NARNIA
New Archaeological Research Network for Integrating Approaches to Ancient Material Studies

University of Cyprus
Archaeological Research Unit

THE NARNIA PROJECT

INTEGRATING APPROACHES TO ANCIENