique complementary to the X-rays one and widely used in many fields of research such as for example biology, archeology, material science and chemistry. The result of an NT experiment is the three dimensional map of neutron attenuation coefficients inside a sample, in other words a three dimensional image reconstruction of how differently the incident neutron beam is absorbed by the sample. The absorption of a neutron (of a defined energy and therefore wavelength) depends uniquely on the chemical nature of the material investigated; it depends on the peculiar nature of the interaction with the nuclei that composes the sample. Thanks to latter characteristics, this technique allows to investigate large samples (thick metals for example), hydrogenous and porous materials, reaching in some cases a very low spatial detail (25 microns); furthermore it is very convenient in case of low contrast between the matrix and the portion of the sample of interest. It has on the other hand the side effect of leaving the material radioactive (secondary source) depending on the exposure time and chemistry of the sample.

We will discuss the fundamentals of the NT and its application on different samples coming from recent underwater research near the shores of Sicily, made by the Soprintendenza del Mare della Regione Siciliana.

New insight on metal finds of the Punic Ship of Lilibeum

Maria Grazia Griffo ([a]), Francesco Armetta ([b]), Maria Luisa Saladino ([b])

([a]) Parco Archeologico di Lilibeo-Marsala (TP), Italy
([b]) Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche – STEBICEF, Università di Palermo, Viale delle Scienze pad.17, Palermo I-90128, Italy.

e-mail of the corresponding author: marialuisa.saladino@unipa.it, mariagraziagriffo@gmail.com

In this paper, the investigation of some finds (two nails, a head and a long shaft nail, and a fragment of Lead sheathing) belonging to the wreck of the Punic ship and exhibited at Museo Archeologico Regionale Lilibeo (Trapani, Italy), is reported. The X-ray Fluorescence Spectroscopy (XRF) allowed us to identify the elements constituting them making some discussion deductions about their composition and degradation occurred.

1. Introduction

During the organisation of the new exhibition of Museo Lilibeo, inaugurated in March 2017, numerous metal finds, belonging to the wreck of the Punic ship, were rediscovered in the deposits. These are very important elements for understanding the ship's construction method and, for this reason, a showcase has been dedicated to them, which is one of the most admired in the exhibition (fig.1).

Figure 1. Overview of the showcases dedicated to the metal finds belonging to the Punic ship.

The batch of finds consists of lead sheets used for the hull lining below the waterline and of several countless pegs and residual heads used for fixing the above sheets, of long and folded nails used to ensure the frames of the hull to the planking, of wooden dowels having nails inside them and of concretions of iron nails.

One of the first questions, asked by the archaeologists themselves at the time of the exhibition, concerned the composition of the alloys. In the literature, the nails are defined *tout court* as "copper nails", but the detailed excavation report, published by Honor Frost, addresses the question in a critical and scientifically way, and deserves further investigation [1].

The English archaeologist reports that the understanding of the alloy nature constituting the nails had involved five years of studies and 17 tests in three different laboratories. Finally, thanks to the investigation of a nail from the Sister Ship, which retained a solid metal core inside a thick corrosion layer, it was possible to deduce that the alloy was a bronze, due to the presence of tin, claiming that the tin was "volatilized" from the outer layers due to the marine environment.

H. Frost reported the conclusion of Mr Jone, responsible of the laboratory: *"Careful examination of the corrosion product layers surrounding the bronze core of the Sister Ship large nails show that, in the conditions pertaining on this site, tin is readily removed during the corrosion process, consequently such corrosion products cannot be relied on to identify* *the original material…all the reports that the nails were originally copper must be altered to 'copper or bronze'* [2].

The question would have remained unsolved if, as H. Frost ironically claims, Merciful Providence had not come to their aid: during the typological classification of the nails, a nail having a metal core from the Punic Ship was identified. The results of the analysis clarified the presence of a percentage of tin of 7.1%, compared to 80% of copper and 12.3% of lead. These results changed the perspective and in the next reports the term *"no metal present, corrosion products of copper"* was used.

The question is still open and herald of interesting research perspectives. In 2017 some researchers of the STEBICEF Department of University of Palermo (Italy) carried out some investigation by means of X-ray Fluorescence (XRF) Spectroscopy on two nails, a head and a long shaft nail, and also on a fragment of Lead sheathing. The XRF technique gives the elemental composition of the analysed surface volumes. Several spots of each find were analysed with the purpose to verify even the variability of the elements in the same finding.

2. Experimental part

XRF spectra were recorded in reflection by using a portable XRF Tracer III SD Bruker AXS spectrometer having a Rhodium tube as an X-ray generator and a silicon drift X-Flash® with Peltier cooling system as a detector. All spectra were acquired with a voltage of 40 kV, a current of 11 μA and an acquisition time of 30 seconds. The identification of the characteristic peaks of an element was carried out using the database contained in the ARTAX 8 software. In each spectrum, the signals of Rhodium (Rh) and Argon (Ar) due to the source and the atmosphere, respectively, are present. The net area percentages of the identified elements were obtained by deconvolution of the peaks after background subtraction.

3. Results and discussion

3.1 Nails

As an example, some representative XRF spectra, acquired on the two nails, a head and a long shaft nail, are reported in the figs. 2 and 3.

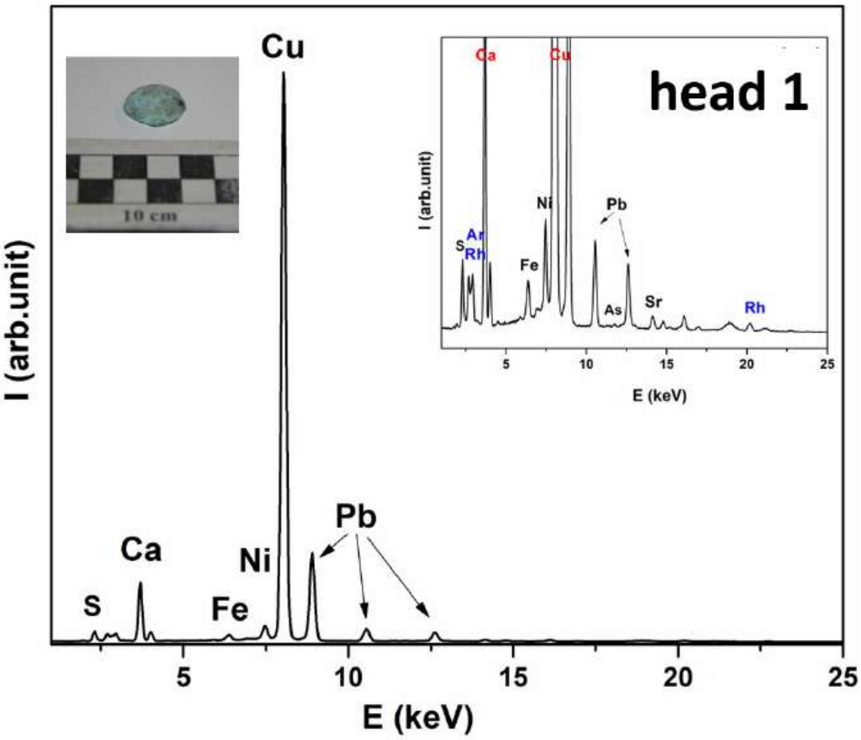

Figure 2. XRF spectrum of the head of the nail (called head 1). The magnification of the XRF spectrum is showed in the inset in order to better visualise the minor elements.

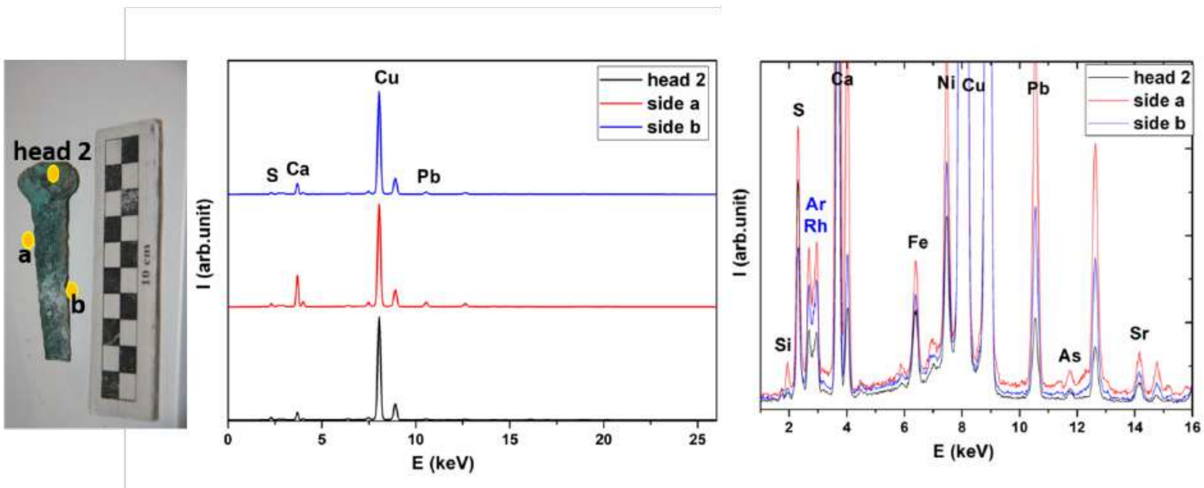

Figure 3. left) analysed spots of the long shaft nail marked in yellow; centre) XRF spectra of the tree analysed spots (called head 2, side a and side b); right) magnification of the XRF spectra in order to better visualise the minor elements.

The main element identified in the head and in the three analysed spots of the long shaft nail (marked in yellow in fig.2) is the Copper (Cu). Lead (Pb) together with Calcium (Ca) and traces of Silicium (Si), Sulphur (S), Strontium (Sr), Manganese (Mn), Iron (Fe), Nichel (Ni) and Arsenic (As) are present as minor components. The presence of iron and arsenic is common for bronze artefacts [3] because they come from the raw materials contamination. In detail, arsenic is an indication of the use of copper sulphides as mineral source [4,5]. The low Fe contents are probably due to soil incorporation on the patina [6]. The presence of lead could be ascribed to the voluntary adding to give a higher fluidity during the casting production.

Some of identified elements (Ca, Si, S, Mn, and Sr) are impurities due to the environment. In particular, the Calcium and Strontium presence is due the sea organism source and the accumulation of these two elements by sea organism is well known as the correlation with the environment microclimatic parameters [7].

A variation on the peak intensity is recognized between the spectra, for this reason the area of the peaks was computed to compare the elemental composition variability in the different analysed spots (Table 1).

Table 1. Net area % of the peaks identified in the nails. Detection limit <0.05%.

element	head 1	head 2	side a	side b
Si	-	0.08	-	-
S	1.89	1.59	1.53	1.01
Ca	**7.2**	**4.9**	**17.5**	**7.0**
Mn	-	-	0.09	0.06
Fe	0.59	0.66	0.86	0.71
Ni	0.44	1.49	2.47	1.89
Cu	**87.9**	**90.0**	**73.6**	**86.7**
As	0.38	0.27	0.53	0.25
Sr	0.15*	0.26	0.42	0.36
Pb	**1.44**	**0.79**	**3.03**	**1.98**

The obtained percentage values do not correspond to atomic composition but help to perform the comparison between the investigated spots and to verify the variability of the finds. The area percentage values of the original alloy elements do not significantly differ, except for the “side a” where the higher quantity of Calcium denoted that it is deposited on the metal. For this reason, we can claim that the Cupper average amount is around 88% with around 1.5% of Lead.

No trace of Tin (Sn) has been identified. The absence of Tin is not surprising and re-opens the question related the nature of the nails (is it copper or bronze?). Considering the penetration power of XRF (few microns), it is possible that the investigated spots are still the patina where the Tin already migrate to outside. Some authors, infact, claim that the accuracy of the XRF data is obtained by analyzing many points and comparing the chemical composition of different corrosion patinas to achieve statistical information of the alloy bulk [8].

However, it is well known that the patinas of bronze are characterised by tin-enriched corrosion layers due to copper depletion. Usually, two layers can be distinguished: (1) an outer layer containing tin species and copper(II) hydrated and/or hydroxyl compounds such as hydroxycarbonate, hydroxysilicate or hydroxysulphate according to the nature of the corrosive environment, and (2) an inner layer, characterised by a lower Sn/Cu ratio than the outer one and containing mainly copper hydroxyl and oxide compounds [9]. On the other hand, some authors reveal that the corrosion rate and patina formation of Sn-bronze are strongly dependent on the environment [10]. In detail, in chloride-rich atmospheres, like the ones of a underwater environment, the stratified patina formed on Sn-bronze is composed of repeated multilayers of Cu_2O- and $Cu_2(OH)_3Cl$-rich sublayers intercalated with Sn-oxides (mainly SnO_2).The stratification of Sn-bronze patina is triggered by repeated events of higher chloride deposition rate, which cause partial dissolution of already formed sublayers, redox reactions between soluble Sn- and Cu-chlorides, and solidification of the main end products SnO_2, $Cu_2(OH)_3Cl$ and Cu_2O after each event [10]. For this reason the presence of tin products in the patina of metal finds from seawater environment is uncommon. On the other hand, MecLaud et al. shown that during the bronze corrosion, under partially aerobic condition, tin usually reacts forming the oxide sulphate $Sn_3O_2SO_4$ [11].

Coming back to the nails of the Punic ship, we analysed only two nails, and, obviously, the XRF investigation should be extended to an higher number of nails to improve the variability and the statistic of the elements. Additional non invasive measurements could be performed such as Infrared Spectroscopy and Neutron Diffraction to investigate the nature of the compounds present in the patina and in the metal core. If possible, the study of the stratigraphy performed by means of optical and electron microscopies could be more useful to solve the question. This investigation should be performed sacrificing one or few nails because, for this kind of observation, the nails should be cut.

3.2 Lead sheathing

As an example some representative XRF spectra, acquired on a fragment of Lead sheathing, are reported in the fig. 4. The area of the peaks, computed to evaluate the elemental composition variability in the different analysed spots is reported in Table 2.

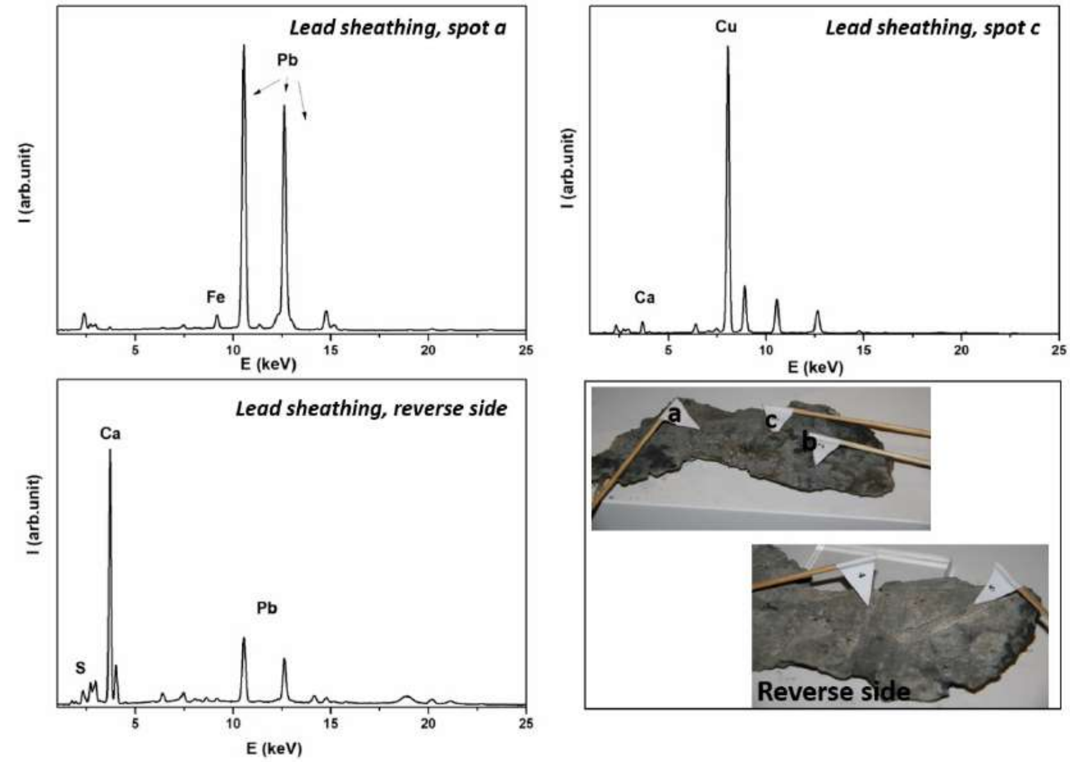

Figure 4. XRF spectra of the analysed area of the Lead sheathing. Some of the analysed spots marked in yellow.

Table 2. Net area % of the peaks identified in the Lead sheathing. Detection limit <0.05%.

element	spot 1	spot 2	spot 3	spot 4 reverse side	spot 5 reverse side
Si	-	0.32	-	0.77	1.04
S	2.71	2.64	-	**3.08**	**2.18**
Ca	**0.62**	**4.03**	**2.79**	**64.3**	**61.5**
Fe	0.32	0.79	2.39	2.95	2.77
Ni	1.27	1.46	1.06	3.79	2.97
Cu	-	-	**82.1**	-	-
Cd	0.38	0.26	-	-	-
Sn	0.22	0.17	**-**	0.14	-
Pb	**94.4**	**90.3**	11.5	**25.0**	**29.6**
Sr	-	-	0.08	-	-

In the spectra acquired on the spot 1 and 2, Lead (Pb) has been identified as the major element. Signals of Silicium (Si), Sulphur (S), Calcium (Ca), Iron (Fe), Nickel (Ni), Cadmium (Cd) and Tin (Sn) are also present as minor elements. In the spectrum acquired on spot 3, Copper (Cu) has been identified as the majority element. This is an indication that this analysed spot has a different nature of the two previous one, in fact it is a nail inserted in the foil having similar elemental composition with the two analysed nails.

In the spectra acquired on the spot 4 and 5, the major elements are Calcium (Ca), Lead (Pb) and Sulphur (S). Since these two spots are acquired on the reverse side of the foil, this can be an indication of the material used to rest on the ship between the lead foil and the wooden hull [12].

4. Conclusions

In this paper, the results of an XRF investigation of two nails and a Lead sheathing belonging to the wreck of the Punic ship and exhibited at Museo Archeologico Regionale Lilibeo of Marsala (Trapani, Italy) is reported.

Results showed the nails are cupper-based, but the tin was not identified and the questions related the nature of metal/alloy used for the nails is still open.

Interesting is that the nail found on the Lead sheathing is similar to the others.

The Lead sheathing is made of lead even if the reverse side seems to be covered with a not-metal layer.

The obtained information are important to define the nature of the composition of the two objects, and useful for the archaeological point of view to improve the knowledge on the metal finds belonging to the Punic ship.

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Modern methods for analysing archaeological glasses

Cristina Leonelli ([a]), Cristina Boschetti ([b])

([a]) Dipartimento di Ingegneria "Enzo Ferrari", Università' degli Studi di Modena e Reggio Emilia, 41125 Modena, Italia
([b]) IRAMAT-CEB, UMR5060, CNRS/Université d'Orléans, 45071 Orléans CEDEX 2, France

cristina.leonelli@unimore.it

cristina.boschetti@cnrs-orleans.fr

Small glass objects, such as beads and pendants and vessels, are reported from the archaeological record as far back as the late fourth millennium BC. During the Hellenism glass was firstly used in architecture, as mosaic tesserae and prestigious vessels were made both in colourless and coloured glass. In Roman times, after the invention and spread of glass blowing, glass vessels became common. Since the first century CE, flat glass was used in form of window panes.

Since the Late Bronze Age, glass objects, but also un-worked glass, were shipped though the Mediterranean with other trade goods and are occasionally found in the cargo of shipwrecks.

The modern methods to investigate antique glass objects are divided into two groups: i) determination of the chemical composition, isotopic characterization for provenance identification (1, 2, 3); ii) determination of physical properties for production technology and degradation process definition (4).

According to the first group, we introduce the main chemical and isotopic groups observed in Hellenistic and Roman glasses from Italy. The theme of provenancing glass runs through the lecture, because the archaeological evidence for primary glass-making sites is extremely poor. The possibility that Italy was a primary glass producer is debated, but it is clear that most of the glass circulating in the region was imported from Egypt and the Levant, flanked by few local glass (5).

According to the second group, we present the use of the heating microscope, a widely used instrument in many industrial applications, to obtain information on the sintering behaviour and, indirectly, on the viscosity curve of glass. We analyse two opacified Roman mosaic glass tesserae and a raw glass from Pompeii. Finally, the relationship between the opacifiers and the thermal behaviour of base glass are presented.

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Study of the state of conservation and the efficacy of conservative interventions on archaeological wood by solid state NMR spectroscopy techniques

Alberto Spinella

Università degli Studi di Palermo, Advanced Technologies Network Center (ATeN Center), Viale delle Scienze pad. 18, 90128 Palermo

alberto.spinella@unipa.it

Abstract

In this work an *excursus* on the determination of the state of conservation of archaeological woods and on the evaluation of conservative interventions by solid state Nuclear Magnetic Resonance (ss-NMR) techniques will be presented.
Particular emphasis will be placed on the study of the state of conservation and on the conservation interventions of waterlogged woods.
Firstly, the discussion will focus on the characteristics of wood from the materials science point of view, presenting its chemical-physical characteristics of natural polymer composite.
The macromolecules constituting the wood (celluloses and lignin) will be described by examining their chemical characteristics and inter and intramolecular interactions and how they determine their macroscopic characteristics.
The degradation a wooden artefact may be subject to in relation to the environmental conditions to which it has been subjected will be described.
A case study of ss-NMR investigations relating to conservative interventions that have been carried out on the Acqualadroni rostrum will be presented.
Qualitative and quantitative results obtained with ss-NMR and how these can be related to the state of conservation of the wood will be illustrated.
In particular, ^{13}C NMR spectra of degraded and non-degraded wooden samples and the importance of determining the degree of crystallinity of the cellulose and the holocellulose / lignin ratio will be described. A method to determine the degree of condensation of lignin will also be presented and the nuclear relaxation times that are related to the dynamic state of the wood components will be discussed together with some results obtained through bidimensional NMR techniques.

Wood chemistry

The principal components constituting dry wood are cellulose (40-45 %), hemicellulose (20-30 %) and lignin (20-30 %). Other organic compounds which are referred to as extractives (5%) are also present.
Cellulose is the most abundant wood component. It is a homopolymer constituted by β-D-glucopyranose units linked together by 1-4 glycosidic bonds.

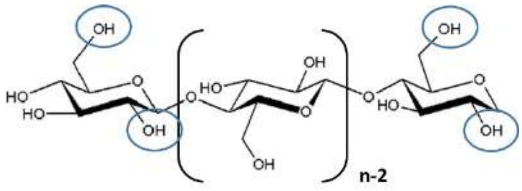

Fig. 1 Cellulose structure

The cellulose main polymerization degree is around 15000. Cellulose molecules are linear and they are characterized by intra and intermolecular hydrogen bonds. Thanks to hydrogen bonds cellulose molecules are aggregated together in microfibrils, in which highly ordered (crystalline) regions and less ordered (amorphous) regions are present. Microfibrils in turn form fibrils and finally cellulose fibers. The cellulose fibrous structure and the strong hydrogen bonds gives it high tensile strength and make it insoluble in most solvents [1].
Hemicelluloses are water soluble heteropolysaccharides with function of supporting material in the cell walls. Hemicelluloses are constituted by D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, and small amounts of L-rhamnose as monomers. Futhermore, D-glucuronic acid, 4-O-methyl-D-glucuronic acid, and D-galacturonic acid are also present. They can be easily hydrolyzed by acids to their monomeric components. The polymerization degree of most hemicelluloses is around 200 and their structures are extensively branched.
Lignin is a very reticulated macromolecule with a high cross linking degree. It is a polymer of phenylpropane monomer units and its biosynthesis involves three aromatic alcohol precursors: coniferyl alcohol (4-hydroxy-3-methoxycinnamyl alcohol), synapyl alcohol (4-hydroxy-3,5- alcohol dimethoxycinnamyl) and p-coumaryl alcohol (4-hydroxycinnamyl alcohol). These precursors differ from each other by the number of methoxy groups (Figure 1.4)

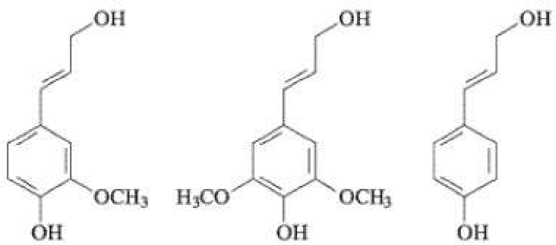

Fig. 2. Monomer units constituting the lignin structure

Depending on plant species the relative quantities of the three monomers are different: softwood plants contain higher quantities of coniferyl alcohol (softwood lignin), hardwood equal proportions of coniferyl and synapyl alcohol (hardwood lignin); finally, lignin grass contains significant quantities of p-coumaryl alcohol derivatives. Even if numerous models have been proposed to represent lignin, its compositional variability does not allow to define the structure. An example of a model is shown in Figure 3.

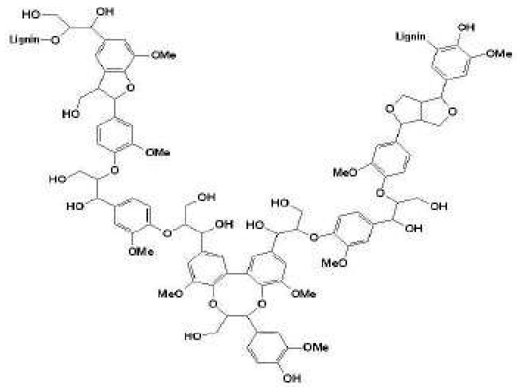

Fig. 3. An example of lignin structure model

Wood degradation

Wood is a material with a high intrinsic resistance. in fact, archaeological wood finds have survived to this day in very good condition. Despite this, there may be various external agents of both biotic and abiotic nature that can cause wood degradation.
The wood abiotic degradation is due to the action of the physical and chemical agents such as temperature, acidity and humidity and prolonged exposure to light. In the case of waterlogged wood (i.e. found in sea or lake beds), humidity is the abiotic factor that causes the greatest damage to the wood structure. The action of water favors diffusion phenomena[2], which lead to extractives loss. The wood biotic degradation is attributable to the action of anaerobic bacteria and particular species of fungi 17[3], which attack mainly its polysaccharide component: the first substance to be degraded is hemicellulose, then amorphous cellulose and finally, crystalline cellulose. In particular, fungi of the soft-rot category, very active even in marine environments, make wood externally soft by their action. Lignin can be damaged as a result of the action of molluscs and crustaceans 18[4]. It usually undergoes partial oxidative degradation and a certain degree of demethylation[5].
Waterlogged wood is a porous and spongy material with cavities filled with water. Moisture content can reach values up to 400%, indicating an almost total degradation of the wood cell wall [6]. As a result of the biotic and abiotic degradation processes, its structure undergoes profound changes, due to the dissolution of starches and sugars and the release of colouring substances and tannins. Water which can be a cause of degradation, can preserve the wood macroscopically as the cellulosic fibres are similar to water-swollen sponges and the residual lignin continues to support the structure [7]. This implies that, as soon as the wood is left to dry, tensions are created which cause distortions, breakages and, if the structure is particularly compromised, complete collapse. Only the gradual replacement of water molecules with consolidating molecules allows to reduce these effects [8].

Consolidation

When a material has undergone degradation processes a consolidation is required. In general, consolidants are liquid substances with low viscosity which diffuse inside the material pores by capillarity. The consolidant choice must take into account the chemical, physical and mechanical characteristics of wood and its state of conservation, as well as the properties that it originally possessed. The consolidants must have good penetration capacity, chemical and thermal stability, good resistance to microorganisms attack and good physical and chemical compatibility with wood. They must not to be toxic to the operator and do not require hazardous solvents for their solubilisation. Finally, it is important that these substances do not form surface films or precipitates that alter the appearance of the wood [9]. There are different methods for consolidant to be applied. The impregnation method which guarantees the presence of the consolidant only in the most superficial areas, the drop-by-drop injection, and immersion. These last two methods allow penetration of the consolidant into the deepest layers of wood, but are applicable only to small objects and have the drawback of dirtying the surface. The most commonly used substances are of natural origin, such as animal glues, beeswax and natural resins. Today, a wide range of synthetic consolidants are also available which, in many cases, can be more effective than natural ones.

Case study

The Acqualadroni roman rostrum was recovered in September 2008, 200 m away from the coast of Messina (Italy), at about 6 m depth. The discovery was considered extraordinary since it is unusual to find this kind of artifacts together with the wooden part of the warship, still preserved. To date, only two rostrums of this kind have been recovered: the Athlit Ram (Steffy JR et al. 1983)[10], and the Acqualadroni rostrum.

Firstly, the rostrum was protected by immersion in streaming deionized water. Then both its wood and metal parts were investigated [11-12-13].

The wooden part of the rostrum was consolidated by immersion in aqueous solutions of Kauramin (a melamine-formaldehyde resin) for eight months, at the “Centro di Restauro del Legno Bagnato” (Pisa, Italy) and it is now exhibited at the Museo Regionale in Messina.

Recently, an analytical survey, in order to assess the state of the wood conservation has been authorized by the “Soprintendenza del Mare della Regione Siciliana (Italy)”. For this purpose, a consolidated wood sample taken by coring was characterized using solid-state NMR (ss-NMR) spectroscopy.

Fig. 4. Core sampling of the wooden part of the Acqualadroni rostrum

The core sample was divided in seven parts and the obtained samples were named from 6I to 6VII in order of increasing depth.

Several ss-NMR techniques were used to obtain information on the structure, dynamics and interactions between wood components. In addition, it was used for evaluating both the conservation state and for the effectiveness of the protective and consolidating treatment. Structure and chemical modifications were assessed by comparing the features of the artifact with modern samples.
^{13}C CP-MAS NMR spectra of all samples are shown in Figure 5.

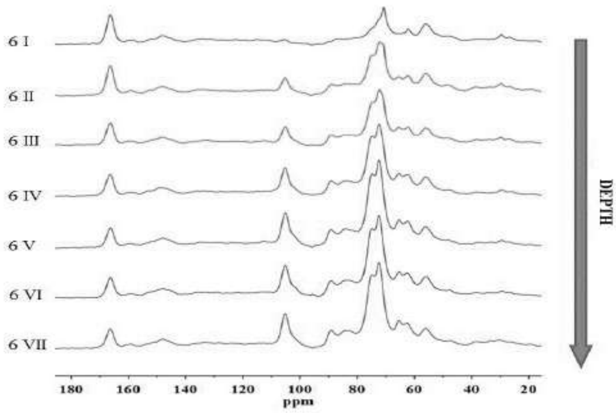

Fig 5. ^{13}C CP-MAS NMR spectra of 6I-6VII samples, normalized to the lignin peak at 147 ppm

The assignment of the peaks attributed to the wood components found in the rostrum has been published in previous works [14-15]and can be found elsewhere.
In Figure 6 the structure of urea melamine-formaldehyde resin consolidant is shown.

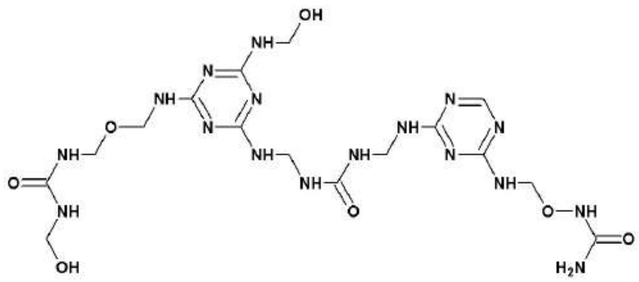

Fig 6. Melamine-formaldehyde and urea resin structure

Kauramin peaks were assigned with reference to the chemical shift values for melamine-formaldehyde resin [16] (Table 2).
By comparing the ^{13}C CP-MAS NMR spectra, it is possible to observe that cellulose signals are more intense in the deeper than in surface samples. This indicates that the waterlogged wood degradation proceeds from surface to the core and primarily affects the cellulose component, as expected.
A resonance at 166.4 ppm due to the quaternary carbon of the Kauramin triazine ring is present in all spectra. This is the only resolved consolidant signal in the spectrum and its intensity increases towards the surface (Figure 7).

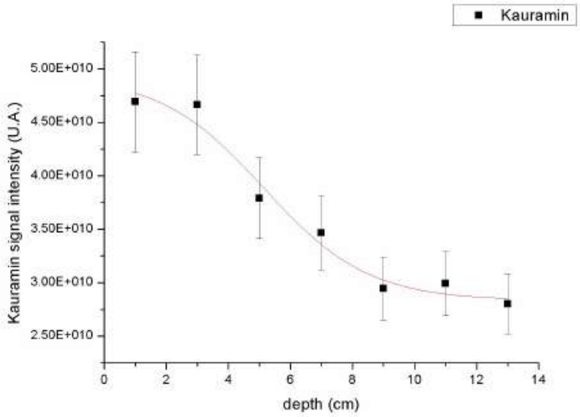

Fig 7 Kauramin quaternary carbon of the triazine ring intensity variation as a function of the depth. The amount of Kauramin is higher in the more degraded surface layers and lower in the deeper, less degraded layers.

Although it is not possible to estimate the maximum consolidant depth penetration following the treatment, the highlighted signals represent a direct evidence that the Kauramin is present in all the examined samples at least up to 14 cm depth.

Wood conservation state

Three parameters were considered for wood state of conservation evaluation. Cellulose Crystallinity Index (CI), lignin degree of condensation and the holocellulose/lignin ratio. The values of these parameters for the examined samples are shown in Table 3 and have been compared with those reported in the literature (Bastone et al. 2016)[17] for a sample of fresh wood taken from a *Pinus Pinaster* stem.
CI was obtained by deconvolution of C4 signals of the cellulose in the ^{13}C CP-MAS NMR spectra by using two Gaussians (Figure 8). The ratio between the area of the crystalline peak (87-93 ppm) and the total area assigned to the C4 peak (80-93 ppm) (Newman 2004)[18] allowed evaluating the CI of cellulose whose values are shown in Table 1.

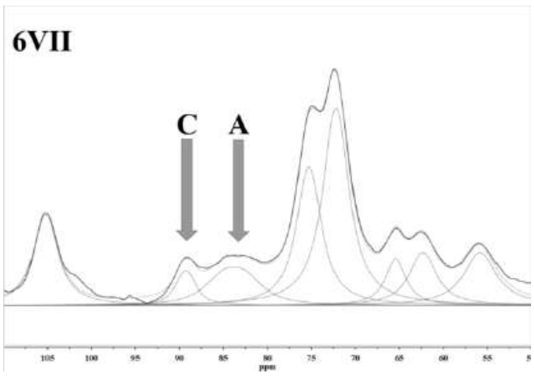

Fig 8 ^{13}C CP-MAS NMR spectrum region of sample 6VII showing amorphous (A) and crystalline (C) C4 peaks of cellulose

Table 1 Indicative parameters of wood conservation state: comparison between the values recorded in 2018, after 10 years from the treatment with Kauramin, and the values reported in literature (XVII) for a sample of young wood, taken from a stem of *Pinus Pinaster*.

Sample	Depth (cm)	CI	Lignin condensation degree	H/L
2018				
6I	0-2	0.63 ± 0.08		0.62 ± 0.05
6II	2-4	0.63 ± 0.08	1.1 ± 0.1	1.03 ± 0.05
6III	4-6	0.48 ± 0.06		1.2 ± 0.1
6IV	6-8	0.36 ± 0.04		1.46 ± 0.13
6V	8-10	0.36 ± 0.04		1.65 ± 0.17
6VI	10-12	0.36 ± 0.04		1.57 ± 0.17
6VII	12-14	0.36 ± 0.04	1.1 ± 0.1	1.65 ± 0.17
Reference				
		0.21 ± 0.02	1.3 ± 0.1	2.3 ± 0.1

The CI of cellulose is widely used to study variations in cellulose structure following degradation processes. The amorphous cellulose is the most sensitive part of wood because it is more easily attacked by microorganisms due to its high hydrophilicity. Thus, when biotic and abiotic degradation occurs, there is an increase in the cellulose CI (Kennedy et al. 2007)[19].

In the case of the examined samples (Table 3), the CI values are higher in the surface samples. The observed trend is an evidence that amorphous cellulose has been conserved from sample 6III to 6VII, while in the superficial areas it has been degraded.

The lignin condensation degree obtained by the non-quaternary suppression (NQS) technique provides an indication of its conservation state (Liitiä T et al. 2002)[20]. In Table 1 the condensation degree values for the surface and for the deepest sample (6II and 6VII respectively) are reported. The lignin condensation degree could not be obtained for sample 6I because of the poor resolution of the NQS spectrum and thus of the high experimental error.

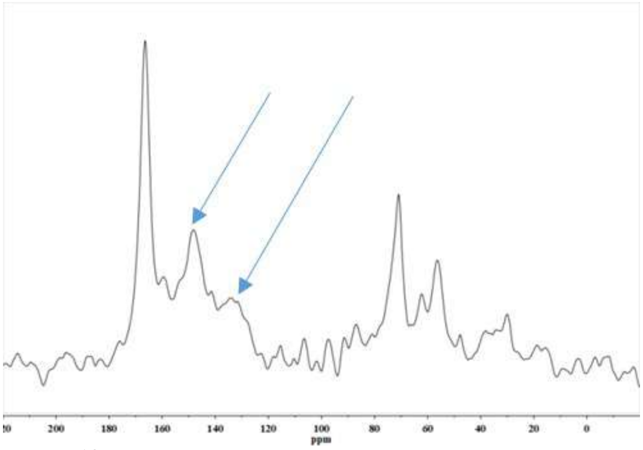

Fig 6 ^{13}C NQS NMR spectrum of sample 6II

The lignin condensation degree calculated by integrating the two signals at 148 and 136 ppm in the ^{13}C spectrum obtained with the NQS pulse sequence, for two samples at different depths (Table 3) does not differ significantly from the value reported for the reference sample. This evidence indicates that lignin has not undergone any appreciable degradation phenomena.
The holocellulose/lignin (H/L) ratio was calculated by VCT experiments considering the holocellulose and lignin formulas proposed by Haw et al (Haw et al. 1984)[21] having a molar mass of 162 and 183 g/mol, respectively.
The H/L ratio is an indicator of the wood conservation state based on a quantitative evaluation of the signals of the different carbon nuclei present in the sample (Macchioni et al 2012; Łucejko et al. 2012)[22-23].
The H/L ratio increases with depth (Table 3). This confirms that the degradation process involves mainly the surface layers and slows down towards the innermost layers, in accordance with the trend observed by ^{13}C CP MAS NMR experiments and CI measurements.
It is worth noting that the values of the H/L ratio are similar to those obtained in one of our previous articles on the non-consolidated rostrum wood (Caruso et al. 2011)[24].

Study of the interactions
In order to obtain information on the interactions between the wood components, a relaxometric analysis was performed and bidimensional Frequency Switched Lee-Goldburg cross-polarization heteronuclear correlation (FSLG CP HETCOR) NMR spectra have been acquired.
Firstly, $T_{1\rho}H$ relaxation times were determined for the characteristic peaks of cellulose, lignin and Kauramin and the obtained values are reported in Table 2.

Table 2 Values of $T_{1\rho}H$ for the characteristic carbon atoms of cellulose, lignin and Kauramin for samples 6I-6VII. Experimental errors are less than 10%. No $T_{1\rho}H$ values are reported for the cellulose of sample 6I because of the low quantity of this compound.

	Cel	Lig	Kau
Structure	C6(c)	OCH_3	C=NH-
ppm	65	56	48

$T_{1\rho}H$ (ms)			
6I		1.6	1.7
6II	1.8	1.7	2.2
6III	1.6	1.8	1.8
6IV	1.8	1.9	1.6
6V	2.0	2.0	1.8
6VI	2.3	2.0	1.6
6VII	2.1	2.0	2.3

It is known that similar values of $T_{1\rho}H$ for carbons surrounded by a comparable proton density indicate a dynamically homogeneous system (Lau et al. 2002; Spinella et al. 2017)[25-26].

Comparing the $T_{1\rho}H$ values for cellulose, lignin and Kauramin, it is possible to notice that they are equal within the experimental error in all samples. This is an evidence of the existence of interactions between consolidant, cellulose and lignin.

This evidence was confirmed by 2D FSLG CP HETCOR NMR spectra. These spectra are ^{13}C-^{1}H bidimensional maps which refer to correlations between carbon and the mainly dipolar coupled protons.

The spectrum relative to the sample 6II is reported in Figure 7, as an example.

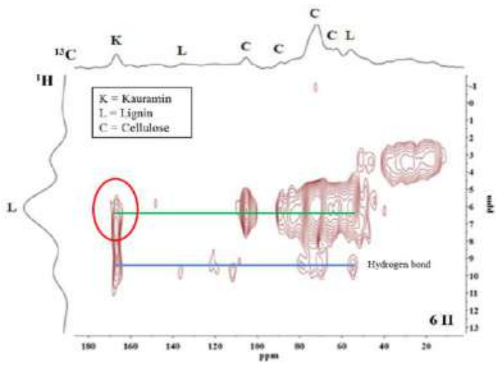

Fig 7 2D FSLG CP HETCOR NMR spectrum of sample 6II. K, L, and C indicate Kauramin, lignin and cellulose respectively. In the x axis is reported the carbon spectrum, in the y axis the proton spectrum. Signals that are on the same horizontal line indicate carbon nuclei on which protons with the same chemical shift cross-polarize.

The range 10-20 ppm is characteristic of protons forming hydrogen bonds (Chierotti et al. 2013)[27]. The signal at 9.5 ppm, therefore, indicates the presence of weak hydrogen interactions between Kauramin, cellulose and lignin (blue line in Figure 8).

The ^{13}C-^{1}H FSLG CP HETCOR NMR spectrum provides a direct observation of the existence of an interaction between the aromatic rings of lignin and the triazine ring of Kauramin (red circle in Figure 8), reinforced by the network of hydrogen bonds.

The functional groups involved in these interactions are evidenced in Figure 8.

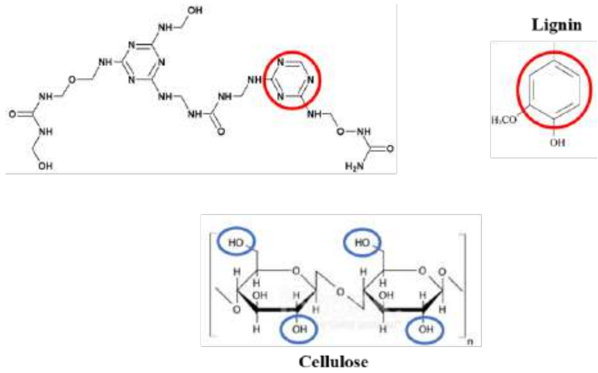

Fig 8 Structures of Kauramin, lignin, and cellulose. Groups among which specific interactions take place are circled in red. Groups between which weak hydrogen interactions are established are indicated in blue.

The hydrogen bond network involving Kauramin and both wood components reasonably stabilizes the consolidating effect of Kauramin. Therefore, the experimental data support the irreversibility of the Kauramin treatment reported in the literature (Fiesoli et al. 2010)[28].

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Multivariate Analysis in the Cultural Heritage Field

Sebastiano Trusso

Istituto per i Processi Chimico-Fisici, CNR, V.le F. S. d'Alcontres 37, 98158 Messina
trusso@ipcf.cnr.it

Principal component analysis (PCA) is one of the most widely used multivariate techniques in statistics. PCA, beside other multivariate statistical methods, is now one of the most important and widely used statistical techniques in many various fields ranging from biology to finance and of course cultural heritage. A search of Google Scholar indicates about 1.5 million papers were published in the last ten years containing some mention of PCA. When the same search is performed adding the '*cultural heritage'* string more than 30.000 papers are found in the last decade, pointing out how statistical methods are nowadays widely used tool in the cultural heritage field. Collection of very large dataset, in fact, is not uncommon in the cultural heritage field. The characterization of work of arts by several experimental techniques like Raman, infrared, X-ray fluorescence or laser induced breakdown spectroscopy (LIBS) can produce very large dataset that originate by performing measurement on several objects and/or at different sampling points of the same objects. Considering that the main goal in the cultural heritage field is not limited to the object's chemical characterization but, even more important, to the correlation to their geographical origin, production methods and dating, statistical methods can aid in handling large dataset identifying a set of variables, smaller than the original set of variables, that nonetheless retains most of the sample's information. In an experiment like Raman or XRF tenth or even hundreds of spectra can be collected, classification of these spectra based on features that are in common or at difference is then very difficult, but it can be performed by the PCA. The original data are organized in a matrix M with R rows and C columns from the input matrix M PCA computes a set of new variables, the principal components, obtained from the original ones trough a procedure of successive axis rotation. The first principal component (PC1) is determined as the one with the largest possible variance with respect to the original data. The second one (PC2) has the largest variance among all the possible components orthogonal to the first one. Under the same constraints, largest variance and orthogonality with respect to the previously determined ones, all of the other components are computed. Usually, the first PCs contain most of the variance, so that a plot of the first two PCs allow the identification of groups of samples with similar characteristics. In this lecture we will recall briefly the PCA mathematical background and some case studies will be presented [1].

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Fluorescence Spectroscopy as Diagnostic Tool for Conservation Studies

Aurelio Bonasera ([a,b])

([a]) Department of Physics and Chemistry - Emilio Segrè, University of Palermo, v.le delle Scienze bdg. 17, 90128 Palermo, Italy.
([b]) INSTM – Palermo Research Unit, v.le delle Scienze, bdg. 17, 90128 Palermo, Italy.

E-mail: aurelio.bonasera@unipa.it

Introduction

Human societies have always given great importance to the protection of artefacts presenting a well-recognized historical and sociological value, thus cultural heritage preservation is an ongoing issue, currently gaining more attention to the public opinion. Nowadays, scientific progression makes available a number of sophisticated tools and techniques, which give the opportunity to deeply study and characterize those assets, with the chance to prolong their lifetime and durability. Preserving artistic patrimony relics is a moral duty for modern societies, but it also represents a florid business, able to support the financial health of several countries around the globe. Cultural heritage universe comprises items with a credited artistic value, such as sculptures and paintings, but other objects like pottery, coins, musical instruments, and clothes, are worth of consideration in numerous cases. Even nowadays very familiar goods (*e.g.*, a personal computer or a locomotive) are becoming or will become cultural assets for the future generations. The preservation of human cultural patrimony moves its focus along with the progression of time, by the way we can already evidence that, looking at those artefacts from the chemist or materials scientist viewpoint, they look like a puzzling object of study, for several practical reasons. These items usually look like a heterogeneous combination of different materials, ranging from organic to inorganic matter. For example, polychrome artworks like easel paintings possess, most of the time, a layered structure where a support, a ground, a coloured paint layers and a protective varnish are combined; their combination is then resulting in peculiar morphological features on both the macro- and micrometric scale. Such complexity has to be deeply investigated and understood before moving the discussion to the preservation strategies; this is the reason why the work of the scientific community allowed to develop several techniques, able to grasp information at the molecular level and guide the understanding of the artefact under the lens.

Fluorescence Spectroscopy – Theory & applications

Among a variety of approaches and techniques, Fluorescence Spectroscopy (FS) is one of the most interesting tools, able to provide information related to the superficial layer of a relic. The technique is based on a well understood photochemical phenomenon, the fluorescence. Fluorescence (1) consists in the emission of light from a molecular-scale emitter, when it is properly "stimulated" by the irradiation of specific electromagnetic radiation (see Figure 1). This "stimulation" is induced when a photon of light with a certain amount of energy is able to promote the transition of an electron located on the emitting molecule or inorganic complex, from its fundamental state to an "excited" state of energy; the excitation lasts for a short period of time, ending up in the dissipation of the excitation energy. Part of this energy is re-emitted as a photon of light, with minor energy if compared with the "exciting" photon (in general, fluorescence lifetime is in the range of $t \leq 10^{-7}$ sec, but there are some exceptional cases (2)). The wavelength of the emitted photons and the bandwidth of the emitted light are information intimately related to the chemical nature of the emitter. Considering that fluorescence is usually (but not exclusively) triggered by UV or visible radiation, emitted light belongs to the visible or near-infrared portion of the electromagnetic spectrum. Fluorescence is generally ascribed to chromophores – dyes and pigments, both inorganic and organic – but not only. In the case of organic materials, fluorescence is typical of materials possessing a portion of the skeleton characterized by delocalized electrons (conjugated π-systems, aromatic fragments), and this is the reason behind the emissive behaviour of materials like binders, resins, and paints.

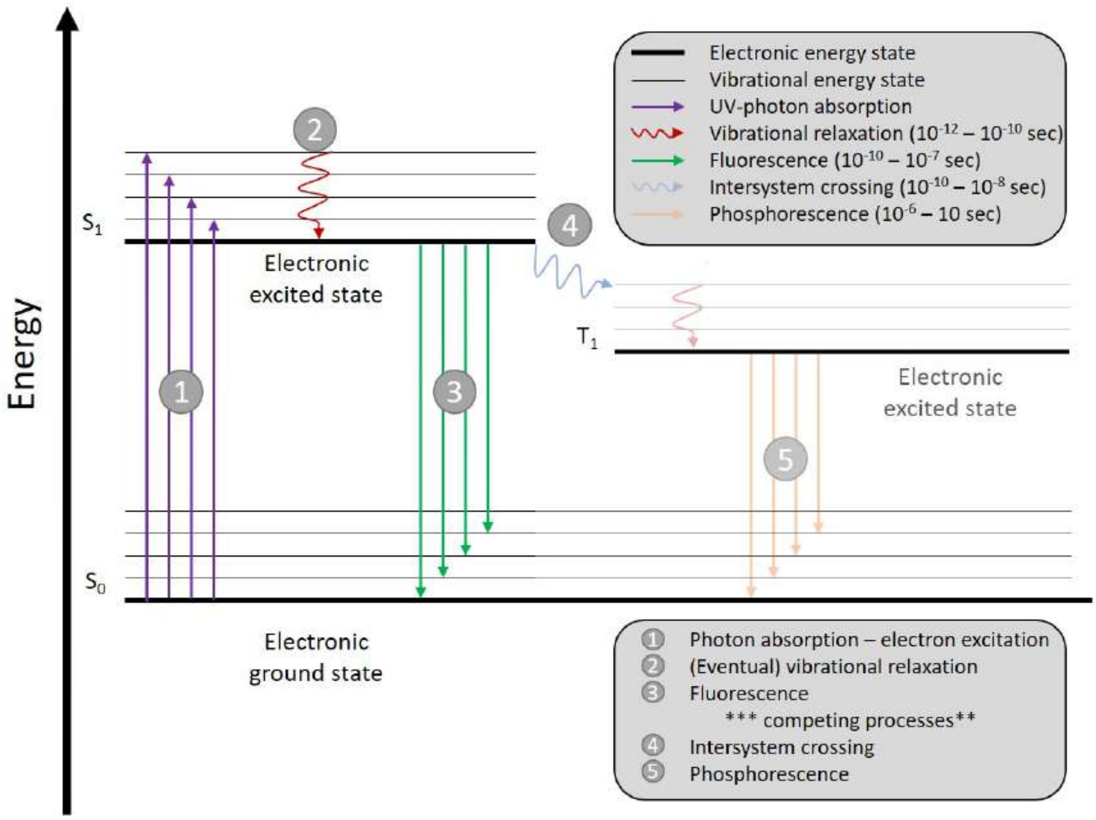

Figure 1. Simplified Jablonski diagram representing the principal events bringing to the fluorescence emission when an emitting molecule is put under UV-photons irradiation. In order to provide a clearer vision, some competing processes (*i.e.* Phosphorescence) are shown as well.

In the literature, several techniques based on fluorescence are present, like UV imaging, (3) UV Fluorescence Photography, (4) Technical Photography (TP), (5) UV-Induced Visible Fluorescence (UVIVF), (6) Laser-Induced Fluorescence (LIS), (7,8) Two-Photon Induced

Fluorescence (TPIF), (9) Fluorescence Lifetime Imaging (FLIM), (10) and there are even more examples. However, for the purpose of this overview, the discussion will focus over the description of the molecular objects which can be targeted following their visible or infrared fluorescence emission, then the pros & cons of this methodology, the most common practical setups for performing the measurements and, finally, the relevance in the cultural heritage preservation will be underlined with some examples. According with these guidelines, specific techniques will be mentioned only from time to time, while the discussion will cover aspects of broad applicability.

As previously mentioned, chromophores are the typical molecular-scale objects producing fluorescence emission; dyes and pigments are ubiquitously present in pictorial artworks (paintings, frescoes, ceramics, etc.), can be found in natural fibres (*e.g.*, the ones constituting clothes), (6) and can be seldom found in sculptures or monuments as decorative surface layers. In this context, FS can be easily employed for shedding light on the superficial layers of an artefact: It can be used for highlighting the distribution of luminescent materials which may be related to aging alterations as well as retouches - fluorescence is more intense in the case of old paintings or varnish layers due to eventual oxidation phenomena occurring through time and exposition to sunlight. (11) Fluorescence measurements offer another significant contribution by revealing details originally visible on an artwork, which are no longer evident under normal light due to the degradation of the chromic layer – the chromophore has been altered but its colourless binder matrix is still present and able to produce fluorescence. (10) FS undoubtedly has some appealing advantages: (i) it is a non-destructive technique, which operates on the surface on the sample and does not require specific pre-treatments, can be performed directly *in situ* and under remote control; (ii) the analysis gives a fast and reproducible response, that is usually converted into a spectral profile (where the fluorescence intensity is function of the wavelength of the light); (iii) it is highly sensible. These advantageous features are counterbalanced by some drawbacks. Among the most important, FS is a surface technique, reason why only surfaces can be analysed unless considering semi- or destructive sampling approaches to get access to inner layers of the artwork. Moreover, fluorescence emitting objects generally have high intensity when dispersed in solution, but the intensity is definitely lowered when they are packed in the solid state, due to intermolecular quenching mechanisms which are depressing the radiative process (*i.e.*, the emission of the light photon). (1) Furthermore, although the technique has high sensibility, some limitations are due to its intrinsically low specificity; emission spectra usually show broad features, so that there are rare chances of an unambiguous proof of the chemical identity of a specific material.

The presence of broad features is a limitation, but there are cases in which fluorescence can immediately provide the right answer: It is possible to distinguish, for example, very similar mineral pigments like Egyptian Blue and Han Blue, (12) where the emitting specie is a copper complex surrounded by a silicate network. Egyptian Blue is a pigment well-known by mankind since millennia; its use is documented since 2500 BC in Egypt, but its presence in artworks is reported during the Roman Period and later in the early centuries of the Medieval Age. From a chemical point of view, it is a calcium copper tetrasilicate, corresponding to the natural mineral named *cuprorivaite*. Similarly, Han Blue has been found in Chinese artefacts produced during the Han Dynasty Age (208 BC – 220 AD), and it is a barium copper tetrasilicate. Both these two blue pigments interestingly present strong photo-induced luminescence, with emissions in the IR when excited with a visible light source. Egyptian Blue emission spectrum is characterized by an intense and broad emission in the infrared range, centred at about 950 nm, while Han Blue emission band is redshifted, with maximum emission localized at ca. 980 nm. The differences between the emission spectra of the pigments are attributed to the chemical environment experienced by copper atoms within the mineral lattice, more technically a different ligand-field. Thus, the luminescence profile becomes connected to the microenvironment copper atoms experience in the two different bulk pigments, and FS can be easily employed as an efficient tool for distinguishing the two pigments when present on an artwork.

Some other attributions can be more difficult to be carried out on the base of just FS data, but this lack in specificity can be tackled by coupling fluorescence measurements with data provided by a complementary technique, reason why it should be coupled with other spectral techniques (*e.g.*, absorption spectroscopy, (13) Raman (8, 13) or FT-IR spectroscopy (14)). A typical combination is given by absorption and fluorescence spectroscopies, whose spectral data are complementary and require similar experimental setup – a light source, filters and a detector, although the geometrical displacement of the components is different; the limited number of components offers the possibility to build up personalized setups with minor effort. (8, 15-16) The significant advantage given by collecting absorption spectra relies on the possibility to use algorithms able to correct fluorescence spectra taking in account distortions of the emission caused by filter effects or self-absorption of the matrix, finally allowing a more precise identification of the sampled artefact. Another possible approach is to create a spectra database, recording spectral data for the highest number of dyes, pigments, binders, etc., in order to have a rapid comparison among the fluorescence profile obtained after sampling an artefact, and the profiles uploaded on the database. A well assessed strategy reported in the literature consist in preparing a library considering the most common and natural organic/inorganic dyes, plus the synthetic ones. (17) Once operated a certain selection, it is important to consider the neat dye but also its combination with a selection of binders, for example. The reason of this operative choice is due to the possibility of an alteration of the fluorescence profile caused by the chemical micro-environment the chromophore can experience in the artwork/artefact. Similarly, the literature suggests to consider typical additives which can alter or contribute to the whole fluorescence spectra, such as ZnO white, with its characteristic intense emission in the visible region (maximum emission at ca. 520 nm), and a descending in the near infrared region. (17)

Fluorescence Spectroscopy – Experimental setup

As aforementioned, one issue making FS appealing to the eyes of restores or other scientists involved in cultural heritage preservation is the simplicity of its setup. From a conceptual point of view, the fundamental components required for performing the analysis consist in: (i) a source of UV radiation; (ii) a cut-on filter; (iii) a sample holder (that is, the most of the times, not necessary); (iv) a second cut-off filter; (v) an image detector. The UV radiation source is one of the components which underwent evident evolution through time. The oldest and most common source for artistic assets application is the Wood's lamp, basically a lamp emitting long-wave ultraviolet light (UV-A) and visible light, although this is a minor contribution; (18) an absorbing material, deposited either on the bulb or in a separate glass filter in the lamp housing (like nickel oxide), filters out the most of the undesired visible radiation without or negligibly affecting the emitted UV-radiation. Lasers (19) are a more recent technology, with excellent performances as UV-sources; due to their tunable intensity, it is possible to investigate samples with high number of photons, so to increase the intensity of the emitted spectra. Unfortunately, prolonged and uncontrolled irradiation could induce photochemical or thermal degradation. (20) Similar pros & cons can be extended to the last product appeared on the market, LEDs technology. (21) Characterized by lower power, they are less harmful if compared to lasers, and definitely less expensive, practical, and simple to be integrated in sophisticated setups. We previously mentioned the importance of filters. Cut-on filters for the UV source are little by little becoming less important due to the wider use of highly monochromatic UV-light sources (laser and LEDs have negligible parasite emission in the visible range, and the emitted light is in a very narrow range of wavelengths). However, filters technology is still quite important for purifying the signal outcoming from the sample, due to the eventually present reflected UV-radiation. Here, there is a wide variety of choices on the market, and several options offer multiple alternatives which can be suited for a wide range of analyses and experimental setups. (22) Finally, the imaging detector is deputed to the conversion of the light stimulus into a digital information, a CCD detector in most of the case. The relevant difference comes later, when the collected signal has to be translated in the final output. In general, there are two possible scenarios. (i) The detector is integrated into a digital camera; thus, the final output is an image file. In this case, the operator can have an overview on a large area of the sample and receive a sort of qualitative map of the distribution of fluorescence over the samples surface. (ii) The detector is integrated with a spectrophotometer, which will finally plot the fluorescence intensity against the wavelength. This setup usually limits the analysed surface to a spot on the millimetre-scale, but the information in turn is quantitative and can be associated to the specific chemical nature of the emitting specie.

Fluorescence Spectroscopy – A study case

After widely scanning the literature, the first consideration to report is that FS application field is mainly relater to pictorial artworks, texts reported on paper or similar supports, with a time window ranging from the Medieval to the Modern Age; only a minor number of case studies concerned archaeological context. Among those, one is herein reported to underline the possibility given by fluorescence measurements to have access to information that would otherwise remain inaccessible. The case reported by Artigas *et al.* considers the investigation of fragments of a Roman amphora found in the archaeological site of Iesso, in Catalunia – Spain (see Figure 1a). (9) Archaeologists found several amphorae near the city walls and, due to the specific place and disposition, they concluded that amphorae were brought by the first legions arriving in Iesso, and probably the wine therein stocked was used when celebrating the city wall building and following the ritual foundation of the settlement. As usually occurring in that period, the pottery reported an inscription mentioning the two consuls ruling at the time of the production of the wine (Figure 2b); this information was considered of crucial importance in order to correctly recognize the foundation year of the Roman village, since the succession of Roman consuls is well documented along the whole story of the Roman Empire. The challenge was related to the central part of the inscription, since the letters indicating the second consul were initially quite deteriorated, and later turning unreadable after a first superficial treatment (humidifying the painted area with a water solution) which should in principle reveal the missing characters but ended up worsening the situation. Plus, shortly after the discovery, photobleaching of the pigments almost cancelled the inscription. Here, FS was considered a key approach, aiming at the detection of pigments or binder traces, whose distribution over the potter should follow the previously present inscription, which was deteriorated or washed out by the time. The authors considered the possibility that binders typically used by the Romans (albumin or casein) could be present, and they luckily offer fluorescence in the visible portion of the spectrum; however, they also considered that an intense UV-light source could increase the risk for the artifact's photodamage. For this reason, they focused their attention on Two-Photon Induced Fluorescence (TPIF), a technique which is based on the contemporary absorption by the emitting molecule of two photons possessing low energy. Their contemporary absorption causes the same excitation induced by an UV-photon with as much energy as their sum. Two-photons absorption phenomena have lower probability to occur, so this operative choice looks like a complication; however, since the employ of low energy photons (in the near-infrared region) reduces the risk of photodamage and photobleaching, it is possible in this case to work with high power irradiation sources without any drawback. Crude TPIF images returned a barely readable sequence of letters (Figure 3c); a combination of histogram equalization adjusts for the total distribution of the signal (Figure 2d) and some image processing techniques (Gaussian blurring and binarization, Figure 2e), provided a clear us to obtain a clear image of the areas and new hints.

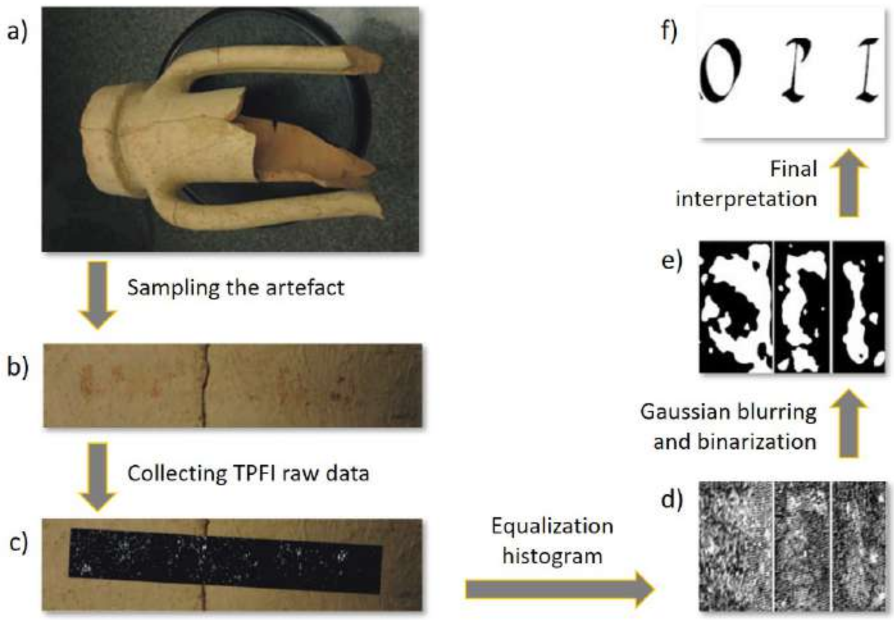

Figure 2. a) The amphora under study and b) detail of the investigated area with clear traces of an inscription. c) Raw TPFI of the painted area. d) The previous images with improved quality after an equalization histogram image processing technique, (e) after a subsequent Gaussian blurring and binarization, and f) the hypothesis for the Roman consul written using *Capitalis Rustica* calligraphy. Adapted from Ref. (9).

The first letters at the left of the inscription suggested that one of the consuls was *Quintus Fabius*; the letters on the right signified "*Consolibus*", a Latin word meaning "being consuls", while the central part suggested *Lucius Opimius* as second consul. Considering that the two consuls were ruling starting from 121 BC, the wine stocked in the amphorae belonged to the 121 BC harvest, so that the foundation of the roman city of Iesso should be dated after this event. From this case study we can conclude that FS is a powerful and versatility technique that is not able to provide the full characterization of an artifact but, combined with other techniques and historical information, it can definitely provide a remarkable support in the cultural relics characterization and contextualization.

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Conservation

To know for conservation: www.analysis.eo

Lorenzo Appolonia ([a])

([a]) Centro Conservazione Restauro, La Venaria Reale (TO); RAVA, Soprintendenza beni e attività culturali;

lorenzo.appolonia@centrorestaurovenaria.it

l.appolonia@regione.vda.it

Premise

www.analysis.eo. It's not a new web page, but only a joke to identify in which way the concept of conservation (1) could be understood. When decrypted the new web-address we can found:

WhyWhenWho.analysis.EnvironmentObject

Introduction

Marco Polo describes a bridge, stone by stone.
- But what is the stone that supports the bridge? - ask Kublai Kan.
- The bridge is not supported by this or that stone, - answers Marco,- but the line of the arch they form.
Kublai Kan remains silent, thinking. Then he adds: - Why do you speak to me Stones? It's just the arch I care about.
Polo answers: - Without stones there is no arch. (2)

This short part of the Calvino's tale could be used like a "manifesto" for the conservation of the Cultural Heritage. In fact, at the end, we can talk of conservation if the monument still exists. Without the stone we don't have a bridge, or tower or others, this mean that without the conservation of the materials that is the visible part of the object this don't exists. This means that when we talk of conservation, we must to take in care that the goal of a conservation process is always the possibility to preserve in the best way the objects (3) materials. For this reason, the knowledge of the matter process alteration (4) and causes are specific knowledge of the Natural Sciences: physic, chemist, biology and others linked with these sciences.

The alterations processes are depending of the knowledge of the object's compositions and the interactions from the matter and the environment. If the science like chemist, biology and physic can describe in a well way the kind of process of alteration, but cannot be enough to understood all the process. The interaction from the matter and the environment could be affected by the shape and the exposition of the object with the environment. For this reason, geometry should be included like a science for the conservation and any kind of conservative approach must to take in care the composition, the environment and also the form.

When we talk about the environment, we must to include all the factors and parameters, the lecture of the contest must to be holistic and start from the general point of view to the detail. All the conservation study know that the water is the must diffused causes of alteration, but the complexity of the system come from the variability of the contribution of: gasses, climate and radiations. For these reasons the experiments and the studies made in the laboratory don't can give us a complete and right result, but only an indicative result that some time must to give a different behaviour in the situ.

Why When Who to make analysis?

A good conservation approach needs a lot of answer about the question linked to the presences alterations and the causes that produced them.

When we approach a CHobject (Cultural Heritage object) for a conservation action we must to consider a lot of questions and only the sciences can give a right answer and, sometimes, more of them together.

Could be obvious but should be necessary to understand why I need to make analysis. In fact different actions can use different analytical procedures.

We can have analysis for the knowledge, this means to characterise the composition of the object. This it's very important to know the composition for a preventive conservation evaluation or which led to a form of alteration. The knowledge is also used for archaeometry analytical support, to know if an object could be original or for the provenance. This is a specific branch of the science for the cultural heritage, but sometime the peoples think that these analyses are the same for conservation. The characterization of the components, even if carried to the measure of traces, cannot be sufficient in order to understand the origin of the factors of alteration that interest the conservation processes.

An important phase where the application of the analytical procedure must to be considered fundamental, is that for the conservation project. Also, the Italian national legislation, concerning public works, provides that the final project must be preceded by an analytical phase (5). It is possible that the humanistic approach of the Italian cultural heritage sector, derived from the philosophical approach of Benedetto Croce and his application made from the Minister Giovanni Gentile, created in Italy, a vision not aligned to the needs of an applied sector that, in its conservation intent, it can not only take into account the value and artistic quality of a work, but also and above all the qualities and behaviors of the materials that compose them. The possibility to caractherise the matter and the interaction with environment and the methods or materials used in the conservation process must to be take in care for any intervention.

In this step of the conservation process, the science can help to optimise the method of intervention. Any process, like cleaning, consolidation or preservative treatment, can use an analytical approach to evaluate the risk about the methods and also the choose for the less aggressive of them.

We can also consider that the analyses made for the project, the same used for the choice of the conservation methodologies, can also applied for the support in the intervention process, especially these made in the situ on the object, or that are not invasive. This part can be a methodology to have a control of the quality of the treatment, a concept not well know in the humanistic approach, but important in an scientific point of view, especially if we have the responsibility in the conservation of the patrimony of the humanity.

But a right conservation proceeding is not complete if we talk only about the previous and during analytical possibility. In any conservation action, we can utilise different analysis to have a right result. Also, at the end of the restoration and for the future of the object, we can monitor the condition with many analytical methods. This kind of approach, contribute in the preventive conservation actions and in the maintenance project for the object.

The analytical context in the conservation, is very wide and general, but we can also take care about the control of the quality of the material for conservation. The low quantity of products used in the restoration don't permit a specific production of compound, this mean that in general the products are sold by the transformer that bough high quantity and produce small package, often with new formulations adapted to the requests of restorers. In this case, but also for the products in general, an analytical control can permit to understand if the product used corresponds to the one requested or reported on the data sheet. Another method for a correct quality control included in a right conservation process.

When someone ask why the analysis are not made in one conservation action, the answer that we receive is that the costs are very high.

It's true that the analytical instruments are very expansive, but the question is: for which kind of interest we make the analysis?

The needs for an archaeometric study include scientific instruments and generally very specific and sometimes very expensive. For this kind of analysis, the more organised are the university laboratory or those in research centres. In this case the cost depends if there are some financial contribution or if the analysis is in a research project.

For the conservation, or the study of the matter, or the development of the treatment, sometimes the analysis necessary are not to complicate or expensive. In these cases, the knowledge could be simply and only in the surface. In general, we can distinguish the analysis for the archeometric like a quantitative approach and these for the conservation treatment like a qualitative approach. It is obvious that some analysis made for the conservation use a quantitative analytical instrument, but the distinction posed is theorical and comprehensive in the complexity for a chemist.

The use of spot test, for example could be enough to know the compounds of the object and this can give us the knowledge necessary to know the possible kind of interaction of this matter with the environment. The same is if we need to know the porosity, we must simply compare the speed of the absorption of a drop of water. Many others kind of analysis can give us the idea of the behaviours of the matter, but it's obvious that any possibility to have a more precise and numeric data about some parameters could be useful. It is evident that when it is possible and the budget it's enough, the possibility of having a thorough analytical result is better condition and to be pursued. The analytical data obtained, as well as all measures for the development of intervention methods, should also be collected in a database. This possibility would create an excellent tool of work and comparison useful for the entire scientific community, allowing, moreover, not to repeat the same type of analysis several times to the advantage of the integrity of the object. In any case the question is that the possibility to have a result came from a scientific analysis, any kind of analysis, is more objective that any others subjective evaluation, usually made in a conservation action without analysis.

The process of conservation, in any case need to have precise questions, in order to be able to have adequate and right answers. The questions may address the choices of the methods of analysis and also the need or the quantity of the sampling necessary to obtain a correct and complete result.

The choice of which could be the analytical techniques is competence of the scientific sector. In general, it's wrong if restorer, architect, archaeology or art historian ask a conservation scientist for a specific analysis. The task of experts in other sciences working in the field of cultural heritage is, therefore, to express questions correctly. If it's clear what we want to know, the experts should give the possible list of analytical possibility, also explaining the limits of the proposed technique or the quantity of sample that we need to have accuracy and quality of the response.

References

1. ***EN 15898***:2019 Conservation of cultural heritage. Main general terms and definitions
   Conservation: All measures and actions aimed at safeguarding cultural heritage while ensuring its accessibility to present and future generations
2. Italo Calvino, Le città invisibili, breve dialogo fa il Gran Kan (Kublai) e Marco Polo, "Supercoralli" e "Nuovi coralli" n. 182, Einaudi, 1972
3. ***EN 15898***:2019 Conservation of cultural heritage. Main general terms and definitions
   1.1.1 Object (synonym: item) Element of tangible cultural heritage
4. ***EN 15898***:2019 Conservation of cultural heritage. Main general terms and definitions
   1.3.4 Alteration (synonym: change modification) Change in material properties
5. Codice appalti, Art. 23, comma 6

La Nave punica: storia e restauro dal ritrovamento alla presentazione nel Museo Lilibeo

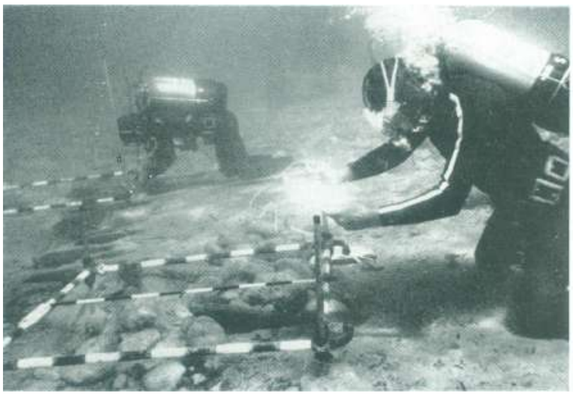
Enrico Caruso

Appena fuori dalla Laguna dello Stagnone, nel braccio di mare che separa Favignana e le isole dello Stagnone, a poche decine di metri a nord dell'Isola Lunga (fig. 1), negli inizi degli anni Settanta del secolo scorso, un fortuito ritrovamento durante il dragaggio del fondo marino per ricavare sabbia da costruzione, fece emergere alcuni frammenti di legno. Proprio in quegli anni era presente in Sicilia Miss H. Frost, abile archeologa subacquea, nota nell'ambiente per le scoperte eccezionali fatte in medio Oriente che venne incaricata dello scavo del relitto.

Miss Frost scavò il relitto nel corso di due campagne alla quale prese parte anche il compianto Sebastiano Tusa, allora giovane e curioso archeologo che portò il suo sguardo sott'acqua per la prima volta e da quel momento decise così che il suo destino di archeologo avrebbe preso una strada che si è poi rivelata vincente per lui e per la Sicilia.

L'insieme di tracce di relitti che si rese allora evidente ha portato all'individuazione di circa 4 insiemi tra i quali emergeva la nave punica e quella che venne da subito definita *sister ship*, nave sorella.

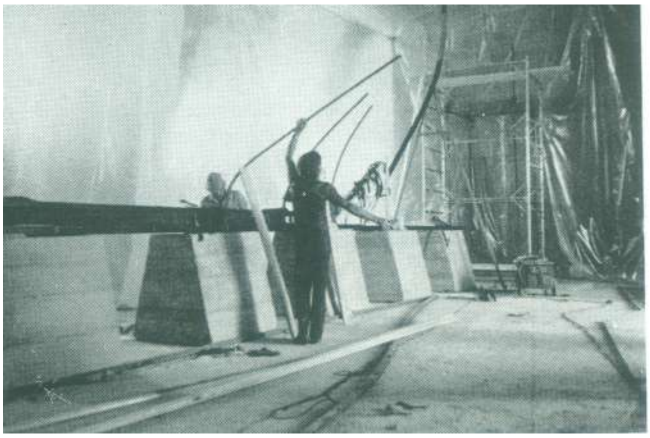
Lo scavo subacqueo era in qualche modo ancora pioneristico e il rilievo delle parti di nave rinvenute (fig. 2) permise l'estrazione degli elementi (fig. 3) che componevano le navi i quali vennero immediatamente portati presso l'azienda vinicola Pellegrino, che offrì riparo nelle vasche di desalinizzazione approntate per l'occasione.



Gli elementi lignei dopo un lungo periodo necessario per la perdita del sale vennero infine immersi in vasche contenente il noto Peg, una cera che avrebbe ricostituito la struttura del legno svuotato dalla lunga permanenza sott'acqua, ricostituendo la solidità perduta. Purtroppo, la tecnica presa a prestito dall'esperienza svedese nel campo del recupero delle navi, ha dato ai reperti il caratteristico colore nero che tuttavia richiama alla memoria il racconto di Tucidide a proposito delle nere navi fenicie.

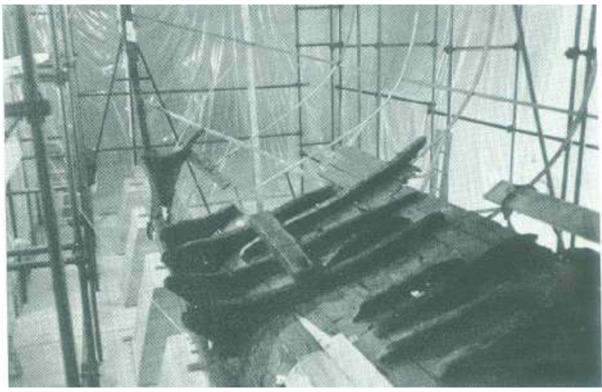
Vennero quindi fatti dei calchi dei frammenti rinvenuti al fine di procedere alla ricostruzione volumetrica della nave e studiare così una struttura adeguata a reggere i frammenti stessi riportati nella loro volumetria originale. A questo punto sorgeva l'esigenza di valorizzare il più antico relitto di nave trovato nel Mediterraneo e quindi immaginare di esporlo in un ambiente fornito della volumetria adeguata a contenere il relitto e la scelta cadde sul più elegante tra i 4 bagli o strutture vinicole erette tra la fine dello Ottocento e gli inizi del Novecento, che sorgono sulla punta di Capo Boeo a Marsala: Baglio Anselmi.

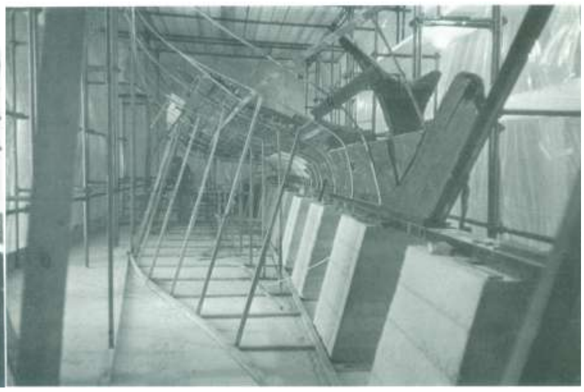
In quegli anni la struttura era già in disuso da tempo ed era quindi vuota per accogliere le spoglie della nave. Le foto di allora mostrano un grande vano scandito da archi acuti trasversali sui quali era posta la copertura in legno e tegole coppi che ben funzionavano per la conservazione del vino nelle botti ma che era però inadatta a dare un clima costante all'interno del grande vano, necessario per la buona conservazione del relitto. Il pavimento era in battuto di terra e su di esso venne stesa una gettata di cemento per pareggiare il fondo e renderlo idoneo a sostenere la struttura portante della nave punica (fig. 4).



Sul piano in cemento vennero poi costruiti dei massicci tronchi di piramide in cemento armato posti in sequenza su cui venne appoggiata una lunga trave in ferro a doppio T alla quale vennero saldati gli elementi che riportavano fisicamente le curve della carena della nave, così come era stata immaginata a seguito dei rilievi e della simulazione verificata con l'aiuto dei calchi in gesso. Tutti gli elementi che ricostruivano idealmente il profilo della carena della nave vennero poi collegati da elementi anch'essi in ferro che vennero poi sorretti da sostegni verticali e inclinati che sostenevano il profilo delle curve della nave (fig. 4).

Al fine di creare un ambiente idoneo a proteggere il relitto venne costruito un ponteggio attraverso il quale si venne a creare un ambiente separato grazie a dei grandi teli trasparenti di plastica necessari a creare un ambiente confortevole, in grado di accogliere gli elementi del relitto mantenendo una temperatura costante (fig. 5-6).





L'ipotesi iniziale che era emersa dallo scavo dei relitti era che la nave punica e la nave sorella fossero due navi identiche e che attraverso il loro assemblaggio, la poppa della nave punica e la prua della nave sorella, si potesse ricostruire idealmente il relitto in tutta la sua forma anche se frutto dell'assemblaggio di due differenti relitti. Una foto d'archivio mostra la prua ricostruita della sister ship con la simulazione del rostro ligneo insieme alla ricostruzione della carena della nave posta in continuità con la nave punica che rimaneva nascosta alla vista dal tendone di protezione. Questa soluzione immaginata possibile all'inizio dello studio venne poi abbandonata quando Miss. H. Frost, approfondendo lo studio dei materiali lignei e dei reperti prese atto di una diversa concezione tra le due navi e decise di eliminare la ricostruzione della prua per evitare confusione possibili tra i fruitori del/dei relitti (fig. 7).

La visione del relitto comincia a essere garantita attraverso un riquadro trasparente (fig. 8) di un buon tendone in resistente materiale plastico sostenuto dall'alto da funi agganciati alla struttura e approntato per sostituire l'invasivo ponteggio che venne eliminato. Tutto ciò in attesa dei lavori di restauro che vennero fatti successivamente e che hanno interessato le coperture rifatte con un tavolato ligneo che garantisce, grazie a opportuni accorgimenti, una temperatura meno soggetta a sbalzi di temperatura.

Il Baglio viene poi restaurato e si pose un nuovo pavimento in cotto rialzato rispetto alla pavimentazione in cemento su cui era posta la nave punica. La nave rimase quindi in una sorta di fossa più bassa di circa 30 cm, adatta a contenere tutte le strutture in ferro approntate per realizzare il suo profilo/volume. Vennero quindi posti lungo il bordo dei dissuasori in legno e corda, sui bordi dell'incavo dei ciottoli per nascondere o mimetizzare il gradino (fig. 9), e vennero inseriti dei cerchi di sabbia circondati da grandi ciottoli per accogliere le anfore trovate con il relitto della nave (fig. 10).

L'esposizione è confusa, la replica della *sister ship* viene appoggiata alla struttura della poppa della nave punica in corrispondenza dei tre sostegni inclinati che sorreggevano senza una reale funzione statica la parte retrostante della nave.

Nel frattempo, era già il 1984, da poco meno di dieci anni il relitto era continuamente visitato, prese forza l'idea di realizzare una mostra sulla città di Lilibeo, la cui importanza nell'antichità non era nota abbastanza per l'assenza di studi e ricerche estese verso il vasto pubblico che non avevano contribuito a una adeguata conoscenza delle potenzialità della città e della sua storia antica. Venne quindi realizzata presso la chiesa del Collegio dei Gesuiti la mostra realizzata da C.A. Di Stefano nel 1984, dal titolo *Lilibeo. Testimonianze archeologiche dal IV sec. a.C. al V. sec. d.C.*, alla quale ebbi la possibilità di partecipare per la redazione dei disegni espositivi e a cui collaborai come aiuto sul campo dei progettisti[77].

Successivamente, per esplicita volontà dell'Assessore BB.CC.AA. e P.I. l'on. Enzo Costa, la mostra fu trasferita presso Baglio Anselmi, dove appunto era già allocata la Nave punica, per realizzare il museo previsto con la legge istitutiva del 1991.

Data la vastità dello spazio a disposizione che impose una nuova riorganizzazione la mostra venne ampliata rispetto all'impostazione originaria, pur mantenendo la formula iniziale adattata alla nuova dimensione. Con il passare del tempo, però, l'esposizione si era arricchita con i diversi ritrovamenti che vennero aggiunti via via al percorso di visita originario, sistemando i nuovi reperti negli spazi apparentemente "vuoti" con il risultato che la visione dello spazio si era appesantita, affastellata e confusa nonché, sempre più occupata da diversi pannelli eccessivamente verbosi aventi forma, dimensioni e colori diversi l'uno dall'altro78.

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[77] Progetto redatto dall'arch. Giuseppe Gini della Soprintendenza ai Monumenti della Sicilia Occidentale e dal Prof. Filippo Terranova. Cfr. GINI 1984, 65-67, figg. 1-12; DI STEFANO 1984, passim; DI STEFANO 1984a, 123-126, figg. 1-7.

78 A. Mottola Molfino, in una guida sui musei siciliani, a proposito dei "musei da rifare" sottolinea che molti di essi "appaiono oggi superati, qualche volta perché troppo piccoli per ricevere il materiale sempre più abbondante che proviene da nuovi scavi […] mortificati da allestimenti datati e ormai obsoleti". L'illustre studiosa prosegue sottolineando che "a Marsala e Mazara, in due contenitori affascinanti come il Baglio Anselmi e la chiesa di Sant'Egidio, la Soprintendenza di Trapani dovrebbe avere il coraggio di evitare l'uso dei propri uffici tecnici nel progettare i nuovi allestimenti interni, ma piuttosto confrontarsi [con] specialisti esterni che sappiano inventare […] modalità espositive che non umilino la suprema bellezza del Satiro di Mazara o della Venere Callipigia di Marsala con apparati didattici, giustificati ma insopportabili per la loro verbosa vicinanza con le opere. MOTTOLA MOLFINO 2010, 28-29. A proposito di Baglio Anselmi la stessa continua: "L'allestimento ha una sua suggestiva dignità; ma nella sala a sinistra dell'ingresso, in cui sono esposti reperti dell'antica città di Lilibeo e da Mozia, è evidente una certa incoerenza espositiva. Spiccano opere di sublime bellezza come la Afrodite "callipigia" di epoca ellenistica (seconda metà del II sec. d.C), in marmo greco […] e posta su una inidonea struttura espositiva". *EAD.*, 116.

Le vecchie vetrine della mostra *Lilibeo* del 1985 sono state recuperate e inserite nel percorso di visita alla meno peggio mostrando interamente il senso del riciclaggio che appesantiva l'esposizione. I materiali usati erano infine innumerevoli.

Su disposizione del Dipartimento dei Beni Culturali quasi tutti i musei sono stati attenzionati e tra essi il Museo Lilibeo dove la scelta era infatti anacronistica poiché frutto dell'esposizione di importanti reperti archeologici provenienti dal Museo archeologico di Palermo, a suo tempo selezionati per la mostra Lilibeo e confluiti in una esposizione finale che manteneva intatte sopratutto le istanze estetiche di una mostra, che è ben lontana e diversa dall'esposizione in un museo.

Il progetto di rinnovo del Museo era stato avviato non meno di tre anni prima dell'avvio dall'ex direttore del museo, dott.ssa Maria Luisa Famà,[79] il progetto è stato poi rivisto ed aggiornato nei criteri museografici, diretto e portato a termine da chi scrive, nel duplice ruolo di Direttore del museo e Direttore dei Lavori, con la collaborazione scientifica della Dott.ssa Maria Grazia Griffo.[80]

La nomina di Direttore dei Lavori del progetto POIn in via di realizzazione nell'autunno del 2015[81] è stata l'occasione per avviare un profondo rinnovamento del museo, rivisto sia negli aspetti estetici ed espositivi che nei contenuti. Il progetto approvato e aggiornato per la sua eseguibilità, purtroppo, non prevedeva la gran parte delle soluzioni poi adottate, a partire dal fatto che non si prevedevano revisioni di alcun genere dei reperti esibiti che avrebbero dovuto riprendere il posto che avevano all'interno delle nuove vetrine previste dal progetto e posti nella medesima posizione espositiva che avevano al momento della redazione del progetto.

Non volendo tuttavia chiudere completamente al pubblico il museo durate i lavori di rinnovamento espositivo sono state realizzate delle mostre. La prima è stata realizzata per accogliere il primo elemento della nave tardo-romana, la trave lunghissima dalla chiglia del

79 La dott.ssa M.L. Famà ha seguito la fase preliminare di progettazione, fino alla consegna dei lavori, il 23 settembre 2015, dato che è andata in quiescenza subito dopo e sostituita quindi nel ruolo di direttore del museo marsalese dallo scrivente che ha condotto e portato a termine i lavori il 30 giugno 2016, come previsto nella gara d'appalto, ad eccezione delle didascalie.

80 Il progetto è stato rivisto soprattutto per gli aspetti e i contenuti scientifici grazie al contributo di un comitato tecnico-scientifico non previsto in progetto e che è stato presieduto chi scrive con la collaborazione della Dott.ssa M.G. Griffo. Molti i componenti, archeologi e studiosi, oltre che di colleghi degli uffici regionali e dell'Università: Francesca Agrò, archeologa medievista; Marco Bonino, docente di "Archeologia navale" presso l'Università di Bologna; Antonietta Brugnone, docente di "Epigrafia greca" nell'Università di Palermo; Rossella Giglio, Dirigente Soprintendenza di Trapani; Maria Luisa Famà, ex Direttore Museo Lilibeo; Antonella Mandruzzato, docente di "Archeologia Classica" nell'Università di Palermo; Leonarda Fazio, archeologa; Antonino Filippi, studioso di Preistoria e Protostoria; Filippo Pisciotta, archeologo, dell'Università di Aix-Marseille; Francesca Oliveri e Philippe Tisseyre, archeologi Soprintendenza del Mare; Vittoria Schimmenti, antropologa Museo Salinas Palermo; Sebastiano Tusa, Soprintendente del Mare.

81 POIn Asse I- Linea d'intervento a titolarità regionale I.1.1 e PAC - Linea d'Azione I "Progetto delle Opere di Valorizzazione del Polo museale – Museo Archeologico Regionale Baglio Anselmi Marsala". Progettazione INVITALIA Attività Produttive di Roma: arch. C. Tesei, S. Gisolfi; R.U.P. arch. S. Biondo, sostituito poi dall'Arch. Natale Canale del Dipartimento BB.CC. Stazione appaltante la Soprintendenza per i Beni Culturali e Ambientali di Trapani. Progetto esecutivo: arch. V. Garbo. Impresa DAMIGA S.r.l. Si sottolinea, infine, la fattiva collaborazione dell'Ing. Roberto Sannasardo, *Energy manager* del Dipartimento BB.CC. per gli aspetti legati alla revisione del progetto in fase di esecuzione relativamente alla climatizzazione.

relitto trovato alla foce del Birgi, esposto al pubblico il 18 dicembre 2015[82] cui seguirono altre su vari argomenti importanti per la conoscenza della città di Lilibeo[83].

Per non arrecare danni ai visitatori del museo si scelse di lavorare in due tempi separati, a partire dalla sala della Nave punica e coinvolgere successivamente anche quella fino ad allora chiamata "Lilibeo".

L'eliminazione di copiosi schermi previsti in progetto per proiezioni che avrebbero finito con il disturbare i visitatori, il ridimensionamento della passerella della nave punica accorciata e ridotta notevolmente in altezza, la riduzione dei totem informativi e tanti altri elementi previsti ma non realizzati hanno infine consentito di dare all'esposizione una nuova veste sia per i contenuti che per la visione d'insieme. Il risparmio ha consentito il rifacimento della pavimentazione con battuto di cemento al posto del cotto preesistente, avente una fuga che amplificava il senso di parcellizzazione dell'ambiente[84], inadatto e assolutamente estraneo al luogo ed alla storia della museografia.

I reperti inamovibili come la Nave punica, sono rimasti nel luogo originario e sono stati reinseriti in un nuovo percorso adeguatamente rivisto anche negli aspetti estetici, come la scelta di nascondere le straripanti e affastellate strutture di sostegno della nave sotto un basamento inclinato che simula l'idea di una spiaggia, come se essa si trovasse tirata a secco per essere sottoposta a riparazione: l'effetto è quello della visione monumentale del reperto non infastidita dalle numerose basi tronco piramidali in cemento armato bruto che non consentivano una corretta visione della nave. Questi elementi a vista finivano con il nuocere alla visione d'insieme e di dettaglio delle parti originali

[82] Allestita in collaborazione con la Soprintendenza del Mare la mostra, intitolata *Dallo scavo al museo: un approdo per la nave tardo romana* ha visto la presenza del Dott. Alberto Di Girolamo, Sindaco di Marsala – il Dott. Vito Damiano, Sindaco di Trapani, nel cui territorio la nave è stata trovata, invitato personalmente dallo scrivente, non si è presentato – del Soprintendente di Trapani Arch. Paola Misuraca e di due relatori: Sebastiano Tusa, Soprintendente del Mare, con *Il relitto di Marausa: scavo, recupero e restauro* e Enrico Caruso, Direttore *ad interim* del Museo Archeologico Regionale "Lilibeo" di Marsala, con *La nave oneraria e l'esposizione in divenire nel Museo "Lilibeo"*.

[83] Una seconda mostra è stata posta all'interno della sala conferenze, smontata per l'occasione e dove è stata trasferita una parte dell'esposizione, utilizzando come sala per conferenze la vicina chiesa di San Giovanni Battista. La mostra è stata dedicata ai lilibetani e aveva come titolo: *Lilibetani. Uomini, donne e abitudini nella città antica*; essa esponeva aspetti della vita quotidiana e alcuni caratteri della cultura artistica.[83] Un'altra mostra metteva invece per la prima volta in vetrina i diversi materiali, poi confluiti in parte nella nuova esposizione del museo, su contesti particolarmente significativi per la storia della città, quali il complesso ipogeico di Santa Maria della Grotta e la chiesa di San Giovanni Battista al Boeo, i cui ritrovamenti sono confluiti nel programma espositivo *Cristianesimo inedito o poco noto a Lilibeo/Marsala tra tardo-antico e medioevo.* Esposti il 26 marzo 2016 nella chiesa di San Giovanni al Boeo. Quelli relativi al contesto dell'area archeologica adiacente alla chiesa e alla "Grotta della Sibilla" sono ancora oggi esposti in una vetrina all'interno dell'edificio demaniale.

[84] Il progetto prevedeva delle lunghe trincee che attraversavano i due saloni nel senso della lunghezza per il passaggio dei tubi della climatizzazione, che andavano poi richiuse con mattoni di cotto simili a quelli distrutti dal taglio. Ciò avrebbe messo in risalto le trincee come una ferita rimarginata messa in evidenza, come i rabberciamenti delle strade di asfalto dopo il passaggio di canalizzazioni: un'immagine non certo congrua con un museo rinnovato.

conservate che sparivano, sommerse da un'enorme congerie di elementi perturbanti, come la buca nel pavimento e le anfore del carico poste all'interno di cerchi di grandi ciottoli con dentro la sabbia.

A lato destro della passerella è stato montato il lato di babordo della Nave punica che un tempo era esposto in un'altra sala del museo. Allora tale elemento era stato inserito in una brutta teca dotata di ruote per il suo spostamento ed aveva un sistema di chiusura esteticamente improbabile e privo di ogni modesto tentativo di rendere l'insieme proponibile alla fruizione (fig. 11)

Nelle vetrine color antracite con all'interno un fondo color porpora – in omaggio all'origine fenicio-punica della città di Lilibeo – sono stati esposti tutti i reperti pertinenti alla nave che erano rimasti per anni nei magazzini[85], dando seguito a quanto previsto dalla L.R. 17/91 che all'art. 4 disponeva il finanziamento di 2.000 milioni di lire "per l'allestimento della nave punica e del suo corredo".

Esposti per la prima volta, i rinvenimenti da "altri relitti" individuati nello stesso sito della Nave punica, al largo dell'Isola Grande che delimita la Laguna dello Stagnone.[86]

Sono quindi stati esposti i relitti medievali dal litorale sud di Marsala e il carico di anforette vinarie rinvenuto in uno di essi, esposto in una vetrina che intende evocare la sezione maestra della nave cui appartenevano (Relitto A di lido Signorino)[87].

Il lavoro è stato utile per ridare ai materiali già esposti o conservati nei magazzini una chiarezza espositiva sia dal punto di vista culturale – come nel caso degli elmi montefortini88 (fig. 12) – che dal punto di vista cronologico e topografico, elementi questi di importanza primaria nella nuova presentazione dei reperti al pubblico.

Particolare attenzione per l'intero museo è stata data in generale ai criteri espositivi che presentano sempre una rigorosa selezione di tipo funzionale, elementi adeguati all'introduzione e alla

[85] Ringrazio a tal proposito la Dott.ssa Maria Grazia Griffo, funzionario direttivo archeologo, che ha ripreso lo studio di quasi tutti i materiali conservati nei magazzini del Museo e della cui infaticabile collaborazione si è avvalso il nuovo percorso espositivo.

86 FROST 1981, 281-296.

87 PISCIOTTA 2018.

88 Studiando i diversi relitti e i loro contesti presenti nel museo per poterli adeguatamente esporre ho avuto modo di accorgermi che due elmi definiti "*cabasset*" dallo scopritore Purpura, nell'articolo apparso nella rivista Kalos, erano stati considerati spagnoli, perché trovati non lontani da un relitto spagnolo prima individuato nelle acque di San Vito lo Capo. PURPURA 1998, 10, figg. 19-20. Evidentemente al momento del loro ritrovamento la conoscenza degli elmi romani non era così approfondita come lo è oggi. Fatto sta che mi accorsi subito dell'equivoco riconoscendoli come Montefortini e così il contesto espositivo non era più quello del tardo medioevo ma piuttosto quello introduttivo della nave punica, dove sono adesso esposti. Cfr. SALADINO *ET ALII* 2019.

conoscenza dei reperti, supportati dall'uso misurato dei pannelli espositivi ed infine completati dalla presentazione dentro le vetrine con l'ausilio ragionato delle didascalie. Queste ultime riflettono un metodo di presentazione bilingue (italiano-inglese), messo a punto da chi scrive in diverse mostre internazionali e che, con un breve testo, fa introdurre il visitatore al contenuto delle vetrine, testo posto sempre a sinistra della fascia delle didascalie e che si ripete in ogni vetrina, accompagnando il viaggio verso la conoscenza. La dimensione delle didascalie è in funzione della lunghezza delle vetrine; essa contiene poi diversi livelli d'informazione, procedendo dal generale al particolare oltre che con la differenziazione nel colore dei caratteri, per i diversi livelli delle indicazioni esplicitate: contesto topografico e cronologia, contesto di scavo e datazione, dati antropologici (quando necessario per i contesti tombali), denominazione del reperto e sua datazione, nonché, infine, i dati relativi a produzione, composizione del materiale e/o decorazione.

Poste queste premesse metodologiche si è scelto di dedicare a un ruolo introduttivo i due piccoli ambienti ai lati dell'ingresso, dotati di porta trasparente che lascia finalmente vedere il giardino durante la visita, dai quali si accede ai due vasti saloni destinati dal progetto all'esposizione museale. Nei due vani minori sono messi in evidenza due aspetti dell'antica città e del suo contesto paesaggistico/funzionale e culturale: la saletta di destra, prima del tutto vuota, ospita oggi alcuni aspetti del porto di Lilibeo[89] con i ritrovamenti nello specchio di mare antistante l'antica città e funge da introduzione alla sezione di archeologia subacquea che segue nel grande vano meridionale.

Nel grande vano sono esposte la Nave Punica nonché i relitti di età islamico-normanna di Lido Signorino, oltre agli elmi montefortini e a vari reperti di particolare importanza quale il braciere fittile, uno dei pochi al mondo così ben conservati, o le anfore studiate ed esposte per la prima volta in una nuova veste, presentate in modo da evidenziare la loro origine storica e la provenienza. L'altra saletta a sinistra, simmetrica alla prima, invece, espone i reperti relativi ai siti fenici presenti nel territorio del Comune di Marsala, Mozia e Birgi90, presentati quali antefatti che precedono la fondazione di Lilibeo.

Così nel salone di sinistra, un tempo denominato Lilibeo, per distinguere il suo contenuto dal contenitore che la legge istitutiva del 1991 definiva "Museo archeologico Regionale *Lilibeo*" di Marsala. Il salone è dedicato al territorio marsalese, a partire dai reperti non numerosi ma importanti di età preistorica e quindi alla città punica, rappresentata e al contempo resa intellegibile da due elementi emblematici della città cartaginese e romana: la *Tessera hospitalis*[91], ovvero una tessera d'avorio che rappresenta due mani che si stringono per sancire un accordo per sé e per i propri discendenti tra un Punico e un Greco, scelti ad emblema di una città multietnica ed ospitale e, infine, l'*Afrodite* o *Venere* tipo "Landolina" di Lilibeo, copia romana del II sec. d.C. di un originale ellenistico che rappresenta l'altissimo livello culturale e artistico presente nella città in età romano-imperiale[92].

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[89] De Vido 1991.
90 Griffo 2019, passim.
91 IG XIV 279; Brugnone 1984, 124, n. 153, Brugnone 2016, 228.
[92] Caruso – Tusa 2004, 103, fig. 11, 105.

Il progetto di ammodernamento del museo, che disponeva di pochi fondi a causa di un capitolato che imponeva peraltro di ridurre i tempi di realizzazione da un anno e mezzo a soli 6 mesi, protratti per altri due mesi e per complessivi 8 mesi di lavoro – pena la perdita del finanziamento – e che imponeva la chiusura dei lavori entro il 30 giugno 2016, quando ancora le didascalie non erano completate, venne, infine, inaugurato il 17 marzo del 2017.

La Nave punica così com'è oggi esposta nel rinnovato museo Lilibeo è stata molto apprezzata dal pubblico perché la sua essenziale esposizione, curata anche con l'attenzione alle luci posizionate in maniera molto attenta e diretta a evidenziare adeguatamente la struttura del relitto della nave (fig. 13), senza farne un'opera illuminata in maniera eccessiva come sovente accade nelle esposizioni di navi.

L'ostensione della nave, la sua esposizione, era stata fin dall'origine pensata da Miss. H. Frost con nuove assi in legno che contribuivano a restituire la struttura originale, integrandola con un assito che aveva un duplice scopo: quello di contribuire con l'integrazione a dare una visione più completa del relitto e, allo stesso tempo, di sostenere i materiali scoperti durante lo scavo e mai esposti come era stato previsto. La nuova esposizione, infine, espone i rami di legno per sistemare le pietre della zavorra, la cambusa, i legni per la cucina e le anfore esposte per la prima volta come un carico (fig. 14) a servizio della navigazione e, soprattutto, degli uomini che sulla nave navigavano.

Metodologie e nuove prospettive per il restauro dei reperti subacquei

Gabriella Chirco ([a,b])

(a) PhD student Dip. Culture e società, University of Palermo, Viale delle Scienze ed. 15, Cap 90128, Palermo - Italy

(b) Restauratrice di beni culturali, Laurea Magistrale in Conservazione e restauro dei Beni Culturali abilitante secondo il D.lgs 42/2004

gabriella.chirco@unipa.it

Abstract

Le problematiche riguardanti i reperti archeologici sono innumerevoli e sono legate a due principali fattori: le condizioni ambientali non idonee alla stabilità dei materiali, nelle quali i reperti si vengono a trovare per moltissimo tempo, e l'attività antropica, sia essa involontaria che volontaria. I beni che vengono ritrovati sono solamente una minama parte rispetto a quelli che l'uomo ha realizzato per sopperire alle sue necessità e pertanto sono una importantissima fonte di informazioni storiche che purtroppo spesso ci giunge frammentaria o degradata. Queste sono le motivazioni per le quali si rende necessaria una corretta conservazione e, quando inevitabile, un adeguato intervento di restauro. A tal proposito, l'intento di questo contributo è quello di illustrare, per le tre tipologie più diffuse di reperti subacquei: legno, ceramica e metallo, i principali fattori di rischio, le metodologie del restauro ad oggi più utilizzate e le nuove prospettive che la ricerca propone e che mirano a rendere sempre più sicure le operazioni dirette sui beni del patrimonio archeologico sommerso.

Introduzione

I reperti archeologici, così come altri beni, indipendentemente dalla tipologia, siano essi in ceramica, legno o metallo, oltre al naturale ed inevitabile invecchiamento che subiscono nel tempo sono, ovviamente, assoggettati agli effetti dell'ambiente in cui si conservano. Infatti, se le opere d'arte in generale sono predisposte a degradi dovuti essenzialmente all'influenza dell'ambiente in cui sono esposte, quindi causati principalmente dalla temperatura non idonea, dallo smog e da livelli di umidità e luce inadeguati, i reperti archeologici subiscono gli effetti dell'ambiente che li "ingloba". Quando il reperto viene a trovarsi sottoterra o sott'acqua si troverà in un ambiente con caratteristiche completamente diverse da quelle per il quale è stato fatto ed in questa nuova situazione subisce una trasformazione che può dipendere da diversi fattori associati alle loro proprietà intrinseche come la composizione, la porosità, la capacità di assorbimento d'acqua o la durezza, che possono incidere ad esempio sull'aspetto, sulla resistenza meccanica e/o sulla forma del manufatto.

Che si tratti di sottosuolo o ambiente sottomarino, le caratteristiche chimiche di questi influiscono fortemente sulle modalità di invecchiamento del reperto e per tanto sullo stato di degrado. Ad esempio, l'interramento di un oggetto in un terreno molto acido può causare danni simili a quelli tipici dell'inquinamento atmosferico [25]. Nella maggior parte dei casi queste trasformazioni porteranno alla perdita dell'oggetto. Meno frequentemente l'oggetto raggiungerà una situazione di stabilità trovandosi in equilibrio con il nuovo ambiente nel quale verrà conservato [14]. Nonostante ciò, benché molto lento, il degrado del materiale è inevitabile e diverse sono le reazioni che ne possono influenzare il deterioramento e la conservazione e che di conseguenza influiscono sulla sua durata, siano esse di tipo fisico-chimico, biologico e meccanico.

Le problematiche connesse al patrimonio archeologico sottomarino

Dovendo, in questa sede, stringere il campo sui reperti provenienti dal mondo sommerso focalizziamo l'attenzione sugli agenti deteriogeni che caratterizzano tale ambiente. Il degrado dei materiali sottomarini è un processo che si sviluppa attraverso eventi ad esempio la colonizzazione biologica da parte di microrganismi che costituiscono una parte della biomassa sottomarina (ad esempio funghi o batteri), la corrosione ionica dovuta principalmente ai sali disciolti nell'acqua, l'ossidazione e le incrostazioni causate dall'attecchimento di alghe, cozze, briozoi e serpulidi, che spesso possono causare gravi alterazioni modificando, oltre l'aspetto, anche la forma del reperto [26].
Quando l'oggetto entra in equilibrio con il sistema che lo circonda questi depositi, che inizialmente si configurano come deturpatori, in un secondo momento possono svolgere una più sana funzione di "conservazione" ponendosi come strato sedimentario di protezione da ulteriori cause di deterioramento, quello che, un conservatore, in altri casi definirebbe "strato di sacrificio".

La conoscenza della materia, combinata con la comprensione dei processi di deterioramento e dei fattori che li causano, è obiettivamente di grande importanza ai fini dell'attuazione di attività di salvaguardia e conservazione che si pongono l'obiettivo di impedire l'ulteriore sviluppo o il protrarsi di processi dannosi. Negli ultimi decenni nel campo dell'archeometria sono stati fatti grandi passi avanti per quanto riguarda lo studio di tali meccanismi attraverso tecniche analitiche che permettono di ottenere tali informazioni in maniera sempre più accurata. Queste tecniche diagnostiche inoltre permettono di acquisire dati in maniera pratica e spesso senza la necessità di effettuare un campionamento, rispettando sempre più l'integrità fisica del reperto (Fig. 1-2).

Fig. 1 Indagini su un elmo condotte *in situ* tramite spettrofotometro in riflettanza con fibra ottica.

Fig. 2 Indagini su un lingotto condotte *in situ* mediante spettrometria FT-IR.

Conoscere a trecentosessanta gradi l'oggetto e i meccanismi che ruotano attorno la sua conservazione è indispensabile anche in materia di recupero infatti, il momento effettivo dello scavo o, in questo contesto, dell'estrazione del reperto dall'acqua, è cruciale per due ragioni: in primis perché è il momento in cui l'archeologo ha la massima possibilità di raccogliere informazioni relative al contesto del reperto e al materiale ad esso associato; in secondo luogo per le conseguenze potenzialmente disastrose derivabili da una mancanza di controllo ambientale su reperti chimicamente e meccanicamente instabili. Proprio il momento del recupero del manufatto è quello in cui esso subisce un ulteriore stress a causa delle variazioni delle condizioni con le quali questo era entrato in equilibrio nell'ambiente che per secoli lo aveva conservato. In ambito di conservazione la consapevolezza di tali dinamiche, unita ad una nuova morale, che oggi più che mai tende a contestualizzare il bene piuttosto che ad estrapolarlo dal ambito nel quale lo si ritrova, spinge verso una nuova direzione per la fruizione del patrimonio artistico che è quella di mantenere il reperto archeologico nel contesto sommerso nel quale viene scoperto portando alla formazione di parchi archeologici che sono veri e propri musei sommersi evitando in tal modo sia di distruggere le informazioni storiche ricavabili da questo sia il rischio della perdita del bene in questione per il sopravvenire delle cause sopra discusse.
Comunque, quando ci si trova a dover affrontare le problematiche legate all'attuazione di una corretta pianificazione di interventi di conservazione o restauro, per i quali la salvaguardia del patrimonio archeologico è l'obiettivo principale, le informazioni ricavate dall'analisi dei dati sono ancora una volta indispensabili in quanto indirizzano sia sull'identificazione dei materiali da utilizzare che sulle scelte metodologiche da attuare.

Dinamiche di degrado e approccio conservativo ai reperti archeologici

I reperti che il mare ci restituisce sono essenzialmente di tre tipologie con caratteristiche materiche molto differenti tra loro: il legno, la ceramica e i metalli. Il primo è di natura organica e viene impiegato tal quale dopo un lavoro di taglio e modellamento, gli altri due sono materiali inorganici che per acquisire le caratteristiche finali hanno subito dei processi di estrazione, lavorazione (talvolta si trovano in miscela con altri materiali) e cottura. Sono pertanto dei materiali molto differenti tra loro che in ambito conservativo e di restauro vanno trattati con metodologie differenti da valutare caso per caso sia per quanto riguarda il trattamento più idoneo alla natura della materia che in base a fattori come lo stato di conservazione, la tipologia e l'avanzamento del degrado e al luogo di destinazione per l'esposizione o la conservazione.

Volendo fare un breve excursus sulle metodologie consolidate e sulle nuove frontiere riguardanti metodi e materiali per il restauro, ed avendo assunto che ciascun materiale ha caratteristiche proprie che vanno trattate individualmente, procederemo ad una disamina delle singole tipologie.

Iniziando dal **legno archeologico imbibito**: questo materiale, altamente idrofilo, si considera tale quando il contenuto d'acqua è maggiore rispetto al punto di saturazione delle fibre [27]. Data la lunga permanenza in acqua, inevitabilmente il materiale subisce un degrado chimico, fisico e biologico che rende i reperti lignei molto friabili a causa della dissoluzione della cellulosa da parte dell'acqua (idrolisi) che la sostituisce quasi totalmente. In tali condizioni l'acqua, anche se rappresenta la principale causa di degrado, comunque ne favorisce la conservazione in quanto la sua massa fa sì che ne vengano mantenute le dimensioni e la struttura [33]. Al momento del ritrovamento il legno di conseguenza, si trova in una condizione di sostanziale equilibrio con l'ambiente circostante, condizione che potrebbe perdurare per un tempo indefinito. All'atto dell'estrazione dall'ambiente marino l'equilibrio acquisito viene inevitabilmente alterato e il legno, se privato dell'acqua, subisce variazioni dimensionali e distorsioni a causa del ritiro delle fibre ed in più si incorre nel rischio di collasso strutturale. Date queste cause vi è la necessità di consolidarlo con materiali che si sostituiscono all'acqua nella funzione di sostegno per mantenerne le dimensioni originarie [33]. Ricordiamo però che oltre al consolidamento è necessaria anche una operazione di rimozione delle incrostazioni e dei depositi marini che, inevitabilmente, ritroviamo sulla superfice del manufatto. L'operazione nella maggior parte dei casi viene eseguita manualmente ed andrebbe attuata prima del consolidamento o in concomitanza di questo.

A partire dagli anni '50 circa, il principale tra i prodotti usati per consolidare la struttura degradata del legno imbibito è stata una soluzione acquosa o in alcoli di polietilenglicole (PEG - polimero sintetizzato dalla polimerizzazione dell'ossido di etilene). A rendere così diffuso l'utilizzo di questo polimero vi è di certo la facilità di penetrazione nella materia, seppur utilizzando soluzioni con polimeri a differente peso molecolare, per garantirne l'accesso anche nelle microporosità, tramite una serie di bagni successivi a temperatura controllata (fino a 60°) [8].

In alcuni studi è riportato anche l'impiego di composti, applicati con lo stesso procedimento del PEG, come ad esempio il D-mannitolo, il saccarosio o il t-butanolo [32]. I risultati non sono sempre soddisfacenti a causa della natura idrofila, è noto inoltre che in condizioni di umidità elevata i PEG trasudano fuori dal legno trattato, e che i reperti lignei impregnati con questo polimero hanno mostrato alcune problematiche come l'igroscopicità o la limitata reversibilità. Un altro degli aspetti negativi di questo tipo di trattamento è la perdita delle caratteristiche estetiche originali del legno in seguito all'annerimento del legno trattato [15] pertanto, reperti che hanno subìto questa tipologia di trattamento, per essere conservati al meglio devono necessariamente essere musealizzati con idonee condizioni ambientali: è il caso, ad esempio, del relitto della nave punica di Marsala o del Vasa (Fig. 3-4).

Fig. 3 Relitto della nave punica al Museo Archeologico Baglio Anselmi di Marsala[94].

Fig. 4 Relitto del Vasa, Museo Vasa Stoccolma[93].

Per ovviare ai problemi ed ai lunghi tempi richiesti da queste tipologie di trattamento, in questi ultimi anni è stata messa a punto una tecnica che prevede la polimerizzazione in situ ossia la polimerizzazione all'interno del materiale tramite l'utilizzo di radiazioni o catalizzatori.
La necessità di dover applicare prodotti sempre meno nocivi per gli operatori del settore ha portato alla messa a punto di trattamenti per via umida che usano come monomero l'isoeugenolo (solubile in soluzioni acquose ed etanolo esplica attività antibatterica ed antimuffa), un equivalente parzialmente idrofobico dei monomeri costituenti la lignina e, come catalizzatori, complessi Salen metallo-centrati, biomimetici degli enzimi: (N,N'-bis(4-sulfosaliciliden) etilendiammino di Rame (II). Ma anche la polimerizzazione di questo monomero presenta i medesimi problemi di scarsa solubilità degli oligomeri [8, 15].
La letteratura riporta esempi di applicazione delle nanoparticelle come riempitivi e deacidificanti del legno archeologico con nanoparticelle di idrossido di calcio che ne aumentano la resistenza, come quelle applicate sul Vasa [16]. L'utilizzo delle nanoparticelle di idrossido di calcio, come metodo alternativo, è stato studiato anche tramite l'applicazione all'interno di nanotubi di halloysite che vengono addizionati ad una miscela di PEG mostrando caratteristiche di deacidificazione e protezione della lignina anche a lungo termine [7].

Passando alla classe dei **materiali ceramici** parliamo di una categoria assai vasta, ma la tipologia dei manufatti ceramici prodotti in epoca antica è riconducibile alla classe delle terrecotte. Sono oggetti che per essere realizzati necessitano di un processo di lavorazione che si suddivide in quattro fasi che nel tempo sono rimaste sostanzialmente invariate e cioè, la preparazione dell'impasto, la modellazione, l'essiccamento e la cottura.
Questa categoria di reperti, data la notevole diffusione in tutte le epoche e la durabilità del materiale, è quella che più facilmente viene rinvenuta nei fondali marini. In quest'ambiente la ceramica è esposta all'accumulo di depositi organici e calcarei ed agli effetti biochimici e fisici di organismi marini viventi. Le alghe hanno un effetto biochimico poiché le loro secrezioni ne dissolvono il substrato, mentre gli organismi marini come lumache o cozze

[93]Immagine tratta da https://www.flickr.com/photos/jlascar/24562295560/
[94]Immagine tratta da https://www.sempionenews.it/cultura/nanotecnologia-incontro-dedicato-alla-nave-del-museo-baglio-anselmi/?cn-reloaded=1, il 23/10/2020.

agiscono meccanicamente sulla ceramica abradendone la superficie [21]. Ulteriore effetto abrasivo è causato dal movimento dell'acqua che sposta sabbia e ciottoli che producono un effetto erosivo sulla superfice degli oggetti depositati sul fondale. Da ciò si deduce che tali oggetti che si trovano sulla superficie dei fondali sono più esposti all'azione abrasive rispetto a quelli trovati sotto la superficie. Questi ultimi, invece, sono maggiormente soggetti all'accumulo di depositi, il più delle volte calcarei.
Inoltre il degrado della ceramica è strettamente legato alla composizione dell'argilla, alla salinità dell'acqua di mare nonché ai diversi tipi di sali che questa contiene, in primo luogo cationi di sodio, magnesio, calcio, potassio e stronzio e anioni cloruro, solfato, bromuro e bicarbonato [12]. I sali solubili, all'interno di un materiale poroso come la ceramica, possono causare danni significativi soprattutto quando i reperti vengono portati in superficie in quanto nel tempo gli oggetti immersi raggiungono l'equilibrio con il livello di pressione circostante, nel corso del quale l'aria dei pori viene sostituita dall'acqua salata.
Al momento dell'estrazione dell'oggetto dal mare e della successiva evaporazione dell'acqua, la soluzione nell'oggetto si concentra ed inizia il processo di cristallizzazione dei sali che, aumentando di volume, causano stress meccanici all'interno della struttura dell'oggetto e possono indurre degradi che vanno dalla desquamazione dello spessore fino allo sbriciolamento dell'oggetto stesso.
Uno dei fattori che influenza la resistenza della ceramica rispetto alla cristallizzazione dei sali è la temperatura di cottura di questa, infatti le ceramiche cotte a temperatura più elevata sono meno porose e di conseguenza meno permeabili, il che comporta un minore assorbimento di sali solubili [34].
Per evitare questi fenomeni è bene far sì che questi oggetti si adattino gradatamente alle nuove condizioni ambientali per ciò sarebbe opportuno che essi rimangano immersi in acqua fino al processo di dissalazione, in modo da escludere la cristallizzazione dei sali e di conseguenza la frattura della struttura del materiale.

Le operazioni di restauro di questa tipologia di manufatti, oltre a prevedere l'acclimatazione e il lavaggio per l'asportazione della frazione salina, si concentrano sulla pulitura della superficie dalle incrostazioni calcaree e dai depositi marini, come conchiglie e trivellatori, e sul consolidamento della struttura (Fig. 5-6).
La dissalazione viene eseguita immergendo l'oggetto in un bagno d'acqua che periodicamente deve essere sostituita. Per evitare il rilascio eccessivamente rapido di sali, che potrebbe causare danni aggiuntivi all'oggetto l'acqua utilizzata deve essere via via più pura per cui inizialmente si utilizzerà l'acqua del rubinetto mentre nelle fasi finali quella deionizzata, al fine di tenere sotto controllo tale operazione è opportuno misurare la conducibilità prima e dopo ogni cambio d'acqua. Quando la quantità di sali (conducibilità) è stata ridotta ad un valore minimo costante, il processo di dissalazione può considerarsi completato e l'oggetto può essere estratto dalla vasca e lasciato asciugare, avendo cura di non esporlo ad oscillazioni di temperatura [13].
Per quanto riguarda la pulitura dai depositi adesi, la metodologia consolidata prevede la rimozione meccanica, di solito tramite l'utilizzo di bisturi o microtrapani, ma per i reperti molto degradati questa metodica non è sempre consigliabile. Per evitare lo stress dell'azione meccanica, che comunque comporta l'applicazione di una certa pressione sul substrato,

negli ultimi anni sono stati utilizzati metodi chimici di pulitura che prevedono l'uso di complessanti come l'EDTA (sale sodico dell'acido etilendiammina tetraacetico) [9], il prodotto viene adsorbito dall'incrostazione e ne indebolisce i siti reticolari permettendone la rimozione [4]. Questa operazione però potrebbe intaccare anche il substrato in quanto dissolve anche il calcio carbonatico della ceramica. Un'altra metodologia già conosciuta ed utilizzata per i dipinti murali che viene applicata, con buoni risultati, anche su questa classe di reperti, è l'utilizzo delle resine a scambio ionico [11] che grazie alla capacità di agire in maniera selettiva solo sullo strato con il quale essa è a diretto contatto, in questo caso sulle incrostazioni carbonatiche [23], permette di ovviare ai problemi che potrebbe dare l'EDTA [4].
Il consolidamento del corpo ceramico è mirato a rafforzare la struttura dell'oggetto. Uno dei prodotti che ha dato buoni risultati, data la capacità di penetrazione, è il Wacker-OH (estere etilico dell'acido silicico) [1]. Il prodotto è applicabile a pennello ed in più presenta il vantaggio di non alterare la colorazione della superficie [19], al contrario di quello che potrebbe accadere con l'utilizzo, allo stesso scopo, del ben più diffuso Paraloid B-72 [29]. Quest'ultimo materiale invece è consigliato per isolare i bordi delle mancanze da reintegrare cosicché durante l'applicazione lo stucco non penetri nella porosità del materiale e l'integrazione sia facilmente rimovibile [20]. Infine sono in corso studi su materiali per la protezione della superfice dei reperti esposti in luoghi dove la mancata possibilità del controllo microclimatico potrebbe portare all'attecchimento di colonizzazione biologica, si tratta di due tipologie di miscele che sembra diano buoni risultati sia dal punto di vista della protezione superficiale che come biocidi, una costituita da un silossano (Hydrophase) e da un biocida (Algophase), l'altra costituita da un polimero florurato (Akeogard P) e da un biocida (Preventol R80) [11].

Fig.5 Fase di incollaggio durante il restauro di una Lekane.

Fig. 6 Fase di stucctatura durante il restauro di un vaso.

L'ultima categoria è quella dei **reperti in metallo** che sono stati realizzati soprattutto in ferro, rame, argento, oro, piombo e stagno, metalli utilizzati con costante regolarità per fabbricare strumenti, armi, ornamenti e altri accessori. Ciascuno di questi metalli è stato utilizzato sia individualmente che in combinazione con altri, per formare leghe come bronzo o ottone. Questi metalli, ad eccezione dell'oro, non esistono in natura sotto forma metallica bensì minerale, di conseguenza dal momento della loro produzione, i metalli e le loro leghe tendono a tornare allo stato iniziale, avviando processi di corrosione che tendono a

convertirli in composti più stabili. Per tanto i reperti sono quasi sempre interessati da accumuli di prodotti di corrosione, che in mare o acqua dolce sono causati principalmente dalla presenza del cloro, inoltre possono essere ricoperti da incrostazioni caratteristiche dell'ambiente da cui sono stati estratti (roccia, sabbia, molluschi, resti scheletrici di organismi marini morti) [17]. Se l'acqua di mare provoca un forte attacco corrosivo, le cui caratteristiche sono una superfice interessata da accumulo di prodotti di corrosione, lacune e alterazione cromatica, questo processo viene intensificato solo quando l'oggetto viene estratto ed entra a contatto con l'atmosfera e, soprattutto nelle leghe ad alto contenuto di rame, in presenza di cloruri, si osservano forme di corrosione localizzata, l'O^{--} degli ossidi può essere sostituito dal Cl^{-} con creazione di difetti e aumento della conducibilità [28] che portano al cosiddetto "cancro" che in breve tempo polverizza il manufatto.
Queste reazioni rappresentano una grande sfida per la conservazione delle opere d'arte metalliche, l'analisi degli strati di corrosione di un manufatto di ferro, infatti, mostra un'alternanza spesso regolare di prodotti di corrosione aerobici e anaerobici, a dimostrazione del fatto che i naturali cicli di esposizione/copertura dell'oggetto modificano le condizioni di alterazione, ma non ne arrestano il processo.
Per prevenire o ridurre la corrosione è possibile utilizzare varie strategie, prima fra tutti la conservazione preventiva, che non interviene direttamente sull'oggetto artistico, in quanto la natura fisica di questo non può essere modificata, ma si basa sul controllo dell'ambiente, dove l'oggetto stesso viene conservato [5]. Il più delle volte i conservatori incorrono in oggetti già degradati che necessitano di interventi diretti.
In primo luogo per prevenire l'ulteriore corrosione, disintegrazione o collasso, questi materiali devono essere mantenuti umidi per tutto il periodo che va dal recupero al trattamento. Durante questo lasso di tempo, le incrostazioni non devono essere rimosse in quanto, in questo momento, fungono da rivestimento protettivo, che ritarda la corrosione, impedisce la conversione chimica dei prodotti di corrosione già presenti e protegge i manufatti da un ulteriore deterioramento. Le soluzioni di conservazione, consigliate solo per la conservazione per brevi periodi, devono avere pH controllato il cui valore dipende dal metallo o dalla lega costituente il reperto. In generale, gli inibitori alcalini più comunemente utilizzati sono idrossido di sodio, carbonato di sodio e sesquicarbonato di sodio [2,21]. Per quanto riguarda la conservazione a lungo termine in bagno, buoni risultati sono stati ottenuti con una soluzione di dicromato di potassio ($K_2Cr_2O_7$) con idrossido di sodio. Molti manufatti in ferro, recuperati da navi spagnole del XVI secolo, sono stati conservati in questa soluzione, mantenuta a pH costante tra 9,0 e 9,5, per più di tre anni senza subire apparentemente un'ulteriore corrosione [18].
Le successive fasi del restauro saranno la messa in sicurezza di eventuali porzioni poco stabili (Fig. 7), l'eliminazione dei depositi incoerenti, come possono esserlo ad esempio residui di sabbia, e quando possibile, e senza incorrere nella perdita di materiale, l'eliminazione anche dei depositi calcarei adesi sul substrato. Quest'ultima operazione avviene meccanicamente ma se l'incrostazione è eccessivamente tenace, la pulitura verrà rifinita mediante sabbiatura o con il processo di elettrolisi che oltre a staccare le incrostazioni dalla superfice agirà sui prodotti di corrosione. Oggi giorno, sui metalli archeologici, viene evitata anche la pulitura chimica in quanto oltre ad agire sulla corrosione potrebbe intaccare la patina superficiale. I solventi utilizzati in questo caso sono

essenzialmente: chelanti come l'EDTA, la TEA (trietanolammina) o l'acido citrico, i quali sono utilizzati di norma in soluzioni acquose a basse concentrazioni al cui uso segue un accurato risciacquo con acqua per l'eliminazione di qualsiasi residuo di solvente [29].
L'operazione più delicata, su oggetti di questa tipologia, è proprio la rimozione di tali prodotti. Il metodo che ad oggi è stato più utilizzato è quello che sfrutta il processo di riduzione catodica dei prodotti di corrosione (cloruri, solfuri, solfati, ossidi e ossidi idrati di ferro), formatisi nel corso della giacitura subacquea e dell'esposizione all'ambiente aereo. La durata complessiva del trattamento varia in funzione dello spessore degli strati dei prodotti di corrosione da rimuovere e in ragione della concentrazione residua nel bagno di trattamento dello ione cloruro (Cl^{-}), primo responsabile della maggior parte di tali processi, sia in ambiente acquoso che aereo. Ma questa tecnica, che in molti casi risulta efficace, può essere distruttiva se utilizzata su oggetti le cui incrostazioni ricoprono modellati o decorazioni non visibili a priori [18], così come possono risultare poco controllabili i metodi di rimozione manuale o di sabbiatura, entrambe affidati alla sola sensibilità dell'operatore.
Una nuova frontiera riguardante la pulitura è l'utilizzo del laser. La tecnica è già consolidata per interventi di restauro su materiali lapidei e per la prima volta è stata ottimizzata per i metalli durante l'operazione di pulitura della Porta del Paradiso a Firenze (Fig. 8). Inizialmente il principale problema riguardante l'applicazione di questa tecnica sui metalli, e ancor più sulle lamine metalliche, era il riscaldamento della superfice da parte del laser ma l'applicazione di sorgenti con impulsi regolabili, come lo Nd:YAG-lasers, ha reso la tecnica sicura anche sulle applicazioni in foglia d'oro [30,31].
Il passo successivo del restauro è quello di rendere la struttura dell'oggetto stabile, quindi ricucire le mancanze che potrebbero compromettere la stabilità della struttura, tramite integrazioni con materiali come resine epossidiche più o meno resistenti da scegliere sulla base del tipo di metallo trattato di cui alcune delle possibili scelte sono l'araldite o la etoond 6066 + indurente [3].
Dopo le operazioni di pulitura e consolidamento di un oggetto metallico l'ultimo passaggio è quello della protezione superficiale. A tale scopo è necessario ricreare le condizioni idonee affinché il processo di corrosione del materiale sia stabile. Anche in questo caso l'operazione più idonea sarebbe quella di agire sull'ambiente nel quale l'oggetto si verrà a trovare terminato il restauro ma molto spesso ciò non è possibile magari perché l'oggetto viene conservato all'esterno oppure in una sala dove si trovano manufatti che richiedono parametri ambientali diversi, pertanto si ricorre all'utilizzo di materiali protettivi e stabilizzanti. Per quanto riguarda i protettivi spesso si applicano resine più o meno diluite a seconda del materiale e delle condizioni climatiche nelle quali verrà a trovarsi. I protettivi più utilizzati per i manufatti archeologici in metallo sono l'Incral 44 e il Paraloid B72 [10] ai quali, talvolta, si addiziona una percentuale di cera, come la Cosmoloid o la Reswax WH; tale addizione è consigliata per le superfici in ferro o piombo [10,22].
Se si utilizzano inibitori di corrosione, comunemente sostanze organiche polari, quelli più diffusi sono ammine, sali alcalini o oli solfatati [29]. Tuttavia l'inibitore più utilizzato soprattutto per i reperti in bronzo è il benzotriazolo 1-H (BTA) in soluzione di etanolo riscaldate a 60 °C. Anche se è stato ampiamente utilizzato il BTA non si è sempre dimostrato efficace, è altamente tossico, rappresentando un grave rischio per la salute e

l'ambiente [5], inoltre altera il colore della superfice [24]. Per ovviare a questi inconvenienti, sono state condotte due linee di ricerca: una che vede il BTA dare i migliori risultati in termini di protezione e inibizione corrosiva, rispetto ad altri materiali, secondo una formulazione che prevede il rilascio selettivo di questo prodotto inglobato all'interno di film nanostrutturati [6]; l'altra riguarda una nuova formulazione green, a base di estratto di Opuntia ficus indica e semi di Nigella sativa (soluzione di NaCl al 3%) già in commercio, che ha dato buoni risultati per la resa estetica, la facilità di applicazione e la durabilità [5].

In conclusione i danni subiti dal patrimonio archeologico sottomarino sono causati sia dai fattori ambientali che dall'uomo. Ai primi sono strettamente connesse le modifiche della struttura dei materiali ai secondi i fattori antropici che spesso deturpano gravemente i siti sommersi.
Gli oggetti dispersi in mare che vengono ritrovati appartengono a quella minima parte di reperti archeologici che in un certo momento del loro percorso di alterazione sono entrati in equilibrio con l'ambiente circostante. Il fattore che altera questo equilibrio è l'attività dell'uomo, infatti, le principali attività antropiche che influenzano il degrado dei siti archeologici sommersi sono ad esempio l'attività marittima, la pesca o lo scarico di rifiuti, in più l'estrazione dai fondali e la manipolazione dei reperti senza le dovute precauzioni possono risultare distruttive per il patrimonio archeologico marino.
Oltre agli interventi mirati che devono essere attuati al momento del recupero, al fine di evitare di sottoporre i materiali a repentini cambi di condizioni ambientali, è imprescindibile l'intervento da parte di personale specializzato che si occupi della conservazione del bene. In questa fase un ruolo fondamentale viene svolto dalla archeometria che, grazie all'utilizzo di tecnologie sempre più avanzate, riesce a dare risposte esatte sulle problematiche conservative dell'oggetto analizzato, così da permettere interventi mirati. Gli interventi eseguiti dovrebbero innanzitutto riguardare l'ambiente nel quale il reperto verrà conservato così da scongiurare il ripresentarsi del degrado che il restauro ha bloccato. Infatti le operazioni di conservazione e restauro molto spesso si rendono indispensabili per recuperare e conservare i manufatti senza i quali parte dei dati e della storia andrebbero inevitabilmente persi. Ciascun intervento deve essere programmato e calibrato sulla base del materiale di costituzione, dello stato di fatto e dei deteriogeni presenti sul reperto per poter eseguire delle operazioni appropriate. A tale scopo, come visto, la scienza non si basa solamente sulle modalità e sui materiali consolidati ma amplia le ricerche per poter migliorare sempre più sia i materiali che entrano in contatto con il substrato che le procedure che vengono applicate in modo da farle risultare sempre meno invasive e sempre più idonee alla conservazione al fine di rispettare la materia, non alterarne l'aspetto e garantire la fruizione e la trasmissione nel tempo del bene e di conseguenza della storia.

Fig. 7 Fase di presconsolidamento e protezione di un reperto metallico[95].

Fig. 8 Pulitura con tecnologia laser di uno dei pannelli della porta del Paradiso di Firenze[96].

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Underwater itineraries in Sicily: submerged museums and new technologies

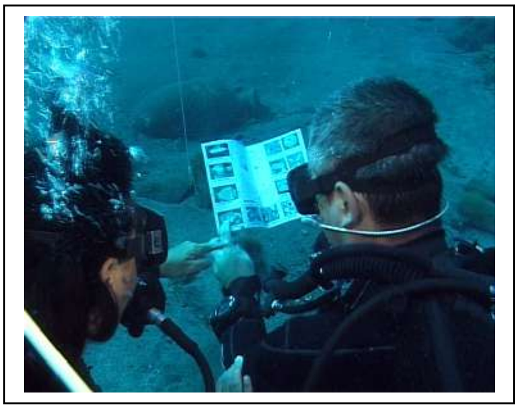
Floriana Agneto ([a]), Pietro Selvaggio ([b])

([a]) Soprintendenza del Mare – Regione Siciliana
f.agneto@regione.sicilia.it; p.selvaggio@regione.sicilia.it

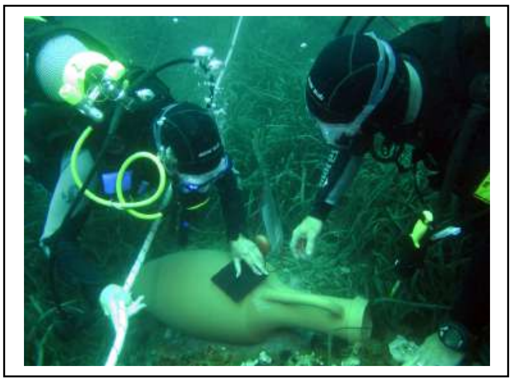
Underwater itineraries in Sicily start from the 2001 UNESCO Convention, supported by the prof. Sebastiano Tusa's great contribute. He carried out several meetings and international conferences among Mediterranean partners in the aim to confirm a general understanding about the underwater heritage protection. Official documents conceived during the meetings by all Mediterranean countries contribute to the Convention final definition.

The conviction that archaeological finds must remain in situ in their original position is the best way to fight against robberies and general indifference, in fact local communities step by step changed their opinions becoming conscious guardians of their underwater heritage, starting at same time a touristic and economic loop by great visibility of media.

The Superintendence of the Sea, created and conducted by Sebastiano Tusa carried out during the years many underwater itineraries available for divers: an authorized guide shows to visitors the way to follow above the site rich in ancient finds marked by plastic floating labels identifying type and age of amphorae, anchors, wrecks, etc. Indeed archaeology meets biology and marine landscapes, an amazing trip for all level of divers. Moreover, dedicated waterproof book-guides provide to visitors further information. The last edition of this system introduced "speaking" floating labels that by a microchip contact provide on the display of the small computer on the diver's wrist some more images text and didactic drawings.



Conceived for non-divers the webcam system also permit the virtual visit on line, available all around the world 24h a day, and special underwater tour was expressly realized for handicapped people and for blind people consisting in authentic and tactile replications finds marked with special labels in Braille language.



Technology gives great emphasis and visibility to underwater finds and in Sicily it has been applied on some cultural underwater itineraries. In particular, at Cala Minnola in Levanzo island and at Cala Gadir in Pantelleria island, a video camera system was installed, in the aim to protect the sites and at the same time allowing the best fruition to visitors. The first experimental project consist in video cameras appropriately placed to monitoring a large visual angle on the rich Cala Minnola's site full of amphorae, with the images transmitted in real time to the display on the video screen inside the old Favignana's tuna fish factory transformed in museum. This system was conceived in 2002 and realized in 2004 by installation of 4 camera protected in underwater housing. Technology at the time was very hard so for transmitting and receiving video signal and power supply we realized a dedicated ground station, from which images were transmitted to Favignana by radio link.

The rapid development of technology allowed in 2006 the installation in Cala Gadir of a new video surveillance system and fruition by 2 webcam, with a big reduction in dimensions of equipment and best quality of images definition.

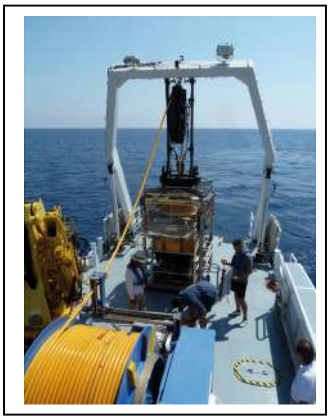
The first webcam placed inside a cylindrical Plexiglas case 2 m. long can be moved along a horizontal rail and can have vertical and horizontal rotation. The second one is installed inside a Plexiglas dome for making horizontal and vertical movements. Images are visible online on dedicated website, camera can be moved 24h a day all around the world discovering different points of view, at the same time watching some moments of sea life. Indeed the site reached in few months the top position among the more visited webcam.

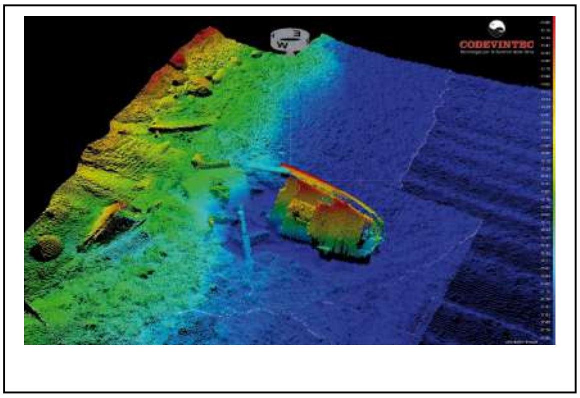
During the realization of video camera projects we conceived and realized in cultural underwater itineraries as a "submerged museums" rich in amphorae, anchors, wrecks and so, available for divers of all level guided by authorized personal. They are simple to visit following the guide and matt Plexiglas labels rectangles in A5 format sustained by a little fishnet floating providing short information on each find. Dedicated plastic guides are made to give to the visitors some more historical and archaeological details as plan of the site and path to follow.

New technology introduces application of "RFID" on plastic labels, which provides some information in new way. Indeed when the diver approaches the floating label his small wrist computer give on historical and archaeological information by pictures and drawings that appear on the display.

Another project, called "I.T.A.C.A." (Innovation Technologies and Application for Coastal Archaeological) experimented underwater archaeological research by study of satellite high-resolution images (TerraSAR-X Cosmo-SkyMed) and multispectral satellite data (World View) combined to derive the relative bathymetry of the sea bottom up to the depth of 70 meters. The resulting data fusion processed using shape detection algorithms specific for archaeological item.

The ARROWS project (ARchaeological Robot system for the World's Seas) developed innovative systems for underwater heritage documentation by experimentation of new technologies for 3D scanning of the seabed with ROV (Remote Operated Vehicle) and AUV (Autonomous Underwater Vehicle) small size. The realization of the project realize the miniaturization of tools with cost reduction for underwater research, especially in the high depth.





The 3D graphic restitution permits the study of the sites, facilitates the understanding of shipwreck dynamics by details till now unknown, mostly to make detailed survey of archaeological sites with information that often escape to traditional survey.

Technology in progress ever provides new solutions for study, protection and fruition of underwater cultural heritage, so we have to research and experiment new solutions that, applied on underwater archaeology, increase the frontier of human knowledge.

Floriana Agneto e Pietro Selvaggio

Pictures Archive © Soprintendenza del Mare

Laboratory Sections

Laboratory of FORS and MO

Maria Luisa Saladino, Veronica Ciaramitaro

STEBICEF Department, University of Palermo, Viale delle Scienze Bld.17, I-90128 Palermo (Italy)

marialuisa.saladino@unipa.it

In this laboratory activity, the Fiber Optic Reflectance Spectroscopy (FORS) and the Optical Microscopy (MO) techniques will be introduced. After a brief introduction about the theory, instrumentations and applications of both techniques, the students will see the application of the following equipment:

-Digivision 1.3 megapixel USB digital optical microscope

-Ocean Optics USB2000 + XR1 portable reflection UV-vis spectrophotometer with DH-mini UV-Vis-NIR source and reflection probe.

The acquisition of MO images and of FORS spectra will be performed on pigments of some archeological ceramics, stones with and without a protective and on patina of metal alloys.

The MO images of each artifacts will be discussed.

Data analysis of FORS spectra will be illustrated. The colour parameters will be also calculated and some considerations about their meaning will be made.

FTIR spectroscopy and its applications: how to study microplastics in marine environment

V. Renda[(a)], D. D'Amato[(a)], G. Marino[(a)], S. Campanella[(a)], V. Ruvolo[(a)]

[(a)] UOC Area Mare ARPA Sicilia, Lungomare Cristoforo Colombo 4521, Palermo (PA)

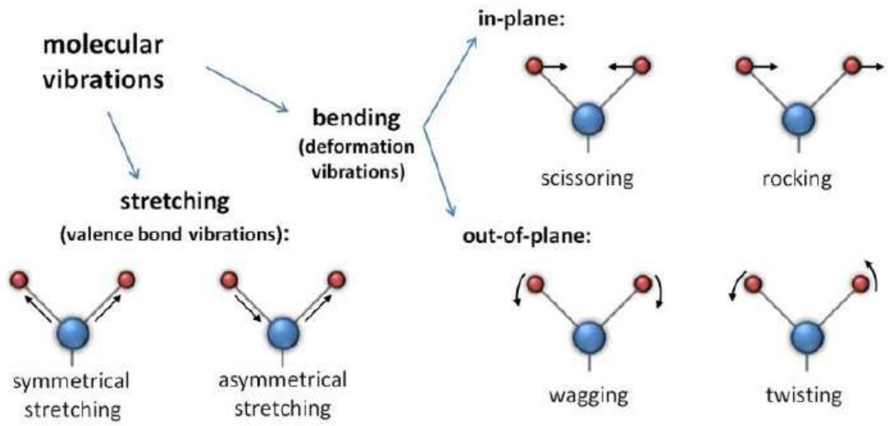
vrenda@arpa.sicilia.it

Fourier transform infrared spectroscopy (FTIR) is a technique that allows the chemical characterization in molecular terms of a very wide class of materials, including composites, and is essential in many cases to carry out preliminary "screening" in an inexpensive and very quick way. This technique has experienced, since its conception, many different developments which have rapidly let it take a key place in a Chemistry lab, in a plethora of fields: from the quality control of materials, foods and drugs, to the monitoring of environmental matrices (water, air, sediment), to evaluations in the field of Cultural Heritage; up to now, FTIR instrumentation is present in almost every chemical analysis laboratory and provides complementary responses to other techniques of both molecular spectroscopy (such as Raman) and atomic spectroscopy (such as ICP-MS analysis). Starting from the fundamentals of the technique, this essay will illustrate various applications, focusing in particular on two subjects: a "hot topic" at an environmental level, such as the monitoring of microplastics, and a Cultural Heritage topic, the protection of stone with nanomaterials.

Theory

Infrared (IR) spectroscopy is a type of molecular vibrational spectroscopy: in this technique, it is exploited the interaction between radiations (of a specific wavelength) and matter, in order to acquire informations about molecular composition of the matrix analysed. In particular, the wavelength range in which we work using IR spectroscopy goes from 0,77 microns up to 1000 microns; conventionally, this range is divided in three intervals: from 0,77 up to 2,5 microns (Near IR), from 2,5 up to 50 (Mid IR), from 50 up to 1000 microns (Far IR). For easiness, since working with commas and decimals has always been quite upsetting, in IR wavelength is expressed as its inverse, the wavenumber.

As already mentioned, the infrared radiation-matter interaction causes a series of vibrations at the molecular level consequent to the absorption of IR radiation by the bonds inside the molecule. But this absorption does not always occur; a vibration is IR active, and therefore observable, in fact only when this oscillation involves a variation of the dipolar moment of the molecule and therefore an oscillating electric field, which interacts with the electromagnetic radiation. According to Hooke's law, a model applicable in the case of bond vibrations, the higher the force constant of a bond, the higher the frequency at which such vibration will be observed. Conversely, the greater the reduced mass of the bond, the lower the frequency at which this vibration will be observed. The types of molecular vibrations detected are mainly of two types, stretching vibrations, elongations that take place along the bond axis, and bending vibrations, which are deformations consisting of movements in and out of the bond plane.



The abundance of active IR vibrations results in the presence of numerous spectral bands within an infrared spectrum. For this reason, an IR spectrum is usually divided into 4 parts for its interpretation, the X-H bond stretching zone, the triple bond stretching zone, the double bond stretching zone and the most important: the stretching and bending of single bonds zone, also called the fingerprint zone. The latter is extremely important in that it is unique to each molecule, thus resulting in a diagnostic criterion for quality control or identification of unknown materials. The power of the technique lies a lot in the fact that from a single measurement it is possible to obtain numerous information, both regarding the molecular identification as it is, intermolecular interactions, adsorption phenomena, or the study of second-order vibrations, which are those deriving from the interaction between two or more vibrational modes.

Instrumentation

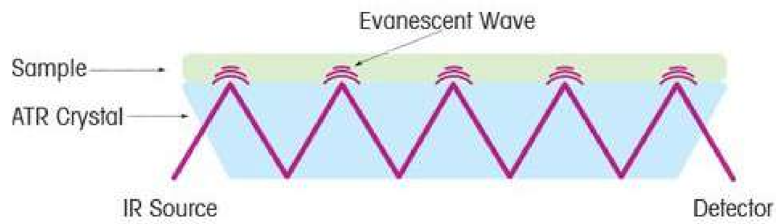
The improvement of the components of the analytical instrumentation has made it possible to have both portable instruments, able to operate, already in the sampling phase, investigations at a low level of precision on the matrix to be analysed, and multifunction bench instruments, which allow to reach a high level of precision, to carry out more complex analyses or to probe small quantities of samples also by creating "chemical images" (such as micro-FTIR).

The first types of infrared spectrometers developed worked in dispersion, providing for the use of a continuous source and a monochromator to select the range of wavelengths to be analysed. This type of instrumentation quickly became obsolete with the advent of "Fourier Transform" instrumentation, as dispersion instrumentations required very long acquisition times (about 10 minutes for 1 spectrum), since each wavelength had to be acquired individually by scanning the selected range. Furthermore, the low power of the continuous source and the attenuation of the signal by the monochromator made acquisition particularly time consuming.

The "Fourier Transform" instruments, since their invention, have become the standard instrumentation for IR spectroscopy analysis. The FT method allows to analyse the polychromatic radiation of the source without placing in-between radiation selection devices. This allows for extremely reduced analysis times (a few seconds), a better signal / noise ratio and the possibility of interfacing the instrument with others, giving rise to hybrid techniques.

A third type of instrumentation, developed more recently, involves the combination of the FTIR technique with the use of a more intense monochromatic source (a QC laser) and allows to achieve almost instantaneous acquisitions and improve spectral resolution, intensity and even lateral resolution. This is why the LDIR (Laser Direct Infrared) technique has been praised for chemical imaging in particular.

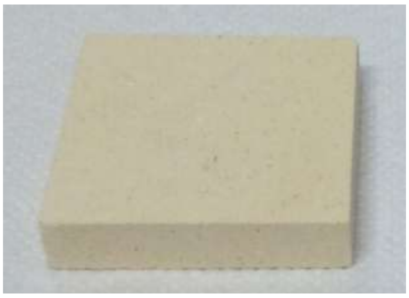
Regarding the methods of signal acquisition, IR spectroscopy was born as a spectroscopy operating in transmission. The evolution of technologies and components has not only led to the transition to FTIR, but also to the development of different methods operating in reflection. In particular, among them it can be mentioned the total reflection (TR) and the total attenuated reflection (ATR). The second of the two has been very successful due to its practicality of use: ATR-FTIR is the methodology currently used routinely in many chemical laboratories that deal with quality control as a key technique for the recognition / certification of materials and food. The technique allows to obtain spectra qualitatively corresponding to those recorded in transmission, even if no preparation of the sample is carried out. In addition, in many cases, the sample can be recovered post-analysis. The second of the two has been very successful due to its practicality of use: ATR-FTIR is the methodology currently used routinely in many chemical laboratories that deal with quality control as a key technique for the recognition / certification of materials and food.



Both TR and ATR exploit the phenomenon of total reflection of the IR radiation coming from the irradiation of the analysed sample. Although the reflected radiation is composed of a diffuse component and a specular component, both techniques only analyse the reflected radiation in a specular way (with the related problems).

The versatility of FTIR has led to a last improvement in the technique, consisting in combining FTIR and optical microscopy (micro-FTIR). The technique has found considerable use in the analysis of Cultural Heritage, as it allows to carry out analyses with high lateral resolution (up to 10 microns with some instrumental settings) in a non-destructive way, a not indifferent feature for this field of application. It also allow to produce "chemical images" by combining the optical images acquired with the microscope lens with the information given by the FTIR analysis on each point.

Case study 1: Cultural Heritage application



The first case study presented concerns a work conducted in the course of a doctoral thesis in Materials Science and Nanotechnologies, at the University of Palermo. The study carried out involved the addition of inorganic oxide nanoparticles to organic film-forming formulations developed for the protection of natural stone. The purpose of adding the nanoparticles was to impart greater strength or self-cleaning properties. ATR-FTIR was used in a first stage for the characterization of the protective polymeric films, before and after the addition of the nanoadditives; in a second step, it was used to investigate interactions at the interface between stone, polymer and nanooxides. In this study, the use of ATR-FTIR in combination with other techniques such as solid-state NMR, allowed to reach a greater awareness on the subject and to give useful indications on the choice of a product containing nanoparticles and their effect on the organic ready-to-use formulation.

Case study 2: Environmental application

The second case study presented concerns a monitoring project currently underway as a result of the collaboration between MIPAAF, CNR ISPRA and ARPA Sicily, concerning the exploiting of μ-ATR-FTIR spectroscopy for the identification of microplastics sampled in Sicilian marine-coastal water bodies. The project stems from the current interest of environmental research on the increasingly consistent presence of microplastics in the marine environment. Microplastics are defined as all those plastic particles with dimensions between 300 microns and 5 mm. Given their very small size, these particles can be easily ingested by marine biota, giving rise to bioaccumulation processes. The sampling of marine waters takes place according to a standardized method in accordance with the methods provided for in the monitoring program for the Marine Strategy (DL 190/2010). The method involves sampling the surface water with a very fine mesh (300 microns), the retained by the mesh is then recovered and stored in 70% ethanol. The sample thus obtained then passes through a sorting phase under an optical microscope. Compared to the Ministerial Directive, this new monitoring project introduces a chemical characterization step of the sorted microplastics in which the individual fragments are analysed with ATR-FTIR (macro or micro based on the size and type of the single sample) and characterized by matching with a spectral database registered on standard materials. The project, still in progress, is beginning to highlight the abundance especially of polypropylene (PP) and polyethylene (PE) microparticles; they are reconfirmed as the most persistent microplastics in the environment, closely followed by polyamide fibers such as nylon.

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Laboratory of X-ray Fluorescence (XRF)

Maria Luisa Saladino[1], Gabriella Chirco[1,2]

[1] Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche – STEBICEF, Università di Palermo, Viale delle Scienze pad.17, Palermo I-90128, Italy.

[2] Dip. Culture e Società, Università di Palermo, Viale delle Scienze pad.15, Palermo I-90128, Italy.

marialuisa.saladino@unipa.it; gabriella.chirco@unipa.it

In this laboratory activity, the X-ray Fluorescence Spectroscopy technique is introduced. The goal of the laboratory is to show to the students the theory and the applications of the above technique in the field of underwater archaeology.

After a brief introduction about the theory and the instrumentations, some case studies are showed.

The students thus see the practice application of the portable XRF Tracer III SD Bruker AXS spectrometer having a Rhodium tube as an X-ray generator and a silicon drift X-Flash® with Peltier cooling system as a detector to some finds saved at the *Museo Archeologico Antiquarium ex Stabilimento Florio delle tonnare di Favignana e Formica*. The identification of the characteristic peaks of an element is carried out using the database contained in the ARTAX 8 software.

In detail, the analysis of metals and alloys and their patina is showed and results are commented and discussed together with the participants of the School. Some consideration about the advantage and the disvantage of the technique are done.

Introduction and application of Raman Spectroscopy

V. Mollica Nardo[1], D. Giuffrida[1], S. Trusso[1] and R. C. Ponterio[1]

[1]IPCF-CNR, Viale F. Stagno d'Alcontres, 37, Messina, Italia

1. Introduction

The phenomenon known as *Raman effect* was discovered by Chandrashekhara Venkata Raman. In 1928, the Indian physicist observed that when a monochromatic light beam traverses a transparent material, a small fraction of the light is and a small wavelength shift is observed. The wavelength shift depends upon the chemical structure of the molecules responsible for scattering, and more precisely on the vibrational properties. [1, 2] Raman spectra can be viewed as a "fingerprint" of the investigated medium, and used to detect and identified molecular species. A typical Raman spectrum features a number of peaks, each peak corresponds to a specific molecular bond vibration, including individual bonds such as C-C, C=C, N-O, C-H etc., and groups of bonds such as in the case of benzene ring breathing mode, polymer chain vibrations, lattice modes, etc. Raman spectroscopy represents a *in force* analytical technique with applications ranging from surface chemistry to biological chemistry and biomedical analysis. [3, 4] The technique, being a non-destructiveness, has been extensively used for the analysis of dyes of interest in the Cultural Heritage field. [5] Identification and characterization of pigments used in works of art play a fundamental role in order to detect a precise geographic area and a specific historic moment. The information gained about the state of conservation and the nature of the constituent materials can help before and during a restoration work. The analytical investigation into archaeological finds should be non-invasive due to their uniqueness, and this main demand is fully satisfied by using portable instrumentation. [6, 7] Many objects cannot be sampled or moved outside museums, or are non-movable by nature because these are part of architectural monuments and, in general, it is easier to reach each object rather than to gather them all in one lab. Mobile Raman spectrometers are deemed in these cases because are able to collect Raman spectra from the artefacts in their location. [8, 9] However, conventional Raman spectra are recurrently affected by the intense fluorescence of the dyes that can hide the Raman peaks, a drawback that always occurs in the case of organic materials. Such organic molecules in fact, are highly fluorescent, making their identification through Raman spectroscopy very difficult. To overcome the presence of high fluorescence is possible to use SERS spectroscopy or FT-Raman. Both of them are efficiently use in the field of Cultural Heritage by several groups. In case of SERS the presence of a nanostructured noble-metal surface is needed, the Raman signal of molecules adsorbed onto the nanostructured metallic surface, in fact, can be enhanced by several order of magnitude with respect to the normal Raman signal, allowing the detection of species even at very low concentration. Moreover, the advent of FT-Raman spectroscopy with near-IR excitation from a Nd^{3+}/YAG laser at 1064 nm, that in principle do not excites the fluorescence, has given a new dimension to art applications, especially for the study of naturally fluorescent biomaterials such as horn, hoof, tortoiseshell, and ivory. [10] Improvements in the generation of Raman spectra and their detection using CCD-visible Raman spectroscopy are now also providing valuable new ways of analyzing often difficult museum specimens.

On the other hand, the selection of a specific Raman technique is intimately connected to the specific case of study. The goal of this communication is to provide a general theoretical and practical overview about the application of Raman spectroscopy in the archaeological field. Below we presented some case-studies of *in situ* measurements about different types of materials, in order to explain the great potentiality of Raman detection.

2. Raman Instrumentation

A conventional Raman spectrometer is composed schematically by a light source, a monochromator, sample holder and detector. Two major technologies are used to collect the Raman spectra, Dispersive Raman spectroscopy and Fourier transform Raman spectroscopy, differences stand in their laser sources and in the way Raman scattering is detected and analyzed. Several type of lasers can be used as the excitation source in a dispersive Raman scattering apparatus, like argon ion (488.0 and 514.5 nm), krypton ion (530.9 and 647.1 nm), He:Ne (632.8 nm), Nd:YAG (1064 nm and 532 nm) and diode laser (630 and 780 nm). FT-Raman spectrometer uses the 1064 nm line of Nd:YAG lasers. The most common modern detectors are now charge-coupled devices (CCDs).

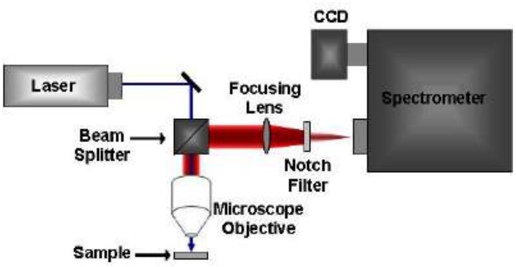

Fig. 1 Schematic of Raman Spectrometer with microscopic attachment (Image by: http://cnx.org/)

2.1 Instrument used in our case-studies

Thanks to technological development, extremely performing portable devices are now available. One of these, the BRAVO spectrometer uses a patented technology to mitigate fluorescence phenomena (SSE™ - Patented fluorescence mitigation) that permits to measure a much wider range of raw materials. Moreover, it is equipped with two excitation lasers with wavelengths (DuoLaser™) centred at 785 and 853 nm. The excitation offers highest sensitivity across the entire spectral range and hence guarantees for maximum unambiguous verification. [11, 12]. Lasers work together to mitigate the fluorescence and it is not possible to separate them by means of the experimental setup. The factors which affect the analysis on Raman spectra may include high signal-to-noise ratio, instrument stability and sufficient resolution. The spectra are collected in the 320–3000 cm^{-1} range with integration times no longer than 60 s.

Fig. 2 Bravo spectrometer

3. Case studies

Specific case studies are presented in this section with the aim to show the potential of this technique. We described the potentialities of Raman measurements on different real materials such as clay masks, reverse painting on glass, wall painting, etc. In particular, we introduced the students of Summer School an overview of Raman applications into some campaigns on artefacts preserved in Museum of Egypt of Turin, Sicilian Regional Museum of forestry and pastoral traditions - Mistretta Museum (ME), Messina Museum, Archaeological Museum of Lipari and Paestum archaeological site. We focalized the discussion on archaeological questions that can be answered with Raman spectroscopy. As mentioned before, the Raman measurements is able to detect inorganic component (like pigments); it can be associated to complementary spectroscopic techniques (FT-IR, XRF) in order to improve data acquired.

A) B)

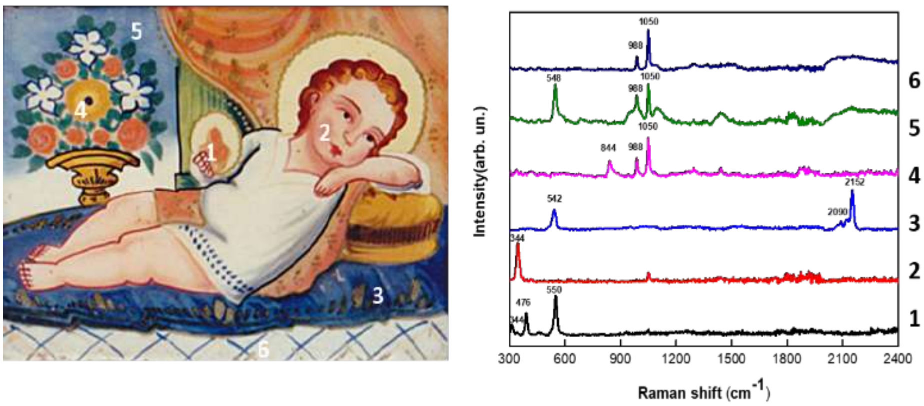

Fig. 3 A) Reverse painting nr. 518 depicting the “Infant Jesus; B) Raman spectra obtained on painting 518 (Image by [13]).

In Figure 3, we show the first example discussed in our contribution. The artwork, painting nr.518, is preserved at the Regional Museum of Forestry and Pastoral traditions of Mistretta (Messina, Italy). The gallery is the first Sicilian demo-ethno-anthropological museum, specifically conceived to give visibility to Sicilian folklore traditions. The aim of this diagnostic campaign (XRF, Raman and IR Spectroscopy) has been the study of pigments and binders of some reverse paintings belonging to different workshops on different geographic areas, in order to identify the materials and methods used in the realization. As mentioned in Introduction, in fact, the analysis of pigments on artworks is of major significance in art conservation as it leads to detailed characterization of materials and is thus important for dating and authentication. Thanks to the use of *in situ* Raman spectrometer on reverse painting nr. 518 depicting the "Infant Jesus" is from the Apulian School (XIX cent.) we detected six different pigments: barium sulphate, white lead, minium, cinnabar, lazurite and prussian blue compatible with historical collocation of painting. The results obtained during the diagnostic campaign have been a support for the restoration of some of the reverse paintings and published in *Microchemical J.* [13]

The second example (Fig. 4) concern a wall painting probably representing St. Francis in the act of receiving the stigmata preserved in in the church of S. Maria delle Palate at Halaesa Arconidea archeological site (Tusa, Messina, Italy). The aim of the work, also in this case, is the characterization of the nature of pigments by combination of Raman and XRF techniques. Raman spectroscopy proved very useful for red, yellow and blue pigments. In Fig. 4 we showed the Raman spectra obtained and published in *Heritage* [14].

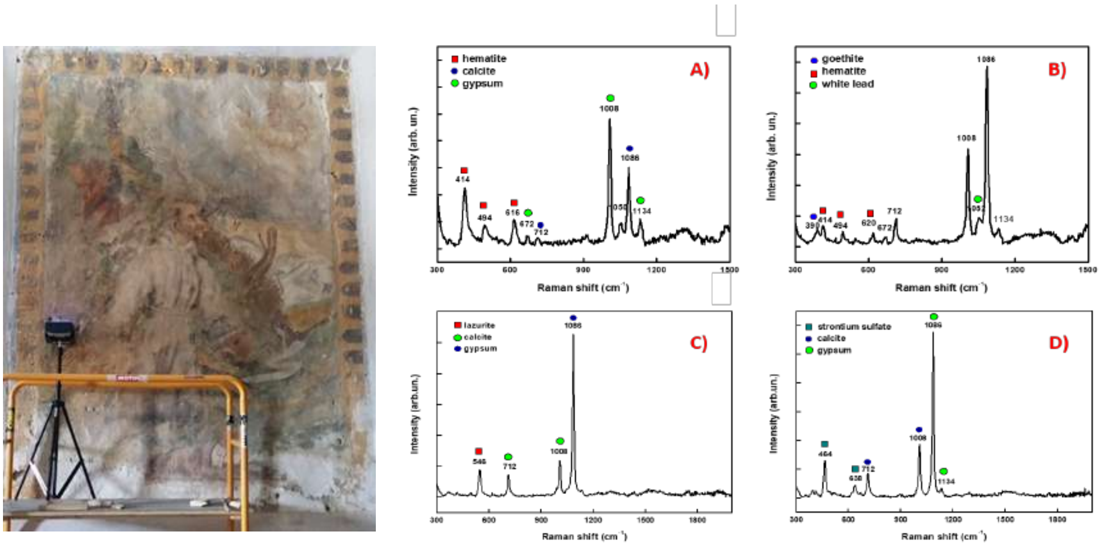

Fig. 4 Wall painting and Raman spectra on A) red; B) yellow; C) blue and D) white area (Image by [14]).

In addition, an *in situ* laboratory was presented in the Summer School in which we explained at the students the use of Handheld Raman Spectrometer and the software OPUS that manages the instrument. In particular, we selected some pigments and the students are guided to collected spectra and to identify the inorganic and organic components of materials. In Figure 5 A) and B) is shown Raman spectra of two different pigments: cinnabar and minium.

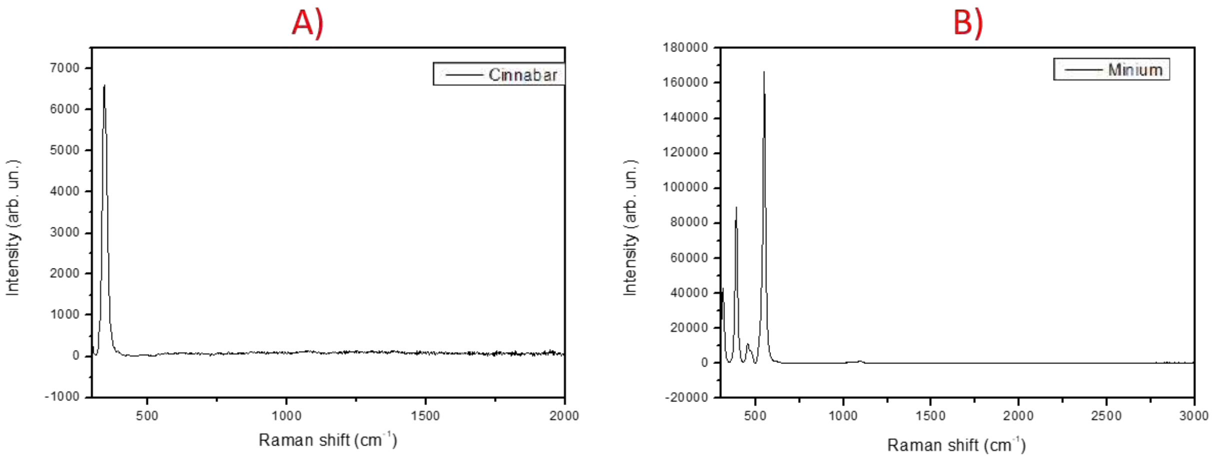

Fig. 5 Raman spectra of A) cinnabar B) minium

The attention was focalized in selection of spectral range and scan numbers of experiment. The identification of the contained molecules was carried out thanks to the use of databases. Specific databases contained spectra of pigments, minerals, ligands etc. are available online. [15, 16]

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Application of laser-scanning and digital photogrammetry techniques in archaeometry

Dario Giuffrida[(a)], *Viviana Mollica Nardo*[(a)], *Sebastiano Trusso*[(a)], *Rosina Celeste Ponterio*[(a)]

[(a)]IPCF-CNR, Viale F. Stagno d'Alcontres 37, 98158 Messina

dario.giuffrida@ipcf.cnr.it

1. Introduction

In the last decade, laser-scanning and digital photogrammetry have become the most common technologies for the survey in the field of cultural heritage [1]. Together with the other methods of diagnostics [2], their deploying can be considered as part of the process that aims to reach a specialist knowledge of a given monument or artifact, prerequisite for any further analysis, intervention or interpretation. In this perspective, the collaboration and the dialog between scholars of humanistic and scientific disciplines has, thus, become necessary both for aspects concerning the historical reconstruction (dating and interpretation) as for other challenges related to conservation, management and communication.

Moreover, the accessibility and the performances of the new portable instruments have strongly promoted their use for urgent on-site measurements, for diagnostic or digitizing campaign planned within the archaeological areas or museums and, in general, for all those situations in which artifacts cannot be moved to specific laboratories (due to their fragility, big sizes, risks of damages, lacks of authorizations etc.) The 3D survey techniques proved to be effective not only in order to collect metric and graphic documentation but also to check the 'state of health' of artworks and buildings and diagnose the degradation processes [3] (e.g. by systematic and controlled iterations of measures over a period of time). Other interesting applications concern the digitization oriented to digital fruition, promotion and preservation of memory in case of destructive events [4].

The goal of this communication is to provide an overview on the main 3D automatic survey techniques used in the archaeological field, trying to highlight its potential and limits by means of some case studies: specifically, we will present two survey projects carried out with the instrumentation of the laboratory "Ardigi3Lab" of the CNR-IPCF of Messina, which have allowed to test and compare different laser-based and image-based techniques on different scales.

2. Methods and technologies for heritage survey

A 3D model of a given artifact or monument can be generated following different procedures [5]:

- Direct survey: the surveyor measures in direct contact an artifact (using a caliper of a measuring tape), in order to generate a drawing, later digitizable through CAD programs.
- Indirect survey: the surveyor uses an instrument (as a total station, a D-GPS, or a camera) to measure a set of single points until the geometrical features of the artefact are defined.
- Automatic survey: a specific instrument, equipped with active or passive sensors autonomously measures and records everything that falls within its range of action, providing metric and morphological details; the surveyor only plans the locations or the movements of the instrument, setting the most suitable acquisition parameters.

The last two methods offer several advantages compared to the first one, as shorter time in data acquisition, higher accuracy, lack of contact, possibility to reach inaccessible zones; instead, only the automatic survey allows to overcome the traditional point-by-point survey and to generate a *dense cloud* of points in which every surface is well characterized.

2.1 Laser-scanning

Laser-scanning is an active and contactless survey technique, based on the measuring of distances by means of electromagnetic waves [6]; specifically, it uses a laser light to measure 3D coordinates of points (x, y, z) on the surfaces of objects. When the light beam reaches the surface of an object, it is partially absorbed, partially reflected and partially transmitted. The reflected wave returns to the source, where it is measured by a detector that processes the signal in order to generate the spatial coordinates of each point. In relation to the systems used for the acquisition and processing of the laser signal, we have different scanners: a) triangulation-based b) time-of-flight-based (TOF) c) phase-shift-based. In the first case, an active sensor projects a laser line or a pattern onto the surveyed object and an imaging sensor, located at a predetermined and calibrated distance (baseline), records the reflected signal in order to derive the 3D geometry of the object. In the TOF laser scanner, a laser impulse is sent towards an object and then the distance between the instrument and the object is computed using either the time of flight of the transmitted and reflected signal (PW scanners) or a phase difference of the transmitted and reflected signal (CW scanners). Obviously, the choice of one or the other technique will strictly depend on the dimensional and morphological characteristics of the object to be detected and on the resolution and accuracy levels requested: for example, measurements with triangulation or manual scanners can provide relative dimensions and positions of small artefacts (with detail down to the micron) but can become uneconomical for buildings (i.e. when the number of points increases) [7].

2.1.1. Instruments used in our study-cases

In the case-studies presented below, three laser-based instruments have been tested, each in relation to different situations and contexts. For the survey of archaeological areas and buildings, we have used a versatile terrestrial laser-scanner, the “Focus 3D S120 by Faro” (fig. 1a). The instrument is characterized by an operative range between 0,6 and 120 m of distance, a wide field of view (360° H and 320° V) and an acquisition speed of 976,000 points per second. It is also equipped with a motorized rotation system and an integrated camera (70 mega-pixels in resolution) for the acquisition of the RGB value.

LASER CARACTHERISTICS	
Laser class	1
Wavelength	1550nm
Beam divergence	Typical 0,19 mrad (0,011 °) (1/e, halfangle)

(a)

Accuracy:	±25 μm (±0.001 in)
Repeatability:	25 μm, 2σ (0.001 in)
Stand-off:	115 mm (4.5 in)
Depth of field:	115 mm (4.5 in)
Effective scan width:	Near field 80 mm (3.1 in); Far-field 150 mm (5.9 in)
Points per line:	2000 points/line
Minimum point spacing:	40 μm, (0.0016 in)
Scan rate:	300 frames/second, 300 fps × 2000 points/line = 600,000 points/sec
Laser:	Class 2M
Weight:	485 g (1.1 lb)

(b)

Figure 1: (a) The Faro Focus 3D S120; (b) The FaroArm and specifications.

For the survey of small artifacts, one of the most performing coordinate measuring machines (P-CMM) has been used the "Quantum^{TM} FaroArm" by FARO (Fig. 1b). This is a transportable device made up by a tripod and a mobile mechanical arm, easily usable on-site as a digitizer or an advanced digital pen. The laser arm meets the most rigorous ISO 10360-12:2016 standards and, suitably connected to the PC, provides a real-time visualization of the point cloud. This kind of instrument has a well-documented background of experimentation for the detection of small-sized objects with irregular and porous surfaces (as ceramic of archaeological interest).

The last tool is the Faro Freestyle 3d (Fig. 2), a triangulation handheld device, equipped with a laser, two cameras with an infrared sensor to provide stereo detection of structured light, a color camera for photographic acquisition and a flash for low light conditions; the system works simply by connecting the instrument via USB to a Windows tablet, which allows a real-time viewing of data. The operativity range of this tool is from 0,5 to 3 m, with an accuracy of 1 mm at a distance of 1 m. As the faro arm, the system uses the surveyed object as a reference between subsequent scanning positions, as long as there is sufficient overlap between adjacent positions. Handheld scanners like this are sometimes marketed as a complement to terrestrial scanners and used to integrate inaccessible areas.

Figure 2: Faro Freestyle 3D scanner

2.2 Digital photogrammetry

Photogrammetry is a passive image-based survey technique through which simple photos are turned into 3d models [8]. It is possible thanks to the use of specific algorithms (e.g. *Structure from Motion*) able to collimate common points from a set of overlapping photos belonging to the same scene and to define the position, the shape and the size of the object taken in exams. Many types of images can be used as input in order to generate a 3D model (satellite, airborne, balloon, UAVs, terrestrial and even underwater images) and this determines different types of photogrammetry (aerial, close-range etc.). In our study case we only used a Canon Eos 7D Reflex Camera (18 megapixels in resolution) and a drone DJI Phantom 4 Pro-Plus (equipped with a 20 MP camera).

3. Case studies

The results achievable from the application of both image-based and range-based techniques are presented in this section with the aim to show the potential of each methods: in particular we will show some survey projects carried out in the last years by the CNR-IPCF of Messina in Sicily and Calabria.

3.1. Lipari

In the frame of a collaboration with the Aeolian Museum of Lipari, between the 2018 and 2019, a selection of finds, belonging to the Classical section, has been analyzed setting up a 3d reconstruction 'mobile laboratory' in situ [9]. In particular the study has included: a) 12 theatrical clay masks (4th cent. BC), with dimension ranging from 6 to 25 cm in height, belonging to the wide collection of theatre-related terracottas [10]; b) 2 figured calyx craters (middle 4th cent. BC); the first (i.n. 340bis), attributed to the Painter of Maron, the second (i.n. 10648) attributed to the painter of Adrastus. c) a Greek stone *arula* characterized by an inscription difficult to read (4th sec. BC); d) a decorated lid of *lekane* attributed to the Lipari Painter.

According to the different requests of study, conservation and dissemination, the measurements have been performed using both laser-scanning (by the Faro Arm and the Freestyle) and digital photogrammetry (by the Canon camera) [11, 12]. The scanning systems allowed to obtain three-dimensional models, metrically correct at very high resolution of all the mentioned finds. A further 3d reconstruction work has been performed on the mask nr. 11114-E [13], different from all the other due to its singular iconography merging two characters (an old man and a young) in a single matrix. The modelling work-flow, carried out by means of specific software (as Geomagic Wrap™), allowed: 1. to dissect the mask and to reconstruct the image of the two prototypes which were blended by the craftsman (fig. 3); 2. to make the digital model available to the scientific community, for the purpose of further study (https://skfb.ly/6QzLw).

Figure 3: The image shows the reconstruction the clay mask 11114-E preserved in the Museum of Lipari.

Another effective application of these two combined techniques has concerned the case of the craters mentioned above: after a scansion with the laser arm (fig. 4a), which has returned a highly metrically correct model, a photo-scansion (with the Reflex camera) has been performed (fig. 4b) in order to generate a photographic texture (not acquired by the laser arm); this latter has been finally applied to the 3d model and used in order to generate a projection onto a plane of the scene depicted on the vessels body (fig. 4c).

(a) (b) (c)

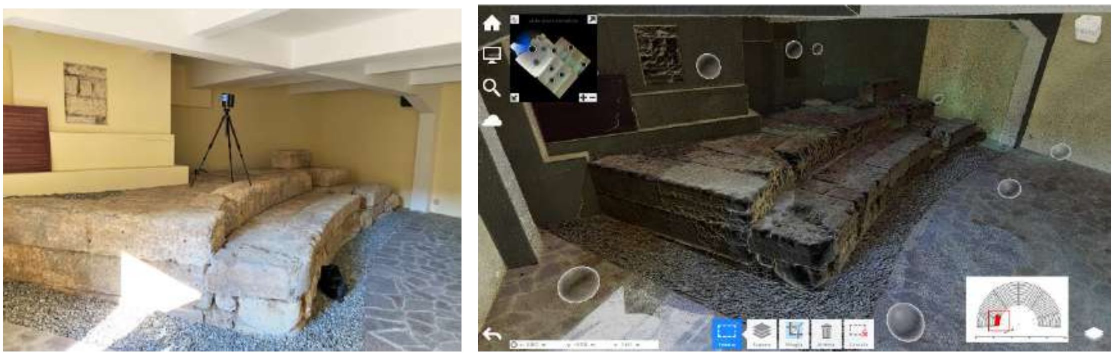
Fig. 4: (a)Acquisition by laser arm photo-scansion; (d) 3d model generated by photo-scansion (in blue the position of each camera); projection onto a plane of the Maron Crater vessel body.

3.1. Reggio Calabria

As part of the project POR CALABRIA FESR 2007-2013, several surveys have been carried out by the CNR-IPCF in the archaeological areas of Reggio Calabria [14] (fig. 5), using the terrestrial laser scanner Faro Focus 3d.

Fig. 5: Reggio Calabria, localization of the urban archaeological areas on satellite image.

The surveys, oriented at the creation of three-dimensional models and some virtual tour, have specifically concerned the following archaeological areas: the site of Piazza Italia, the Roman Baths and the Hellenistic fortifications (located along the city waterfront) the *odéon* of via XXIV Maggio, the "Aragonese" castle, and the extra-urban site of Motta S. Agata. The architectural complexity of the structures has, often, required a careful planning of the number and positioning of scans and acombined use of terrstrial laser-scanning and drone photogrammetry [15].
In the case of the *odeon* (of which only a small part is still preserved), the 3d model generated through terrestrial laser-scansions (fig. 6a), has been used as a support to reconstruct the volumetric development of the building: merging our accurate 3d model with a well-known hypothetic planimetry (fig. 6b), a 3D reconstruction of the missing parts has been finally perfomed through the software Rhinoceros 6.0.



(a) (b)

Fig. 6: *Odeon*: acquisition using the FARO terrestrial laser-scanner; (b) results of the first processing.

The second case study concerns the Roman *Thermae* (area of 290 m^2) and the and the Hellenistic fortification walls of Reggio: in the first case (fig. 7a) a project of 23 laser scans integrated with a drone flight (45 photos) has hallowed to develop a digital model and a virtual tour of the archaeological urban area (the latter is available online at http://wwgis.ipcf.cnr.it/vr/vr-terme/); in the second case 44 laser-scanner position have been necessary to cover the whole strip measuring 16 x 120 m (fig. 7b). The use of the terrestrial laser scanner proved to be particularly useful for the survey of the underground site of Piazza Italia (fig. 8), where the use of the photogrammetry was impossible.

(a) (b)

Fig. 7: View from drone of the Roman *Thermae* (a) and of the Greek fortification (b).

Fig. 8: (a) The archaeological area of Piazza Italia, Reggio C; (b) Scanning by Faro Focus 3D S 120.

4. Notes on data processing

Data processing (filtering, registration of adjacent scans, meshing, application of texture, editing and exporting) was performed combining some dedicated software as Autodesk Recap Pro, FARO SCENE and JRC 3D Reconstructor. Using Pano2VR, the 360° photos recorded by the Faro CAM2 built-in camera were also used to create a virtual tour for each area; these products will be accessible from specific web pages or from off-line applications and will offer the visitor a better experience of fruition. In two cases (Roman Bath and Greek Walls areas) it was possible to fly over the archaeological areas with a DJI Phantom 4 PRO drone, in order to acquire an integrative photogrammetric (image-based) survey, which has been processed through Agisoft Metashape.

5. Discussion and Conclusions

As shown above, laser scanning and photogrammetric modelling techniques have a lot of common and useful features, thanks to which they have became very popular in the field of cultural heritage survey [16]:

- they can also be used employing basic hardware instrumentation and user-friendly software;
- they allow to save time for the survey on field;
- they can provide a complete 3D virtual model in a short time;
- they allow to perform 3D measurements and extract 2D drawings (plans and sections) and ortho-images.

Despite the two methodologies are able to produce similar three-dimensional models through different procedures, the choice of most appropriate technique can depend on several factors: the object or the area to be surveyed, the user experience, the budget, the time available and the goals of the research. Photogrammetry is often preferred in order to provide textured and photorealistic 3D scenes and due to its low-cost applications.

One of the difference is that the photogrammetric processing requires a correction of the distortion and the scale of the model with external measurements (as control points) to be acquired using other instruments; the point cloud of a laser scanner is instead "correct" metrically but positioned in a local coordinate system; if we wanted to geo-reference it correctly, we would have to integrate GPS points.

Nonetheless, the two techniques are complementary and integrable within a survey project in order to generate 3d models usable for study analysis, monitoring of the state of conservation, enhancement, evaluation of risks and degradation phenomena, supports for restoration and web sharing etc. [17] Finally their integration allows to overcome the limits of both techniques and obtain a good balance among geometric resolution, costs, and time can be achieved [5].

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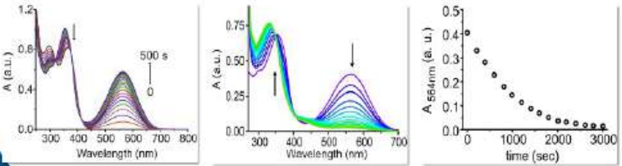
Visita allo Stabilimento Florio

Student posters

Aurelio Bonasera - graphic resume

University of Palermo, Dept. of Physics and Chemistry - Emilio Segrè
viale delle Scienze, bdg. 17, rm. 1/B6, 90128 Palermo, Italy
E-mail: aurelio.bonasera@unipa.it

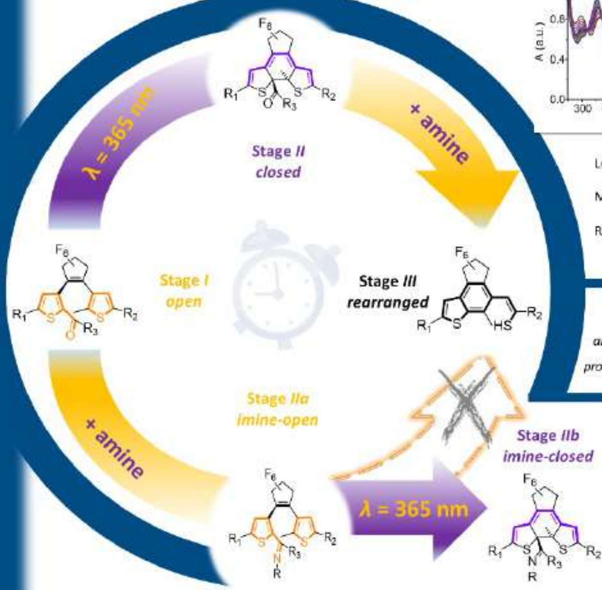
Period	Institution	Position	Topic
2006 – 2011	*University of Messina*	Bc. & Ms. student in Chemistry	Organic synthesis
2012 – 2014	*University of Trieste*	Ph.D. student in Chemistry	Dyes & pigments synthesis, photocatalysis
2014	*Université de Mons*	visiting Ph.D. student	Dyes & pigments, computational models
2015-2018	*Humboldt-Universität zu Berlin*	Marie Skłodowska-Curie fellow	Photochromic molecules (diarylethenes) synthesis
2017	*University College London*	visiting researcher	Photochromic OLEDs development
2018	*BASF SE*	visiting researcher	Dyes synthesis, organic memories
2020 - ongoing	*University of Palermo*	associate researcher (RTD-A)	Dye-Sensitized Solar Cells (DSSCs)



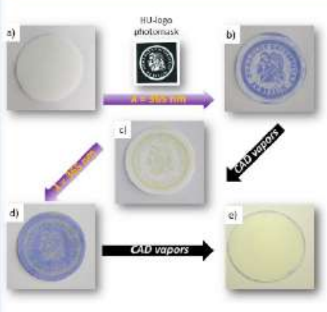
Left: Typical UV/vis spectrum evolution for a photocromic probe (CH_3CN, $4.0 \cdot 10^{-5}$ M) under irradiation @ 365 nm, until reaching the photostationary state (PSS)

Middle: Typical evolution of the UV/vis spectrum of a photocromic probe at the PSS ($2.4 \cdot 10^{-5}$ M) after the addition of benzylamine (BA, $1.7 \cdot 10^{-2}$ M)

Right: Decrease of the band @ 564 nm, corresponding to the formation of the rearrangement product.



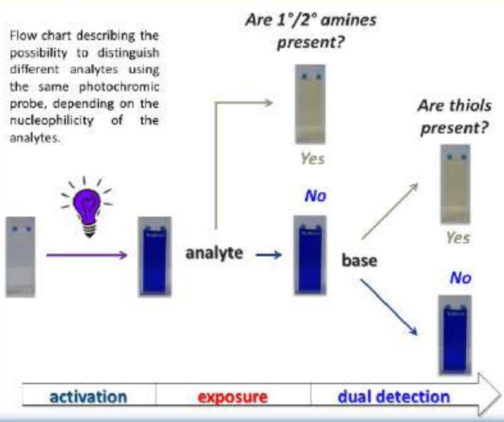
- *Practical: rational molecular design, simple and versatile synthesis*
- *on-demand activation of the probe (JUST a commercial UV table lamp, NO sophisticated equipment needed)*
- *defined place and initiation time of reaction*
- *selectivity (1° and 2° amines, NO 3° amines).*



Amine-sensing performed on light activated filter paper:

a) coated filter paper with a solution of the photochromic probe
b) *in situ* activation by irradiating @ 365 nm
c) exposure of the filter paper to cadaverine (1,5-diaminopentane, CAD)
d) CAD vapor removal, and subsequent re-activation of the non-irradiated areas
e) color evolution once exposed again to CAD vapors.

Flow chart describing the possibility to distinguish different analytes using the same photochromic probe, depending on the nucleophilicity of the analytes.



2° Summer School
Archeometria e Archeologia subacquea – *Sebastiano Tusa*
Favignana 6 - 12 settembre 2020

Dott.ssa Veronica Ciaramitaro

Borsista presso il dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche - STEBICEF e INSTM UdR - Palermo, Università di Palermo

LAUREA MAGISTRALE IN CHIMICA

Il ***Tempio G*** del Parco archeologico di Selinunte, il più esteso d'Europa, è uno dei templi più imponenti della Magna Grecia. Il tempio, in costruzione dal 530 al 409 a.C., oggi è completamente distrutto a causa di un forte sisma avvenuto in epoca medievale. Il materiale da costruzione proviene dalle antiche e rinomate Cave di Cusa, situate a circa 2 km dall'acropoli di Selinunte, dove si trovano rocchi di colonna semilavorati ancora attaccati al banco roccioso e capitelli riconducibili per loro dimensioni al colossale Tempio G.

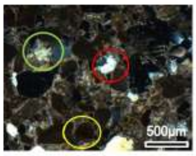

Tempio G


Cave di Cusa

Dall'odierna proposta di ricostruzione del Tempio per anastilosi, nasce il mio lavoro di tesi, in quanto sulla pietra in opera esistono pochi studi di ricerca relativi al deterioramento, alla conservazione e alla protezione.

L'obiettivo è stato duplice:
- verificare l'***efficacia protettiva*** di tre differenti formulazioni polimeriche sulla "pietra di Cusa";
- conferire alle tre formulazioni polimeriche ***proprietà autopulenti*** mediante l'aggiunta di nanoparticelle di biossido di titanio.

Caratterizzazione petrografica della Pietra di Cusa



Micrografia di una sezione sottile della pietra di Cusa con filtri polarizzatori, 40x_xpl.

La pietra è una calcarenite: grani di quarzo (cerchio rosso), grani di micrite (cerchio giallo) e grani di calcite spatica (cerchio verde).

Formulazioni polimeriche

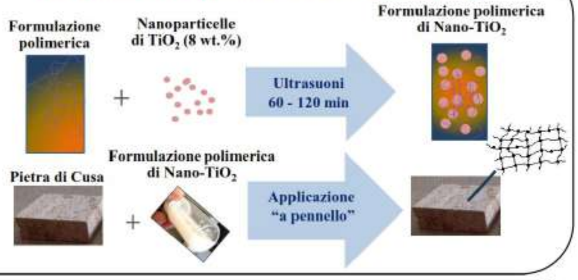
PROTETTIVO	POLIMERO	COMPOSIZIONE
Fluoline HY	Esafluoropropene / fluoruro di vinilidene	Sol. 3 wt.% in acetone / butil acetato (1:6)
Wacker 290	Silossano oligomero	Sol. 10 wt.% in acetone / butil acetato (1:1)
Fluo AQ	Fluoroelastomero tipo Fluoline HY	Sol. 5 wt.% in acqua

Preparazione dei provini

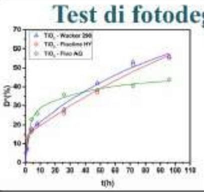
I provini sono stati preparati secondo le indicazioni della UNI EN 10921.

a) 5x5x2 cm b) 5x5x1 cm

Formulazioni polimeriche di nano-TiO_2



Test di fotodegradazione del blu di metilene

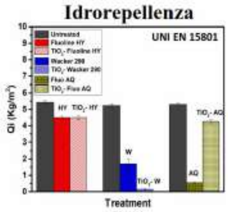


L'aggiunta di nano-TiO_2 conferisce alle formulazioni polimeriche proprietà autopulenti.

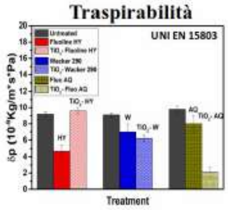
Efficacia protettiva

Variazione delle proprietà fisiche dopo il trattamento con le formulazioni polimeriche e le formulazioni polimeriche di nano-TiO_2

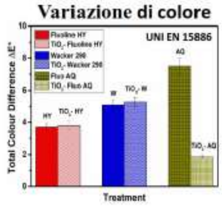
Idrorepellenza



Traspirabilità

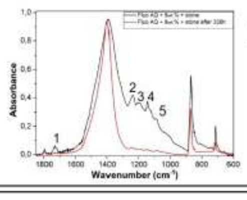


Variazione di colore



L'aggiunta di nano-TiO_2 alle formulazioni polimeriche migliora le proprietà protettive del Fluoline HY e del Wacker 290, ma provoca una diminuzione delle proprietà protettive del Fluo AQ.

Indagine FTIR: effetto del nano-TiO_2 sulla struttura chimica del Fluo AQ



- *Fluo AQ + 8 wt.% TiO_2 sulla pietra dopo 24h (linea nera)*
- *Fluo AQ + 8 wt.% TiO_2 sulla pietra dopo 96h (linea rossa)*

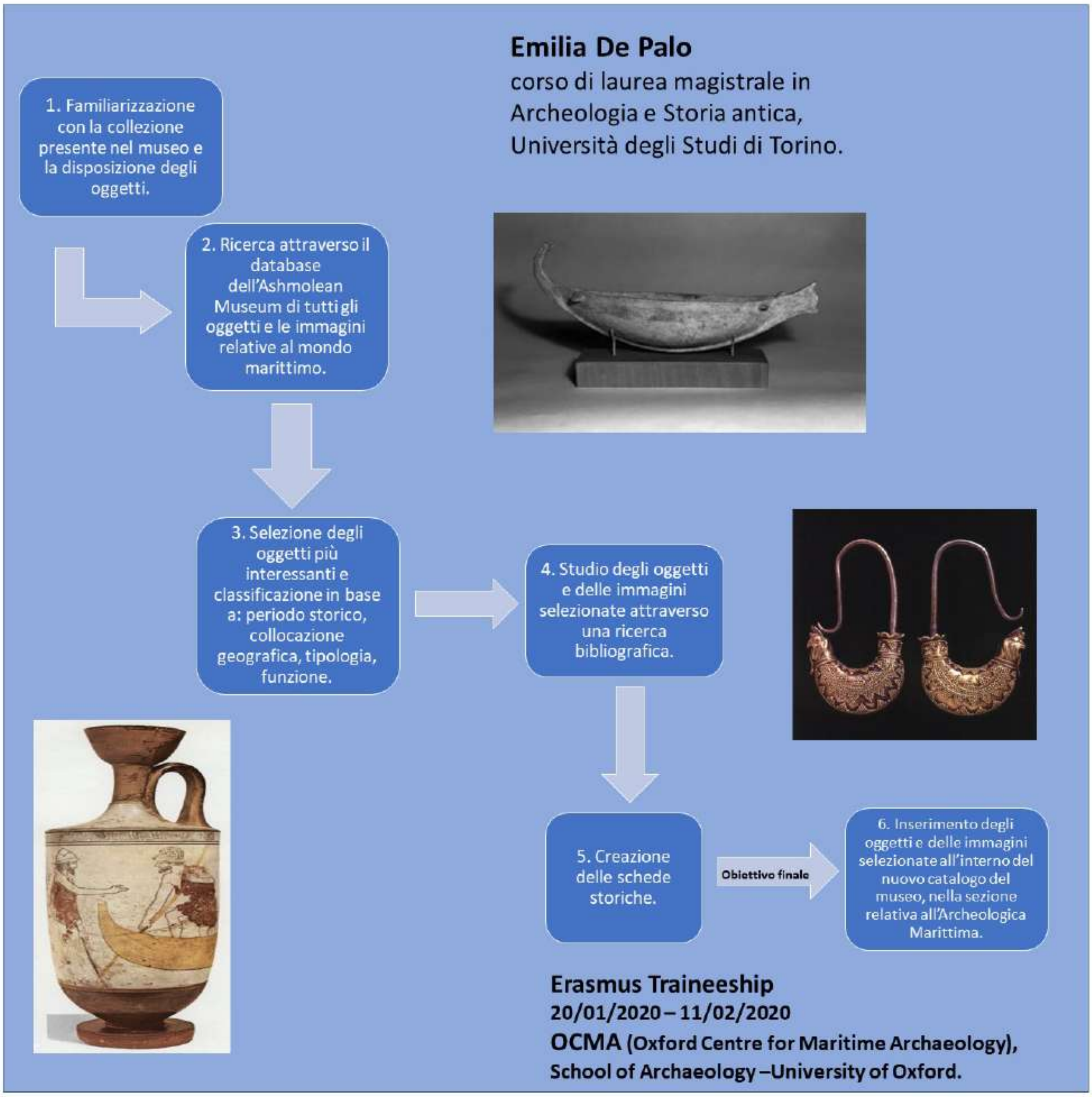
La scomparsa dei picchi caratteristici del polimero (1, 2, 3, 4 e 5) indica la degradazione del Fluo AQ.

La perdita delle proprietà protettive del Fluo AQ in presenza del nano-TiO_2 è da attribuirsi alla degradazione del polimero.

Conclusioni

- Le tre formulazioni conferiscono proprietà protettive alla pietra di Cusa. Il Fluo AQ può essere considerato il formulato che conferisce le migliori prestazioni, se si accetta un leggero effetto bagnato sul substrato lapideo.

- L'aggiunta di nano-TiO_2 alle formulazioni polimeriche conferisce proprietà autopulenti, ma provoca la degradazione del Fluo AQ. Le proprietà protettive del Wacker 290 sono mantenute, quindi può essere considerato il formulato con nano-TiO_2 che offre le migliori prestazioni sulla pietra.


Emilia De Palo
corso di laurea magistrale in
Archeologia e Storia antica,
Università degli Studi di Torino.
1. Familiarizzazione con la collezione presente nel museo e la disposizione degli oggetti.
2. Ricerca attraverso il database dell'Ashmolean Museum di tutti gli oggetti e le immagini relative al mondo marittimo.
3. Selezione degli oggetti più interessanti e classificazione in base a: periodo storico, collocazione geografica, tipologia, funzione.
4. Studio degli oggetti e delle immagini selezionate attraverso una ricerca bibliografica.
5. Creazione delle schede storiche.
Obiettivo finale
6. Inserimento degli oggetti e delle immagini selezionate all'interno del nuovo catalogo del museo, nella sezione relativa all'Archeologica Marittima.
Erasmus Traineeship
20/01/2020 – 11/02/2020
OCMA (Oxford Centre for Maritime Archaeology),
School of Archaeology –University of Oxford.

2° Summer School
Archeometria e Archeologia subacquea – *Sebastiano Tusa*
Favignana 6-12 settembre 2020

Esperienze della Dott.ssa Gabriella Chirco

Dottoranda in Scienze Umane: Dinamica dei Sistemi, Patrimonio Culturale, Studi Culturali con indirizzo archeologico presso l'Università degli Studi di Palermo, Dipartimento di Culture e Società

Laurea in Conservazione e Restauro dei Beni Culturali
Caratterizzazione e Restauro delle Tavolette Fuori Posto


Abbraccio di due amanti

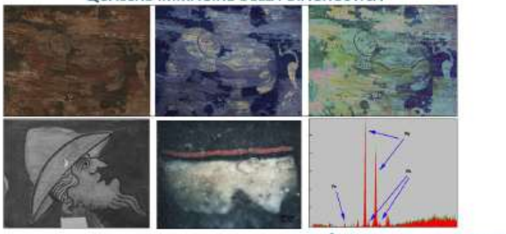

Capriolo


Dama seduta in verziere


Drolerie

Durante la tesi di Laurea mi sono occupata della caratterizzazione dei materiali e del successivo restauro delle «Tavolette fuori posto». Si tratta di dipinti su tavola (conservati preso la Galleria interdisciplinare di Palazzo Abatellis a Palermo) la cui provenienza ipotizzata, dai documenti del museo, era il soffitto ligneo dell'Aula Magna dello Steri di Palermo.
La caratterizzazione è stata eseguita *in situ* con tecniche di immaging (nel Vis, nell'UV e nell'IR) e spettroscopia XRF e in seguito approfondita con in laboratorio mediante osservazioni al microscopio delle cross section di alcuni frammenti e analisi di spettroscopia NMR. I risultati, oltre ad essere stati di grande aiuto per la progettazione e l'esecuzione dell'intervento di restauro, hanno confermato la provenienza delle opere. Anche il restauro è stato eseguito *in situ* e si è configurato come un intervento di tipo conservativo, che ha rispettato le stratificazioni storiche delle opere.

Qualche immagine della diagnostica



Alcune fasi del restauro

Alcune delle campagne di diagnostica e dei restauri

Il progetto pilota del restauro sul soffitto ligneo dello Steri di Palermo


Fregio con doppio intreccio di fettucce


Girali vegetali con volto di Cristo

Partecipazione al progetto pilota condotto dall'Università di Palermo in vista del restauro dell'intero soffitto ligneo.

È stata eseguita una campagna di caratterizzazione dei materiali, tramite indagini non invasive eseguite *in situ*, e micro prelievi. Inoltre è stato eseguito il restauro di due tavole appositamente prelevate.

Campagne di diagnostica

Alcune delle campagne di diagnostica a cui ho partecipato. In particolare 1.Madonna delle Grazie, Cappella Palatina (FT-IR); 2.Lingotti in oricalco, Museo Archeologico Gela (FORS); 3.Affreschi grotta del Crocifisso Lentini, 4.Dipinto murale di A. San Filippo (Vis-IR); 5.Crocifissione con Addolorata e S. Giovanni, chiesa di S. Sebastiano di Augusta; 6.Cristo Davanti a pilato, collezione privata (Radente); 7.Madonna dell'Elemosina, Cattedrale Biancavilla (Vis-Radente), 8.Giocatori di dadi, collezione privata (Vis-UV).

Restauri

Alcuni dei lavori di restauro eseguiti su opere facenti parte di collezioni private. I restauri si sono configurati come interventi conservativi, i materiali e i metodi impiegati sono stati accuratamente scelti seguendo i principi di compatibilità e distinguibilità nel rispetto dell'opera d'arte. 1.Madonna con Bambino, olio su tela (prima e dopo l'intervento), 2. Apparizione di Maria a San Stanislao Kostka, olio su muro (volta) (prima e dopo l'intervento), 3.Cristo davanti a Pilato, olio su tela (prima e dopo l'intervento), 4.Crocifisso in carta pesta (prima dell'intervento).

Il Dottorato in Scienze Umane – indirizzo archeologico

Il progetto di dottorato "I vasi di Centuripe"

Si tratta di opere databili tra il III e il II secolo a.C. prodotte a Centuripe, generalmente di grandi dimensioni (80 cm e più di altezza). Rappresentano un caso di grande interesse dell'applicazione di tecniche pittoriche su supporti ceramici, sono caratterizzati da decorazione a rilievo, spesso dorata.
Numerosi esemplari sono esposti nei musei sia nazionali che esteri, ed un gruppo cospicuo si trova nei magazzini del Museo Archeologico di Siracusa. Solo un numero limitato, in cattivo stato di conservazione, proviene da scavi regolari, invece la maggioranza, rinvenuta in circostanze incontrollate, ha alimentato sin dagli inizi del '900 il mercato antiquario, dove sono stati immessi anche prodotti falsificati. Il progetto si pone l'obiettivo di affrontare, tentando per la prima volta un approccio più sistematico, le problematiche legate alla distinzione tra i vasi autentici e i falsi-storici tramite lo studio delle tecniche di esecuzione, dei materiali utilizzati e del loro modo di impiego in un'ottica di interdisciplinarità scienziato-archeologo.

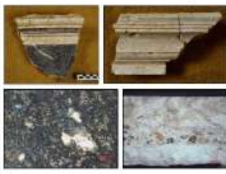
Le esperienze correlate

Parte del periodo all'estero è stato svolto presso la Missione Archeologica Italiana della Scuola di Atene a Gortina di Creta durante il quale, in parallelo con lo studio dei materiali rinvenuti durante gli scavi degli anni precedenti è stata eseguita la conservazione, la pulitura ed in due casi il restauro completo dei reperti in questione.

Nell'ambito del progetto Pinxerunt sono state studiate e catalogate le pitture delle case del quartiere Ellenistico Romano di AG. Si è prestata attenzione alla conservazione dei reperti ed è stata restaurata un'antina.
Dal progetto è nata una mostra e un catalogo a questa correlato.

Le collaborazioni

In seguito alle esperienze alle quali ho partecipato sono nate alcune collaborazioni con colleghi archeologi. In particolare,



insieme al collega M. Benfatti (UniBo) ho analizzato e caratterizzato i materiali costituivi di quattro reperti in stucco modanato provenienti dalla casa III M del quartiere Ellenistico-Romano di AG. Dalle quali è stato stabilito che insieme ai materiali tradizionali degli stucchi, la calce e la sabbia di fiume (in questo caso originata da rocce bio-calcarenitiche), nella malta è stata trovata una, meno diffusa, componente lipidica e che il pigmento apparentemente nero era in origine di colore blu (a base di alluminosilicati).

Con il collega D. Giuliano (UniPA) è stato avviato uno studio, ancora in corso, su alcuni frammenti di malta, che per aspetto si distinguono notevolmente da altri con la medesima provenienza. I dati preliminari indicano la presenza, di inerti costituiti da materialevulcanico.

3D SURVEY AND MODELING OF MASKS AND CALYX CRATERS FROM LIPARI: INTEGRATION OF LASER AND PHOTO SCANNING SYSTEMS

D. Giuffrida ([a]), V. Mollica Nardo ([a]), M. A. Mastelloni ([b]), O. Adinolfi ([c]) & R. C. Ponterio ([a])

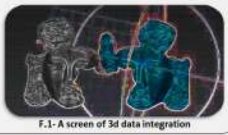
([a]) IPCF-CNR di Messina, Viale F. Stagno D'Alcontres, 981158, Messina
([b]) Former Director of Polo, Parco Archeologico e Museo "L. Bernabò Brea" di Lipari
([c]) FARO Europe GmbH & Co. KG

Study context

The poster shows the result of a 3D survey campaign carried out by **IPCF-CNR** of Messina at the Aeolian Archaeological Museum of Lipari. Within a wider study of characterization and diagnostic performed through non-destructive methoilologies (see also poster n.16), many artifacts have been surveyed using a portable **laser scanner** in order to record their geometries as accurately as possible; in some specific cases the technique has been combined with **digital *sfm* photogrammetry**, based on photo-scanning, for a better photorealistic rendering of some painted surfaces.

Aims

The aim of the work is to show the potentialities of a combined use of range based and image-based survey techniques on archaeological artifacts in order to obtain useful tools for **analysis, diagnostic, digital restoration and virtual fruition within the Museums**.

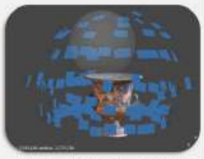

F.1- A screen of 3d data integration

Materials & Methods

Using non-destructive and non-contact methods we have analyzed: n. 9 terracotta comedy theatre masks (datable between the 5th and 4th centuries BC and discovered by L. Bernabò Brea and M. Cavalier in the second half of XX cent. in the Greek necropolis of Contrada Diana.), n. 2 figured calyx craters (mid 4th century BC), a stone inscription, a fragmentary clay head and a lekane lid.


F2.- Some of the finds surveyed


F.3- The Pittore di Adrasto crater (n.i.10648) and the arm laser-scanner


F.4- Position of the cameras around the object

The pieces were digitized with a **Faro® Cam2 laser arm** (model Quantum M FaroArm): with a point probe the digitizer has allowed to collect 3D data points with an accuracy ranging from 0.0007" to 0.004".
In addition, a scaled SfM model of some clay masks and of two figured craters was created using a **Canon Eos 7D** camera in order to integrate the model with photographic texture, not acquired by laser arm. In particular the vases were entirely photo-scanned following a 'converging axes' schema, taking care to get an overlap and sidelap between the frames ranging from 60% to 70% (F.3).


F.5- The Faro LaserArm and 3d data point


F.6- Acquisition with Faro Laser Arm


F.7- Acquisition and restitution of mask i.n. 14584

Data processing

1. Using "Geomagic Wrap®" the results of each laser scansion related to a specific find have been cleaned, repaired, merged and processed in order to create 3d meshed models.
2. The photo-scansion of craters has been processed in "Agisoft-Photoscan" following these steps:
- Correction of optical distortion of camera (by Agisoft-Lens)
- Alignment of the frames by tie points between adjacent frames;
- Building of of dense cloud;
- Generation of polygonal mesh (three-dimensional surface);
- Generation of texture (only for vases);
- Exporting of models;


F.8- A restored fragmentary clay head

Post-processing of calyx craters: texturing and unwrapping

Finally, the high-resolution texture of vases made up by Photoscan was transferred to the vertices of the model using MeshLab, colouring the surfaces.
In addition, a **cylindrical projection** of the decorative apparatus of craters was also carried out using Agisoft Metashape® (FF.7-8).


F.9 – Cylindric projection of Maron crater (i.n. 340bis) depicting the myth of *Hippolytus* and quadriga of horses


F.10 – Cylindric projection of Adrasto Painter crater (i.n. 10648) depicting the quarrel between *Tydeus* and *Polyneikes*

Results

These non-contact methods has allowed to obtain 3D models of all the finds listed above, useful for scopes of **research**, **preservation**, **monitoring** of conservation status, **restoration** activities (without intervening directly on the object), **promotion**, interactive **fruition** of unexposed pieces and **accessibility**.

Conclusions

Although the laser-scanner method is the most accurate way to define the geometry of objects (and the only one suitable for all that activities which requires maximum precision as digital restoration), it is very poor in photorealistic rendering in relation to the high cost of equipment and elaboration software, which require as long processing times and high modeling skills.
The technique of photo-scanning, thanks to the structure from motion algorithm, allows, once the acquisition scheme is accurately designed, to partially automate the processes using low cost and user-friendly tools, having a less geometrical accuracy but a more effective photorealistic rendering. The two methods are however absolutely complementary in order to finally get an 'integrated model', as well proved.

In the case of craters, in fact, the combined use of both tecniques offers an efficient and precise way for executing drawings of painted vases thanks to **stylistic analysis** of which it is possible to identify in some case painters and workshops: only a meticulous fine documentation of details may reveal the particularities and characteristics of a painter and can help to recognize these on other vessels.

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See more

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F.11- Point cloud and 3d mesh of mask i.n. 11248


F.12- Mask i.n. 13558


F.13- Mask i.n. 11114E

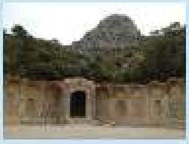
2nd Summer School
Archeometria e Archeologia subacquea “Sebastiano Tusa”
Favignana 6-12 settembre 2020

Presentazione Dott. Dario Giuliano
Dottorando in Scienze della Cultura
Curriculum in Scienze del Patrimonio Umano.

GLI ANNI DELLA FORMAZIONE

Il percorso formativo inizia con la Laurea Triennale in Beni Culturali Archeologici presso l’Università degli Studi di Palermo, che si conclude con una tesi in Preistoria e Protostoria sui beni di prestigio nel Bronzo Finale nell’area Tirrenica. Nello stesso Ateneo frequento la Laurea Magistrale in Archeologia durante il quale partecipo al progetto Erasmus presso l’Università di Göttingen in Germania con cui collaboro al Kamarina Survey. Successivamente partecipo al DO.RE.MI.HE. (Doctoral de recherche pour la mise en valeur de l’heritage naturel et culturel), un progetto nato dalla collaborazione dell’Università di Palermo, di Tunisi e della cattedra UNESCO di Evora. L’obiettivo era la formazione di studenti esperti nella gestione e valorizzazione dei siti archeologici, dei beni naturali e dei beni immateriali e del contesto in cui si trovano. La tesi di laurea, in Archeologia della Magna Grecia, si occupava dello studio del contesto e dei materiali, inediti, rinvenuti durante uno scavo condotto il località “Fontana di Paolo” nel comune di Casteltermini (Agrigento). Diverse le campagne di cui scavo a cui ho partecipato, sia con Atenei italiani (Palermo, Bologna, Siena) che stranieri (Institut of Fine Art of New York, Universität Bonn).




LE SUCCESSIVE COLLABORAZIONI

Conclusosi il ciclo accademico ho frequentato un corso di speleologia; in seguito ho collaborato con l’archeologo Dottor Gianluca Furcas nel progetto di esplorazione, studio e rilievo degli ipogei dell’antica città di Akragas. Altre esplorazioni speleologiche hanno interessato cavità artificiali (cisterne e miniere) sia nell’agrigentino che nel nisseno. Per l’Università di Aix-en-Provence ho condotto il rilievo di parte dell’acquedotto Galermi, nota struttura idraulica del siracusano, all’interno del progetto “Hydromed” sotto la guida della Professoressa Sophie Bouffier.

Dal 2018 collaboro con l’Università di Bologna nelle campagne di studio che questo Ateneo conduce ad Agrigento, sia nel Quartiere Ellenistico-Romano con lo scavo della casa III M (all’interno delle Field School "Pitture ellenistiche, dalla Macedonia alla Sicilia" e “Le forme dell’abitare nel Mediterraneo”), sia nel quartiere artigianale di Porta V.

Al di fuori dell’ambito accademico ho lavorato nel settore della didattica, e nell’accompagnamento turistico per Akhet Srl, Coopculture e FAI.







IL DOTTORATO DI RICERCA

Nel 2019 comincio il dottorato di ricerca presso l’Università di Palermo in Scienze della Cultura, curriculum Scienze del Patrimonio Culturale. Il progetto di ricerca, la cui idea matura durante la stesura della tesi Magistrale, si occupa dello studio dei sistemi di copertura, nello specifico tegole, in Sicilia dalla loro comparsa alla conquista romana. Lo studio prende in esame due casi studio: la città di Himera, in cui è attestato il più antico tetto fittile in Sicilia, e Agrigento in cui, grazie alla sua lunga vita è possibile riscontrare le variazioni nei tipi e nei modelli dei laterizi, dalla fase greca a quella romana. La ricerca è resa possibile grazie alla disponibilità e alla proficua collaborazione con il Parco Archeologico e Pesaggistico della Valle dei Templi, che mi ha permesso di partecipare ad una campagna di scavo dalla quale sono venuti in luce interessanti dati per la ricerca; con l’Ateneo di Catania, permettendomi lo studio dei materiali provenienti dagli scavi del teatro di Agrigento e del cd. tempio Ellensitico-Romano; con l’Università di Bordeaux e con il Parco Archeologico di Himera, Solunto e Monte Iato.

Contemporaneamente alla ricerca del dottorato proseguo sia la collaborazione con il Dottor Furcas sullo studio degli ipogei agrigentini, sia nuovi progetti quali uno studio sulle anfore provenienti dal comune di Casteltermini - con l’analisi degli impasti - di prossima pubblicazione all’interno del progetto Fa.Ce.M. Con la collega Dottoressa G. Chirco abbiamo avviato lo studio di alcuni frammenti di malta, rinvenuti durante lo scavo della casa III M di Agrigento, interessanti poiché sembrerebbero caratteazati dall’utilizo di inerti vulcanici nel loro confezionamento.






Glass supports characterization of a large collection of reverse glass paintings by a multivariate statistical approach

V. Mollica Nardo, V. Renda, M. L. Saladino, E. Caponetti, F. Armetta, G. Anastasio, C. S. Vasi, S. Trusso, R. C. Ponterio

IPCF-CNR, Viale Ferdinando Stagno d'Alcontres, n. 37 Messina 98158, Italy

Email: mollica@ipcf.cnr.it

We present an X-ray fluorescence spectroscopy (XRF) study combined with a multivariate approach that allow to detect compositional differences and similarities among the glass supports of a large set of reverse glass paintings belonging to the collection of the Mistretta museum. Reverse painting on glass is an old decorative technique used since the Roman time consisting in applying a cold paint layer on the reverse side of a glass support. The collection show a large spreading of provenience and dating of the items. In consideration of the current classification solely based on stylistic criteria, we applied a multivariate analysis on the XRF measurements data set to find a more objective classification criterion based on the elemental composition of the glass support. Results showed that glass supports can be divided into four different typologies on the basis of their different elemental composition. Assignment of these typologies to the current assignment to a given geographical area or a given period is not straightforward, probably due to reuse or original erroneous attribution.

The case study

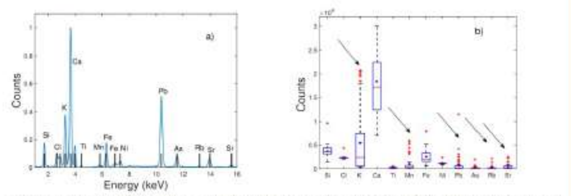
'Miracula in vitro' *Regional Museum of Forestry and Pastoral Tradition, Mistretta*

High variability in the provenance of the collection pieces

Conservator question:

The elemental composition of the glass supports correlate with the current attribution?

X-Ray Fluorescence analysis (XRF) performed on 50 items of the collection



a) XRF spectrum of the glass #54; b) Box-plot of the intensity of the XRF emission lines. Lower and upper box boundaries 25th and 75th percentiles, respectively, line inside box median, dot inside box mean, lower and upper error lines 10th and 90th percentiles, respectively. Crosses are data out liers falling outside 10th and 90th percentiles. Arrows indicate emission lines for which a meaningful statistical deviation from mean values is observed, as evidenced by outliers.

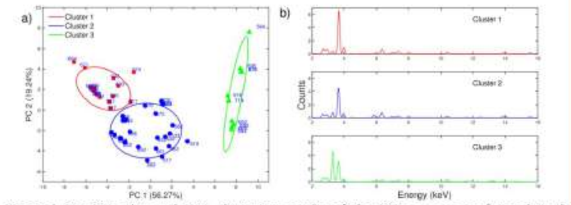


Fig 2 a) PC1-PC2 plot and HCA clustering results of the PCA process performed in the energy range between 2 and 16 keV; b) Average spectra of the different cluster.

As it can be seen, in Fig.2a) the three groups appear well separated in the PC1-PC2 plane (see symbols and colors). Spectra belonging to the different clusters are shown in Fig.2b). From the latter figure it can be seen how clusters are mainly classified by the spectral differ ences in the 3-4 keV energy range, and more precisely by the I_K/I_{Ca} intensity ratio values. All spectra belonging to a given cluster show a nearly I_K/I_{Ca} constant value. Nevertheless, differences among spectra classified in the same cluster are evident in high energy side region. As a consequence of this finding, we follow a different strategy. Looking at Tab.1 three energy ranges can be identified where intensities variation of the constituent elements occurs: in the energy range between 3 and 4 keV are emission lines from K and Ca, between 4 and 10 keV emissions from Ti, Mn, Fe, Ni, Cu and Zn, while between 10 and 16 keV emission from from Pb, As, and Sr. PCA analysis, then, was performed in limited energy ranges in order to identify differences in the elemental composition of the glass supports

Multivariate analysis on XRF data

A multivariate approach was applied to the XRF data for the recognition and the detection of common patterns

FROM XRF SPECTRA... ...AND HCA ANALYSIS

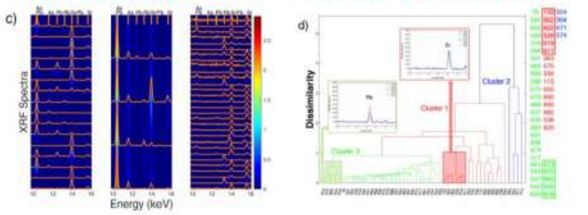


Fig. 3 c) Emission intensity maps (color bar) in the 10-16 keV energy range of XRF spectra belonging to the different clusters, Pb and Sr emission lines positions are reported; d) Dendrogram along PC1 and PC2 of the glass supports.

Finally the energy range between 10 and 16 keV is considered; in this range emission from Pb and Sr were identified, and spectra were classified into three groups (Fig. d). In the first one, composed by few glasses, showed an intense emission by Pb Lα at 10.5 keV, the second cluster is populated by two different kind of glasses, characterized by the presence of Sr or Pb, but the intensity emission from Pb is weaker with respect to the one observed in spectra belonging to the first cluster. The third cluster is the most populated one and spectra show emissions from both Sr and Pb, but emission intensities are very weak compared to the one observed in cluster #1 and #2. The corresponding dendrogram is shown in d), the three clusters are well separated at different levels of dissimilarity. Nevertheless in the dendrogram cluster 1 and 3 show the presence of two subgroups with a higher level of similarity within the two clusters. Looking at the corresponding XRF spectra one of the subgroups is characterized by the presence of Rb emission line while the second by Sr emission line, as it can be seen from the corresponding XRF spectra reported in the inset of d).

Conclusion

Comparison of **Fe** intensity emissions allowed the identification of **two groups**, with different geographical origin: **northern Italy** (Europe) and **southern Italy** (Campania and Sicily). We investigated by XRF spectroscopy a large collection of reverse glass paintings. XRF data were processed by multivariate analysis in the attempt to check the current classification of their geographical and production period, currently based on a stylistic analysis. Processing of the data in different energy 305 interval, where peculiar elemental emission were observed, allowed to group glasses with similar composition. The presence 310 of Mn was identified mainly in Fe rich glasses, as an additive introduced to remove green color typical of Fe rich glasses. Potassium was identified as a fluxing material in most of the glasses, whose provenience is attributed to southern Italy, pointing out how soda-potash was used beside soda-lime in these 315 region up to recent times

References:

[1] - M.L. Saladino, S. Ridolfi, I. Carocci, G. Chirco, S. Caramanna, E. Caponetti, Amulti-disciplinary investigation of the Tavolette fuori posto of the Hall of Barons wooden ceiling of the Steri (Palermo, Italy), J. Microchem. 126 (2016) 132137.

[2] - V. Mollica Nardo, V. Renda, G. Anastasio, E. Caponetti, M.L. Saladino, C.S. Vasi, R.C. Ponterio, A combination of portable non-invasive techniques360 to study on reverse glass paintings at Mistretta museum, J. Microchem. 146 (2019) 640644.

UN MUSEO PER TUTTI

Un museo di connessione e la *digital trasformation*

Silvia Pariti

I musei sono spazi democratizzanti, inclusivi e polifonici per il dialogo critico sul passato e sul futuro. Riconoscendo e affrontando i conflitti e le sfide del presente, conservano reperti ed esemplari in custodia per la società, salvaguardano ricordi diversi per le generazioni future e garantiscono pari diritti e pari accesso al patrimonio per tutte le persone.

I musei non sono a scopo di lucro. Sono partecipativi e trasparenti e lavorano in partnership attiva con e per le diverse comunità al fine di raccogliere, preservare, ricercare, interpretare, esporre e migliorare la comprensione del mondo, con l'obiettivo di contribuire alla dignità umana e alla giustizia sociale, all'uguaglianza globale e al benessere planetario.
(Kyoto 2019)

E' necessario essere contemporanei per promuovere azioni che migliorino l'accesso al patrimonio culturale, soprattutto per i giovani e le persone svantaggiate, al fine di aumentare la consapevolezza sul valore, sulla necessità di conservarlo e preservarlo e sui benefici che ne possono derivare (art. 12 della Convenzione di Faro)

La scelta di far vivere un museo virtuale può essere dettata da varie esigenze: raccogliere opere sparse in tutto il mondo, ricostruire attraverso animazioni e modelli 3D, oggetti oppure opere o siti andati perduti; dare la possibilità a ogni utente, nel mondo, di visitare il museo e di personalizzare la visita, il percorso, non essere legato a orari d'ingresso.

«Lo storytelling digitale ha dimostrato il suo ruolo innovativo come strumento importante anche per lo sviluppo delle industrie culturali e creative e di strategie di promozione culturale e territoriale.»
(E. Bonacini in «I musei e le forme dello storytelling digitale», p. 29)

Il Museo danese delle navi di Roskilde

Il Museo delle navi vichinghe, con la mostra del 2011 «Archeologia sott'acqua», ha permesso ai suoi ospiti di avvalersi della realtà aumentata per esplorare mondi storici sommersi, in un connubio di ricostruzioni storiche, effetti sonori in grado di coinvolgere emotivamente e di trasmettere in maniera più semplice ed efficace quella che è la storia dei suoi ritrovamenti, facendo sentire gli spettatori più vicini ad passato che fino a pochi anni prima era sommerso e dimenticato.

Le pareti del museo e le navi ricostruite prendono vita, navigando fra le onde, sotto il sole, nella notte o tra le tempeste più violente, in un paesaggio di alberi scricchiolanti, col rumore del vento, delle onde che sbattono contro i fianchi delle navi e addirittura i comandi dello skipper.
L'installazione analogica offre agli ospiti del museo di sperimentare in prima persona le forze, i sensi e i sentimenti in gioco quando si naviga in mare aperto.

(Cfr. CRUMLIN-PEDERSEN O., 2010)

2° Summer School ARCHEOMETRIA E ARCHEOLOGIA SUBACQUEA "SEBASTIANO TUSA"
Favignana, 6-12 settembre 2020

Antonella Privitera *Esperto scientifico dei Beni Culturali*

PhD student, Università degli Studi Roma Tre, via della Vasca Navale 84 – 00146 Roma

ROMA TRE UNIVERSITÀ DEGLI STUDI

antonella.privitera@uniroma3.it | PUBBLICAZIONI E PRODUZIONE SCIENTIFICA: https://uniromatre.academia.edu/AntonellaPrivitera

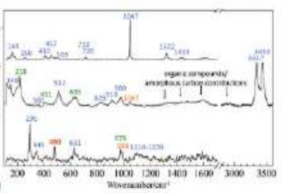
2019 ad oggi

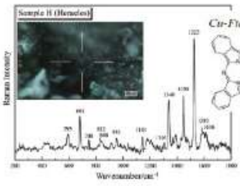
SCIENZE Dipartimento di Eccellenza

Dottorato di Ricerca in Scienze della Materia, Nanotecnologie e Sistemi Complessi
Dipartimento di Scienze, Università degli Studi Roma Tre

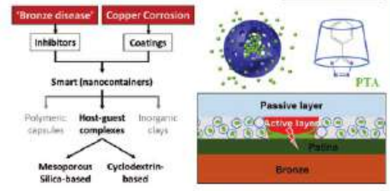
SpectRa Lab

Prodotti di corrosione artificiale del bronzo:
Rouaite $Cu_2(NO_3)(OH)_3$
Atacamite $Cu_2Cl(OH)_3$
Cuprite Cu_2O
Tenorite CuO
Chalcanthite $CuSO_4 \cdot 5(H_2O)$
Langite $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$
Covellite CuS





Autenticazione di bronzi e studio delle patine di corrosione



Nanomateriali per la conservazione di manufatti in bronzo

2020 ASSOCIAZIONE NAZIONALE DEGLI ESPERTI DI DIAGNOSTICA E DI SCIENZE E TECNOLOGIE APPLICATE AI BENI CULTURALI (ANEDBC)
socio ordinario 2019-2020

2020 **Perito e Consulente Tecnico d'Ufficio (CTU)**
Ministero della Giustizia, Tribunale di Catania

2020 **Scuola Nazionale di Chemiometria applicata ai Beni Culturali**
Alma Mater Studiorum - Università di Bologna (sede di Ravenna)

2019 **Corso di Alta Formazione e tirocinio in "Tecnologie per la conservazione e fruizione di beni archeologici"**
Dipartimento di Antichità, Sapienza Università di Roma

2019 **MOOC "Engaging the European art market in the fight against illicit trafficking in Cultural Property"**
UNESCO, segretariato della Convenzione del 1970 in partnership con l'Unione Europea

2019

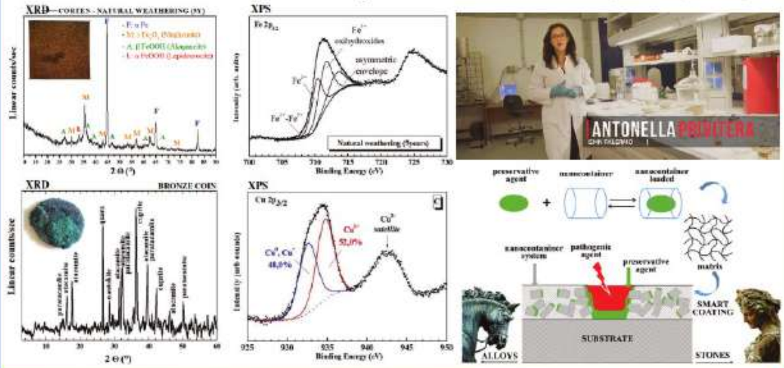
CENTRO PER GLI STUDI CRIMINOLOGICI GIURIDICI E SOCIOLOGICI — OSSERVATORIO INTERNAZIONALE ARCHEOMAFIE

Master in Archeologia Giudiziaria e crimini contro il Patrimonio Culturale
Centro per gli studi criminologici (Viterbo)

2015-2018

PON Ricerca e Competitività 2007-2013 — CNR ISMN

Borsa di formazione (annuale) e Assegno di ricerca (biennale) in Nanomateriali e Nanotecnologie per la conservazione sostenibile di manufatti metallici e lapidei del Patrimonio Culturale
Istituto per lo Studio dei Materiali Nanostrutturati (CNR-ISMN, Palermo)

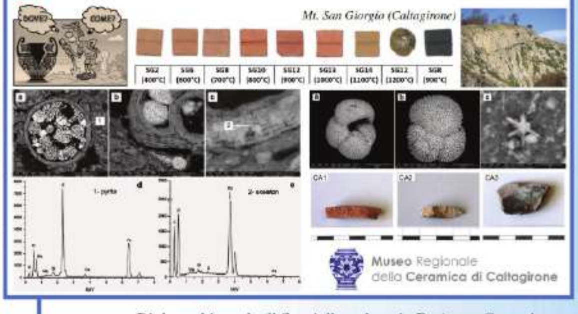


2016 **Corso di Alta Formazione 3° Training Camp Iperion CH.it sulla Diagnostica avanzata non invasiva sui Beni Culturali**
E-RIHS.it (ex IPERION CH.it)

2012

UNIVERSITÀ DELLA CALABRIA

Laurea Magistrale in Scienze e Tecnologie per la Conservazione e il Restauro dei Beni Culturali (LM11)
Università della Calabria (Arcavacata di Rende, Cosenza)



Museo Regionale della Ceramica di Caltagirone

2010

UNIVERSITÀ degli STUDI di CATANIA

Missione archeologica, Leptis Magna (Libia)
Facoltà di Lettere, Università degli Studi di Catania

2010 **Diploma biennale di Specializzazione in Restauro Ceramico**
Istituto Statale d'Arte per la Ceramica - ISAC "Luigi Sturzo", Caltagirone (CT)

soprintendenza del mare | Università degli Studi di Palermo | unipa 2020 la terza missione | PARCO ARCHEOLOGICO LILIBEO MARSALA | DIPARTIMENTO DI SCIENZE E TECNOLOGIE BIOLOGICHE CHIMICHE E FARMACEUTICHE (STEBICEF) | "Labor Artis CR diagnostica S.r.l." | ASSOCIAZIONE ITALIANA DI ARCHEOMETRIA

Corrosion and decloruration for cultural heritage: analytical and electrochemical studies.

Rosalinda Sciacca[a], Mario Berrettoni[b], Paolo Conti[b], Silvia Zamponi[b]

[a]Dept. Industrial chemistry -"Toso Montanari", Alma mater studiorum University of Bologna, UOS Campus Rimini, Via dei Mille, 47921, Rimini, Italia; E-mail: rosalinda.sciacca2@unibo.it ;

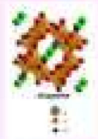
[b]School of Science and Technology, Chemistry Division, via S. Agostino 1, University of Camerino, 62032 Camerino, Italy

Analytical studies

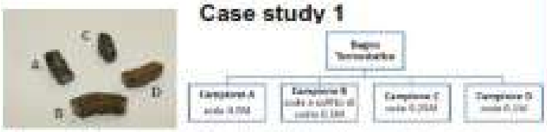
The corrosion of archaeological iron is affected by the surrounding environment conditions such as humidity, temperature, wet time, chemical composition, and contamination in air. In particular, the chloride ion arising from the air-borne salt or de-icing salt is one of the major factors of the corrosion. Desalination treatments have been employed for several decades to stabilize iron archaeological artefacts.

The chloride contents after desalination procedure has determined by Atomic Absorption Spectroscopy and by ion chromatography to check the desalination method efficiency. *[1; 2]*

Iron (II) hydroxide can be oxidized to iron (III) compounds, Hydroxide or oxyhydroxides, such us Goethite (α- FeOOH), Lepidocrocite (γ-FeOOH) and Akaganeite (β-FeOOH). Their structure is characterized by the presence of tunnels that are partially occupied by chloride anions that give to the crystal its structural stability. Conservators point out the removal of chlorine ions from objects could be a good preservation option.

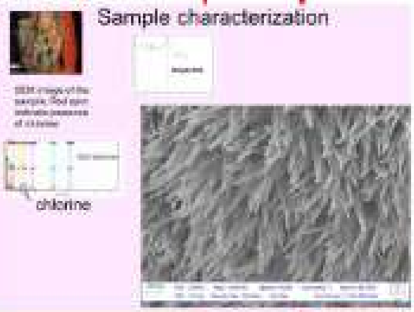


Case study 1

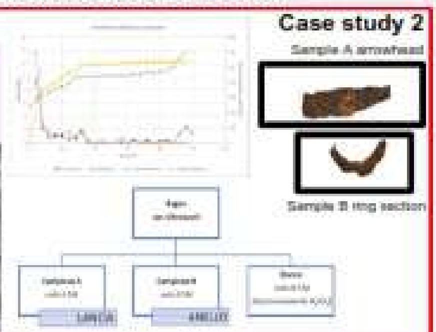


Iron sample from a ring, dated IV century BC, found in the archeological site of ancient Carsoli (AQ) Italy

Sample characterization



Case study 2

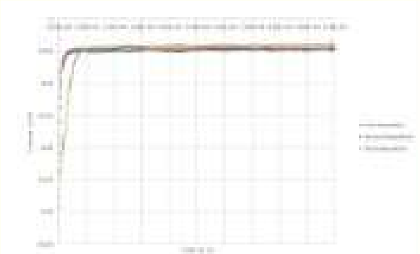


Electrochemical studies

Iron oxides/oxyhydroxides are abundant materials and their films are useful in many scientific and technological applications. These compounds are implicated in corrosion processes as different species.

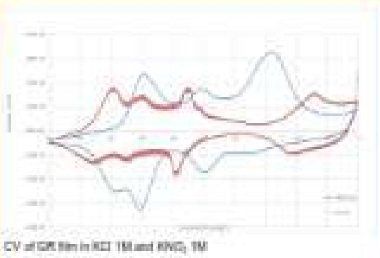
The corrosion layer growth and evolution is a difficult process to follow because of unclear redox-species involved in its formation. *[3]*

GR Solution with 0.2 M $(NH_4)_2SO_4$, 0.02 M $(NH_4)_2Fe(SO4)_2$, 0.4 M NH_4Cl, 0.02 M $FeCl_3$, pH set at 8.1 [4]



GR film was electrodeposited by amperometry for three times at -400mV on GC working electrode vs Ag/AgCl.

Film electrodeposited appears with a yellowish-colored as soon as it is in contact with O_2

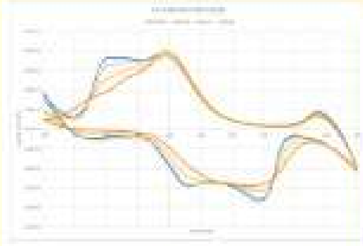


CV of GR film in KCl 1M and KNO_3 1M

To check the role of Cl- ion the film is studied in different support electrolyte, as KCl and KNO_3.

Characterization of GR film in KCl 1M and $KNO_3$1M shows a similar shape with three peaks, ascribable to three redox-species.

When electrolyte KNO_3 is used the current is higher than in KCl.



Potentiodynamic analysis of GR film in KCl 0.01 M

To investigate the rule of Cl^- on the corrosion process, GR film in several molarity of KCl was studied.

The voltammogram above shows 7 isosbestic points, that are common when a chemical reaction is in progress, suggesting the correlation between several species during the process.

Conclusion

- ✓ Suitable analytical techniques are been proposed to follow the decloruration process and to evaluate its efficiency.
- ✓ Using the ultrasound bath as decloruration method is the best choise from a kinetic point of view.
- ✓ The electrochemical studies could clarify the corrosion process and they could be helpful to choose a specific decloruration method.

Reference:

1. F. Kergourlay, C. Remazeilles, D. Neff, E. Foy, E. Conforto, E. Guilminot, S. Reguer, Ph. Dillmann, F. Nicot, F. Mirambet, J. Robbiola, Ph. Refait (2011) Mechanisms of the dechlorination of iron archaeological artefacts extracted from seawater 2474–2483
2. C. Bonafide Pérez, J. Hernández Méndez, Ma. J. Fonseca Rivero, and A. Ma. Bernal Melchor (1983) Indirect Determination of Chloride as Chromyl Chloride by Atomic- Absorption Spectrophotometry
3. Sugae K, Kamimura T, Asakura R, Doi T, Miyake H, Kudo T. Electrochemical reduction and re-oxidation behavior of α, β, and γ-iron oxy hydroxide films on electrodes. Materials and Corrosion. 2019;70:187–195 [illegible]
4. Kyoung Woo Chung, Kwang Bum Kim, Seong-Ho Han, and Hyungkeun Lee, Novel Synthesis of Nanosized Cellular Iron Oxide/Oxyhydroxide Thin Films I. Electrochemical Synthesis of Green Rust Thin Films and Their Chemical Oxidation.

LECTURERS SHORT BIOGRAPHIES

Floriana AGNETO

Floriana Agneto, diver and functionary at Superintendence of the Sea Department of Culture - Regione Siciliana, responsible for editorials initiatives and translations, relationship and communication in English French Spanish languages, cooperation in European Projects and underwater itineraries, organization of meetings, conferences, exhibitions and fairs.

Franco ANDAROLO

Franco Andaloro direttore del Sicilian Marine Center della Stazione Zoologica di Napoli è un ecologo marino che studia gli effetti delle pressioni naturali e degli impatti antropici sul biota marino attraverso un approccio olistico e una visione ecosistemica. Su questi temi ha condotto 80 progetti di ricerca e pubblicato oltre 250 lavori ISI. E'stato membro di numerose commissioni ministeriali e fatto parte della delegazione italiana in COP di CBD, Barcellona Convention, FAO-GFCM, IOTC. Ha svolto attività di consulenza e/o ricerca per MATTM, MAE, MIPAAFT, FAO, UNDP, IUCN, UE, Regione Sicilia. E accademico delle scienze subacquee di Ustica e di Terramadre. Ha ricevuto, tra gli altri il tridente d'oro, il premio Merli, il premio Rossana Maiorca, il premio Sanremo libro del mare. E' nei consigli scientifici di Marevivo, di Slowfish e di WWF di cui è anche il delegato per la Sicilia. Negli ultimi anni è anche impegnato nel recupero del patrimonio storico e immateriale della pesca. E' istruttore subacqueo per WASE, ISDA e PADI e operatore subacqueo scientifico.

Francesco ARMETTA

Francesco Armetta, graduated in chemistry in the 2013 is a Materials Engineering PhD in Information and Communication Technologies at the Università degli Studi di Palermo. He was also a research grant holder at Centro Nazionale delle Ricerche, performed a six months Advanced Training at the ISIS neutron spallation source of Science and Technology Facilities Council (STFC) in United Kingdom and he worked for six months on "Chemical physical investigation on archaeological samples" at the Università di Camerino. Since 2019 he is three years Researcher at STEBICEF Department of University of Palermo.

His interest has been focused on the development of luminescent nanomaterials and archaeometry. He is author of papers concerning the development new synthesis method and characterization of nanomaterials in journals of chemistry and engineering and, more recently, on characterization of archaeological metallic objects recovered in the seabed in collaboration with Soprintendenza del Mare of Sicily.

He was several times guest, also for long period, of foreign research institutions in United Kingdom, Germany and Poland. He also attempted to several high level summer school on Neutrons and on Cultural Heritage. Recently he was involved in the organization of Archaeometry and Underwater Archaeology Summer School and of several dissemination events.

Mario BERRETTONI

Il prof. Mario Berrettoni è nato a Muccia il 7 febbraio del 1958 e si è laureato in Chimica presso l'Università di Camerino il 23 marzo 1983; dal 1998 è professore associato all'Università di Bologna, SSD CHIM01, presso il dipartimento di Chimica Industriale "Toso Montanari" ed è incardinato nel Campus di Rimini. Il 1° settembre 2020 si trasferirà all'Università di Camerino, Scuola di Scienze e Tecnologie.

I principali interessi di ricerca sono:

- Applicazione della spettroscopia di assorbimento X
- Caratterizzazione chimico fisica di materiali da utilizzare come componenti attivi in batterie al litio ione
- Sviluppo e caratterizzazione di nuovi materiali elettrodici da utilizzare come sensori amperometrici e potenziometrici
- Sintesi e caratterizzazione di esacianometallati misti per applicazioni fotovoltaiche e fotocatalitiche
- Applicazione di metodologie analitiche al settore ambientale
- Applicazioni di metodologie analitiche ai beni culturali

È autore di circa 100 pubblicazione scientifiche.

Cristina BOSCHETTI

Cristina Boschetti was born in 1977. She holds a laurea (equivalent BA+MA) in Art History (2001, University of Parma, mark 110/110 cum laude), in a diploma in Conservation of Painting (2004, ENAIP Botticino, Brescia) a second laurea (equivalent MA+BA) in Classics (2005, University of Parma), a PhD in Archaeological Science (2009, University of Padua). Since the completion of her PhD she occupied postdoctoral research positions in international (Nottingham, UK; Cairo, Egypt) and Italian Universities (Padua), obtaining prestigious research funding (British Academy Grant, Marie Curie e Al-Idrisi Erasmus Mundus Fellowships). Since 2007 she is curator of the room Magic, at the Museum of Jewellery of Vicenza. Since 2018 she is temporary lecturer at IRAMAT-CEB CNRS, Orléans, where she is member of the ERC research project GlassRoutes, directed by Nadine Schibille. She is author of 46 scientific publications on glass from the Hellenistic period to the High Middle Ages, and on Roman mosaics and wall paintings.

Eugenio CAPONETTI

Eugenio Caponetti (1948) currently is Professor of Physical Chemistry at the Department of Biological, Chemistry and Pharmaceutical Sciences (STEBICEF), School of Basic and Applied Sciences at the University of Palermo.

In 2004 he started an activity aimed at the diagnosis and characterization of artefacts of historical and artistict interest. Within the framework of the European Chemistry Thematic Network (ECTN), he was a member of the Organizing Committee of 12 International Residential Summer Schools (ECTNA). From 2007 to 2012 he was President of the Bachelor's Degree in Cultural Heritage Sciences and Technologies, with headquarters in Petralia Soprana (PA). Since 2007, he has been the chief of the Centro Grandi Apparecchiature (CGA) (http://www.unipa.it/cga) at ATeN Center of the University of Palermo. CGA was the home of the 2nd Residential Summer School, Chemistry and Conservation Sciences in 2008.

In 2017 he co-founded a university spin-off Labor Artis CR Diagnostica srl, whose main activity is non-invasive diagnostics by using portable equipments. He is responsible for the DELIAS project "Development and Application of Innovative Processes and Materials for Diagnostics and Restoration of Cultural Heritage" - District of high Technology for innovation in the field of cultural heritage in the Sicilian region.

His scientific activity over the last 10 years is documented by numerous congressional communications and 90 publications in international journals, of which one half are related to cultural heritage topics and the rest concerns the synthesis and characterization of nanostructured materials and polymer nano-composites.

Maria Pia CASALETTO

Graduated in Chemistry, PhD in Materials Science, CNR Director of Research, Dr. Maria Pia Casaletto is an expert in Surface Science specialized in X-ray induced Photoemission Spectroscopy from both conventional and Synchrotron radiation sources. Her research activities deal with the study of the surface reactivity of innovative and ancient materials. The main application fields concern: Heterogeneous Catalysis; Biomaterials, Conservation of Cultural Heritage. In the latter area, she deals with the application of innovative investigation methodologies, the synthesis of nanostructured materials for the conservation of metal and stone artefacts and the recovery of ancient production techniques. The study of the mechanism of degradation is devoted to the design and synthesis of low toxicity and eco-compatible materials and formulations of natural products to be used as protective and/or corrosion inhibitors for the preservation of metal and/or as biocides for the conservation of stone artefacts.

Monica DE CESARE

Monica de Cesare is professor in Classical Archaeology at the University of Palermo, Italy. She has researched into Greek archaeology and history of Greek art, with a particular interest in vase painting and iconography. She has done research on archaeology and topography in Magna Grecia and Sicily, in Greek and non-Greek sites; she has also researched into the history of classical archaeology, with particular reference to aspects of archaeological research and collecting between the 19th and the 20th centuries, forms of the sacred in the Greek and indigenous world of the West. She is co-director with E.C. Portale of the archaeological excavation mission and research of the University of Palermo in Agrigento (the southern area of the Olympieion). In Segesta she coordinates a research project on the 'Grotta Vanella dump' and the sanctuary of the Contrada Mango (studies of the finds and archival material of the old excavations). She has published several essays, including some interdisciplinary ones, at national and international level.

Stephan DOEMPKE

Stephan Doempke, born 1955 in Muenster, Germany, studied psychology, cultural anthropology and science of religions in Muenster, Wichita/Kansas and Berlin. Throughout his life he has committed himself to the rights of indigenous peoples, a nuclear-free world, and the preservation of natural and cultural heritage. In 1989 he joined the founding team of the House of World Cultures in Berlin, and from 1993-1998 coordinated projects in Russia and Central Asia for the German Nature Conservation Union NABU. He supported the revitalization of felt-making in Kyrgyzstan and was a free-lance consultant before he became UN Programme Coordinator for Culture and Heritage in Albania in 2008, and from 2010-2014 worked as a World Heritage expert in Gjirokastra, Albania. He is the founding chairman of World Heritage Watch, a Berlin-based global network of NGOs monitoring World Heritage.

Salvatore EMMA

Technical diver for underwater archeology within the Superintendency of the Sea of the Sicilian Region since its establishment, he has made numerous documentaries and photoshoot collaborating with numerous newspapers in Italy and abroad. He specializes in underwater video shooting and technical photography with particular reference to underwater photogrammetric survey. He has made numerous 3D surveys during the excavation campaigns of the Superintendency of the Sea in Sicily and abroad. He participated in the missions on the deep Sicilian wrecks with mini submarine creating the 3D survey of the wrecks of the Aeolian islands. He has participated in numerous archaeological missions and underwater excavations in Italy and abroad (Japan, Libya, Lebanon, Tunisia, Kenya, Jordan) as a diving technician and photographer / documentary maker.

Maria Grazia GRIFFO

MARIA GRAZIA GRIFFO, teacher of History of Art for many years in the High School, is a Classical archaeologist and works at the Archaeological Park of Lilibeo -Marsala since 2010. She is curator and author of various books about Marsala and its hinterland, and also of many scientific articles about archaeological subject on proceedings conferences and specialized papers.

She is involved in preservation, interpretation and communication of the archaeological heritage at the Lilibeo Museum where realized both scientific, both museological activities. She collaborates with University of Palermo, Department of Culture and Societies, University of Amburgo, and University of Geneve for the excavation campaigns in the Archaeological Park of Lilybaeum.

Her research is related to the Punic Shipwreck of Marsala, and also to the funerary rites and grave goods of Punic Necropolis, like Birgi (Motya hinterland), and Lilybaeum.

Cristina LEONELLI

Degree in Chemistry in '86 at the University of Modena, after several experience supported with national fellowships in Modena and in U.S.A., she got Ph.D. in Chemistry in '91. From '92 to '98 she got the position of researcher/assistant professor at the Faculty of Engineering (Modena University) specializing in the field of Chemistry Applied to Ceramic Materials. After one year as associate professor at the Faculty of Engineering of the University of Naples "Federico II", she was back to Modena and Reggio Emilia University in 2000 where she is still active at the Department of Engineering "Enzo Ferrari"- DIEF. She got full professorship in 2005 in Chemical foundations of technologies (SSD: CHIM/07). She has coordinated several national research projects and some international cooperation projects on the themes of preparation and characterization of ceramics, glasses and inorganic compounds. She has been publishing the results of her research work in over than 330 scientific publications and 8 patents.

Fabrizio LO CELSO

Graduated in Chemistry in 1993 at University of Palermo, in 1998 he obtained the Ph.D. in Chemistry at the same University, the title of the final thesis was: "Phase Separation in Multicomponent Mixtures" under the supervision of Prof. R. Triolo. The research project was partially carried out at the Computational Physics group of the Technical University of Delft (The Netherlands, supervisor : Prof. S. de Leuuw). In 1998 he had a postgraduate fellowship at the Physics and Astronomy department of University of Missouri (USA) working within a research project concerning the modelization of disordered systems for the SAXS (small angle x-ray) data analysis. From 2000 to 2004 he was a postgraduate fellow at the Physical Chemistry Department of the University of Palermo on a research project based on the Critical Micellization Density concept. From January 2005 is a faculty staff at the Physical Chemistry Department of the University of Palermo. His research has been mainly addressed to the modelization and analysis of neutron and x-rays scattering data to obtain structural properties of condensed matter systems (i.e polymer and block copolymer solution in various solvents). Another field of interest has been the use of Neutron Tomography applied to object of cultural heritage importance. His current interest are aimed at the study of structural and dynamical properties of ionic liquid systems by means of both experimental scattering techniques and classical molecular dynamics.

Francesca OLIVERI

Francesca Oliveri – Archeologa specialista in Antichità Puniche, ha studiato presso l'Università degli Studi di Palermo, l'Università La Sapienza di Roma e la Hebrew University of Jerusalem. Attualmente è Funzionario Archeologo presso la Soprintendenza del Mare, Regione Sicilia, Palermo ed è responsabile di zona per l'area marina e costiera delle province di Trapani (Egadi comprese) e Agrigento; coordina studi e ricerche sulla cd Strada sommersa di Mozia; fa parte del gruppo di ricerca Egadi Islands Survey Project; si occupa di mostre ed allestimenti museali; progetta e realizza Progetti Scuola Museo per le scuole siciliane su temi relativi al Mediterraneo antico, la portualità, le esplorazioni, navigazione e commerci, la cucina del mondo antico (Punico, Greco e Romano). Annovera numerosi articoli scientifici comparsi su riviste specializzate riguardanti le sue ricerche.

Filippo PISCIOTTA

Partanna (TP), 25/06/1978.

Dottorando presso l'Università di Aix-Marseille in cotutela con l'Università di Palermo.

Di recente vincitore di una borsa di ricerca presso l'Università di Palermo nell'ambito del progetto di ricerca "Harvisting Memories". I principali campi di interesse sono metodi e tecniche di rilievo tradizionale e 3D applicati all'archeologia mediante l'utilizzo di strumentazione e software per la documentazione grafica e fotografica sia nell'ambito dello scavo archeologico che dei reperti. Esperto in cultura materiale tardoantica, bizantina e medievale (IV-XII secolo). Ha conseguito la laurea specialistica in archeologia presso l'Università di Palermo con il massimo dei voti e con una dissertazione sulla ceramica tardo antica e protobizantina di contrada "Case Romane" a Marettimo (Campagne di scavo 1994, 2007-2008). Lunga esperienza nel campo dell'archeologia (scavo e documentazione); collaborazioni con diversi istituti nazionali e internazionali come l'Università di Palermo, l'Università La Tuscia di Viterbo, il CNR di Catania, il CNRS Francese, l'Università la Sapienza di Roma, l'Istituto Germanico Archeologico di Roma, l'Università di Bonn, e vanta una periodica collaborazione con l'Institute of Fine Arts della New York University. Negli ultimi anni impegnato in diverse attività di ricerca e valorizzazione partecipando attivamente a convegni e campagne di scavo (parco archeologico di Selinunte, missione archeologica dell'Università of Fine Arts di New York; parco archeologico e valle dei templi di Agrigento; Corleone, presso il sito di Contrada Castro); collaborazione nelle mostre museali del parco archeologico di Selinunte e nel nuovo allestimento del museo Baglio Anselmi di Marsala.

Vincenzo RENDA

Vincenzo Renda has graduated with full mark in Chemistry at the University of Palermo. He has been a former PhD student in Materials Science and Nanotechnology at the University of Palermo (in collaboration with UNICT), conducting his research in the group of Prof. Caponetti (Dip. STEBICEF - CGA). During his PhD, he studied the aspects of consolidated methods for the testing of materials for the protection and consolidation of various materials of artistic interest, with particular attention to the stone surfaces, and aimed to develop the chemical aspects linked to the use of innovative nanomaterials in the field of Cultural Heritage. As part of his research, he has also improved especially in the use of FTIR spectroscopy, XRF spectroscopy and UV-VIS spectroscopy, both applied in the field of diagnostics for Cultural Heritage through the use of portable instrumentation and in the research field. He has also become familiar with the use and maintenance of bench type FTIR and μ-FTIR spectrometers. He worked at CNR IPCF of Messina as part of the project STBIC "Scienza e tecnologia per il recupero e la fruizione di beni di interesse culturale", dealing with the preparation of metal nanoparticles by using physical methods for application in the diagnostic of Cultural Heritage materials and also improving his spectroscopy skills with Raman techniques. He is currently employed in ARPA Sicilia, working on monitoring marine and coastal waters and especially microplastics identification in those matrices.

Maria Luisa SALADINO

Prof. Maria Luisa Saladino - MS in Chemistry in 2001; PhD in Chemical Sciences in 2008. Since 2019 she is Associate Professor at STEBICEF Department of University of Palermo. The research activity is related to the development of innovative nanostructured materials, such as luminescent nanoparticles, mesoporous silica materials, polymer nanocomposites and controlled release systems for the protection of stone surfaces. She is also involved in the development of analytical methods for the investigation of artefacts in the field of Cultural Heritage, by using non invasive techniques and multianalytical approaches. She is the scientific coordinator of the Canaletto Project "Multianalytical approach for the dating and authentication of archaeological ceramics" financed by the Executive Programme for Scientific and Technological Cooperation Between the Italian Republic and The Republic of Poland for the years 2019-2020 and of ICONS Project "Old Believer Faith icons" of VETKA Museum (Gomel Region, Vetka)" financed by KEP Programme of Central European Initiative in collaboration with Institute of Low Temperature and Structure Research, Polish Academy of Sciences (Wrocław, Poland) and Francisk Skorina Gomel State University (Gomel, Republic of Belarus). Scientific production: about 100 among papers, proceeding books and book chapters, about 250 conference presentations/seminars/lectures, in the field of Physical Chemistry, H-index=20, citations>1100. She is author of one Italian patent and editor of two peer-reviewed international journals (Orcid: https://orcid.org/0000-0002-7481-8556).

More info at http://www.unipa.it/persone/docenti/s/marialuisa.saladino

Pietro SELVAGGIO

Pietro Selvaggio, engineer and naval archaeologist, dive instructor, functionary at Superintendence of the Sea Department of Culture - Regione Siciliana, responsible for European Projects and underwater itineraries

Alberto SPINELLA

Born in Palermo 31/08/1971

MD in Chemistry.

Ph.D. in Chemical Engineering and of Materials.

Since 02/07/2007 he manages the Nuclear Magnetic Resonance (NMR) Laboratory at the Centro Grandi Apparecchiature (CGA) – ATeN Center of the University of Palermo.

His research activity focused on the characterization by liquid and solid state NMR of polymer matrix composites as well as structural and functional nano materials and nano composites and on the applications of NMR spectroscopy in the field of Cultural Heritage. He contributed to solve specific scientific problems by applying the most advanced NMR pulse sequences. Among other collaborations he has been responsible of a research commissioned by the “Laboratorio Arvedi” at the “Museo del Violino” in Cremona about supramolecular interactions between components of ancient varnishes for stringed musical instruments, in particular for the violins made by Antonio Stradivari.

He is co-author of 37 publications on international journals and numerous communications at national and international congresses.

Francesco TORRE

Francesco Torre, già titolare di Cattedra di Geomorfologia e Geoarcheologia all’Università di Bologna, ha lavorato come geologo per tre anni per il Governo Sudafricano, Department of Mines, Geological Survey. È stato responsabile geologo marino nella spedizione scientifica nel Mar Nero (agosto-settembre 2000): scoperte le tracce del “Diluvio Universale”. Dall'anno 1995 collaboratore dell’Institute for exploration, (Istituto americano della “Division of Sea Foundation,inc.”. Ha partecipato come Responsabile geologo nella spedizione scientifica in Egitto sul Delta del Nilo e nella spedizione per ricerche archeologiche e geomorfologiche marine nel Mediterraneo, nella zona di Banco Skerki, con una nave oceanografica ed un sottomarino strategico nucleare della Marina Militare Americana, NR-1, scendendo, primo italiano a farlo, alla profondità di 800 metri. Scoperte 5 navi romane. Direttore della ricerca il Prof. Robert Ballard, famoso scienziato americano, geologo, scopritore del “Titanic”. Nel 2006 ha partecipato, come responsabile geologo, con una nave oceanografica del MIT, allo studio di tutti i vulcani sommersi del Mediterraneo.

E’ laureato in geologia, Biologia, Scienze naturali e Scienze Turistiche.

Lingue studiate e parlate: Inglese, Francese, Tedesco, Spagnolo, Arabo, Turco, Swahili, Afrikaans.

Edoardo TORTORICI

Graduated in Classical Literature (1972) at the University of Rome "La Sapienza" with a thesis in Topography of Rome and Ancient Italy.
Archaeologist Inspector at the Archaeological Superintendence of Lazio (1980-81).
Faculty of Letters of the University of Rome "La Sapienza": researcher of Ancient Topography (1981-92).
Faculty of Letters of the University of Catania: associate professor of Archaeological Methodology (1992-1996) and Ancient Topography (1996-2000);
From 1 April 2000: full professor of Ancient Topography.
From 1 November 2001: director of the Department of Archaeological, Philological and Historical Studies of the University of Catania.
From 1 January 2002: Professor of Ancient Topography at the Italian Archaeological School of Athens.
Director of the Experimental Cartography Laboratory for Ancient Topography and Underwater Archeology of the University of Catania.

Retired from november 1st 2019

STUDENTS PROFILES

Aurelio BONASERA

Aurelio Bonasera è un Chimico attivo nel campo della sintesi organica; ha ricevuto il diploma di Laurea Magistrale in Chimica presso l'Università degli Studi di Messina occupandosi della sintesi e caratterizzazione di composti eterociclici biologicamente attivi. Successivamente, ha conseguito il titolo di Dottore di Ricerca in Chimica presso l'Università degli Studi di Trieste, dove ha sviluppato un progetto riguardante l'isolamento e caratterizzazione di pigmenti utili per la fotocatalisi omogenea. Successive esperienze di post-dottorato in Germania ed Inghilterra lo hanno coinvolto nello studio di composti fotocromici, da impiegarsi quali elementi attivi di dispositivi elettronici organici e di innovativi sensori colorimetrici per matrici alimentari. Oggi è Ricercatore a tempo determinato (RTD-A) presso il Dipartimento di Fisica e Chimica – Emilio Segrè dell'Università degli Studi di Palermo, dove realizza celle solari di nuova generazione basate su coloranti organici. I suoi interessi di ricerca spaziano dalla chimica di coloranti e pigmenti (sintesi, caratterizzazione, investigazione computazionale) alla chimica delle interfacce.

Gabriella CHIRCO

Gabriella Chirco è una restauratrice laureata all'Università degli Studi di Palermo nel 2014 in Conservazione e Restauro dei Beni Culturali, laurea magistrale abilitante alla professione ai sensi del D. Lgs. N. 42/2004, presso la quale si è specializzata nel PFP 2 (Manufatti dipinti su supporto ligneo e tessile; Manufatti scolpiti in legno; Arredi e strutture lignee; Manufatti in materiali sintetici lavorati, assemblati e/o dipinti). Durante il periodo di tesi di laurea ha iniziato a familiarizzare con le tecniche di diagnostica per i beni culturali, con particolare interesse per le tecniche di caratterizzazione non invasive, che post laurea ha potuto approfondire e fare proprie grazie alla partecipazione a diverse campagne di diagnostica in collaborazione con il dipartimento Stebicef dell'Università di Palermo.

Tra il 2014 e il 2016 ha conseguito un master di II livello in Ricercatore esperto in nanomateriali e nanotecnologie per i beni culturali all'università di Palermo, durante il quale si è occupata di micoremulsioni per la pulitura di superfici dipinte.

Attualmente è dottorato di ricerca in Scienze Umane: Dinamica dei Sistemi, Patrimonio Culturale, Studi Culturali con indirizzo archeologico presso il dipartimento di culture e società dell'Università di Palermo. La sua attività di ricerca si focalizza sulla caratterizzazione di materiali ceramici dipinti con oggetto principale i Vasi di Centuripe dei musei archeologici Antonio Salinas di Palermo e Paolo Orsi di Siracusa.

Veronica CIARAMITARO

Laureata in Chimica Magistrale presso l'università degli studi di Palermo, curriculum Chimica dei Materiali, nel 2019. Durante il mio lavoro di tesi sperimentale dal titolo "Protezione della Pietra del Tempio G di Selinunte. Efficacia del trattamento ed interazioni tra il substrato lapideo e i protettivi utilizzati", mi sono occupata di valutare l'efficacia del trattamento di protezione sulla "pietra del Tempio G di Selinunte" di tre protettivi, scelti sulla base delle loro diverse proprietà, e di studiare le possibili interazioni tra questi e il substrato lapideo, mediante spettroscopia di Risonanza Magnetica Nucleare a Stato Solido, con l'obiettivo di valutarne la compatibilità chimica e di correlare le proprietà macroscopiche con le proprietà microscopiche.

E' stata titolare di una borsa di formazione presso il IAMC-CNR di Capo Granitola riguardante il monitoraggio dell'ambiente urbano, extraurbano e marino.

E' vincitrice di borse di studio nell'ambito del progetto Materiali di nuova generazione per il restauro dei Beni Culturali: nuovo approccio alla fruizione – "AGM for CuHe" presso il Consorzio Interuniversitario Nazionale per la Scienza e la Tecnologia dei Materiali; con un programma formativo di ricerca che prevede la caratterizzazione di consolidanti e lo studio delle interazioni con il substrato materico mediante tecniche spettroscopiche attraverso l'uso di protocolli analitici.

Svolge attività di didattica presso l'Accademia delle Belle Arti di Palermo in qualità di docente a contratto.

Emilia DE PALO

Mi chiamo Emilia De Palo e mi sono laureata in Beni Culturali il 7/11/2018 presso l'Università degli Studi di Torino e attualmente sono studentessa iscritta all'ultimo anno della Magistrale in Archeologia e Storia antica, sempre a Torino. Sono appassionata di Archeologia e di Subacquea sin da quando ero bambina, infatti appena mi è stato possibile ho conseguito vari brevetti ricreativi (attualmente mi trovo in possesso del brevetto "advanced open water diver"). Quest'anno (dal 20-01 al 11-02, con rientro anticipato causa emergenza sanitaria covid-19), ho potuto lavorare con l'OCMA (Oxford Centre for Maritime Archaeology) presso l'Università di Oxford, grazie al programma Erasmus+ Traineeship. Insieme all'OCMA e in collaborazione con l'Ashmolean Museum abbiamo portato avanti un progetto basato sulla realizzazione di un database di oggetti e immagini subacquee per la pubblicazione di una guida al materiale subacqueo presente nel museo e nei magazzini. È stata un'esperienza molto importante e formativa perché ho potuto partecipare, non solo al progetto, ma anche a conferenze e lezioni frontali che mi hanno permesso di approfondire le mie conoscenze in campo subacqueo, tuttavia ancora molto labili.

Dario GIUFFRIDA

Laureato in Archeologia del Mediterraneo (LM-2) presso l'Università di Messina, nel 2018 ho conseguito il Diploma di Specializzazione in Beni Archeologici presso l'Università di Firenze.
Attualmente sono dottorando di ricerca in Scienze Storiche, Archeologiche e Filologiche presso l'Università di Messina e associato con incarico di collaborazione presso il Consiglio Nazionale delle Ricerche (Istituto per i Processi Chimico-Fisici di Messina), nell'ambito delle attività sul Patrimonio Culturale condotte dal Laboratorio di ricostruzione 3D "Ar3Digilab".
Durante la mia esperienza al CNR, ho avuto modo di acquisire un ampio know-how nel campo del rilievo strumentale (laser-scanner, fotogrammetria terrestre e da drone, D-GPS), nonché sull'utilizzo dei principali applicativi GIS e CAD per la ricerca, analisi e restauro digitale del patrimonio archeologico e storico-architettonico.
In ambito universitario ho preso parte a numerose attività di ricerca sul campo in Sicilia e Calabria (scavi e survey) e dal 2015 sono membro del team della missione di ricerca archeologica italo-greca presso il sito di Skotoussa (Tessaglia).
Come libero professionista ho inoltre collaborato a diverse consulenze finalizzate alla redazione del "documento di valutazione di impatto archeologico" (ViArch) ed effettuato sorveglianze durante progetti preliminari o esecutivi di opere pubbliche. Il mio profilo è inoltre arricchito da numerose competenze in ambito informatico (linguaggi html, php, javascrip, gestione database) finalizzate alla fruizione remota dei beni culturali.

Dario GIULIANO

Inizia il suo percorso di studi presso l'Università di Palermo dove si laurea con il massimo dei voti nel corso di Laurea in Beni culturali Archeologici con una tesi in Preistoria e Protostoria. Presso lo stesso Ateneo frequenta il corso di Laurea Magistrale in Archeologia, durante il quale partecipa al progetto Erasmus presso l'Università di Göttingen in Germania. Nel 2015 partecipa al progetto DO.RE.MI.HE – una collaborazione tra le Universià di Palermo, Tunisi ed Evora – per la messa in valore del patrimonio naturale e cultura sia esso materiale che immateriale. Si laurea con il massimo dei voti nel 2017 con una tesi in Archeologia della Magra Grecia. Nel 2019 inizia il dottorato di ricerca presso l'Università degli Studi di Palermo in Scienza della cultura con un progetto sui sistemi di copertura, nello specifico tegole, in epoca greca in Sicilia dalla loro comparsa alla conquista romana esaminando i siti di Agrigento e Himera.

Viviana MOLLICA NARDO

Laureata in Chimica nel 2011 presso l'Università degli Studi di Messina e Dottore di Ricerca in Scienze Chimiche nel 2015. Dal 2016 la mia attività di ricerca si è concentrata sullo studio di manufatti di interesse storico-artistico con metodologie spettroscopiche, in particolare la spettroscopia Raman, e nello sviluppo di materiali nanostrutturati innovativi (substrati SERS). Dal 2016 ad oggi, sono stata anche impegnata in campagne diagnostiche con strumentazione portatile. Alcune delle ricerche più importanti hanno riguardato: reperti conservati nel Museo d'Egitto di Torino, alcuni dipinti su vetro del Museo delle Tradizioni silvopastorali di Mistretta (ME), due dipinti di Antonello da Messina al Museo Regionale di Messina, una vasta collezione di maschere del Museo di Lipari e alcune lastre tombali dipinte del sito archeologico di Paestum. Inoltre un aspetto importante della mia attività di ricerca si incentra sull'applicazione di metodi computazionali allo studio dei pigmenti organici.

Silvia PARITI

Sono Laureata in Beni Culturali con indirizzo Archeologico presso l'Università degli Studi di Torino. Frequento la magistrale di Archeologia all'Università degli Studi del Salento e desidero specializzarmi in Archeologia Subacquea. Il mio percorso formativo si è arricchito nel settore della Grafica Pubblicitaria, della Fotografia e del Video Editing. Sono una ragazza molto intraprendente e socievole. Desiderosa di imparare sempre più e di mettermi alla prova. Ho un grande spirito di adattamento, lavoro bene in squadra e ho anche doti di leadership. So affrontare ogni situazione a mente lucida e ho un'ottima capacità di problem solving.

Antonella PRIVITERA

Antonella Privitera è Conservaton Scientist. Dopo la laurea ha collaborato con la missione archeologica a Leptis Magna (al-Khoms, Libia) del Dip. S.A.Fi.St, Università di Catania. Nel 2014 ha collaborato con il laboratorio PH3DRA (PHYSICS for Dating Diagnostic and Dosimetry Research and Applications) del Dip. di Fisica e Astronomia dell'Università di Catania, nel campo dell'Archeometria e della Fisica applicata ai Beni Culturali. Tra il 2014 e il 2018 ha svolto attività di ricerca presso il Consiglio Nazionale delle Ricerche, all'Istituto per Studio dei Materiali Nanostrutturati CNR-ISMN di Palermo, nella tematica "Nanomateriali e nanotecnologie per la conservazione sostenibile di manufatti metallici e lapidei del Patrimonio Culturale". È esperta in Archeologia Giudiziaria e Crimini contro il Patrimonio Culturale e svolge attività di consulenza tecnica in ambito giudiziario e stragiudiziale, iscritta all'albo dei Periti e CTU del tribunale di Catania. Attualmente svolge il Dottorato di Ricerca in Scienze della Materia, Nanotecnologie e Sistemi Complessi, presso il Dip. di Scienze, Università degli Studi Roma Tre.

Rosalinda SCIACCA

Nasce a Paternò (CT) il 18/05/1992. Consegue la Laurea Magistrale in Chimica e tecnologie farmaceutiche nel 2017 presso l'Università degli Studi di Catania con una tesi dal titolo "Preparazione di (R) - ed (S) -pranoprofene mediante biocatalisi: una risoluzione non convenzionale". Durante il lavoro di tesi, svolto presso l'Istituto di chimica biomolecolare del CNR di Catania, si concentra sulla sintesi asimmetrica biocatalizzata di sostanze di interesse farmaceutico.

Da Novembre 2018 è dottoranda in chimica analitica presso il Dipartimento di Chimica Industriale "Toso Montanari" Università di Bologna- UOS Rimini. Gli interessi di ricerca sono rivolti allo studio dei processi di corrosione relativi ai beni culturali, di materiali zeolitici per diverse applicazioni ed allo sviluppo di batterie al litio ione, utilizzando tecniche elettrochimiche.

Justine VERNET

Currently post-doctoral researcher at the Institute of Chemistry of Condensed Matter and Technologies for Energy of the National Research Council (ICMATE-CNR), in collaboration with the Department of Chemistry and Industrial Chemistry of the University of Genoa (DCCI -UNIGE), my researches mainly deal with the metallurgical practices from Prehistory to the Contemporary Era and on long-term corrosion processes of metallic materials. In particular, I am specialized in the metallographic characterization of non-ferrous alloys and in the multivariate statistical study of the correlations between chemical composition, microstructural properties and mechanical properties of ancient alloys. Lately, my research activities focus on the archaeometric investigation and in-situ conservation of submerged metallic artefacts.

AUTHORS INDEX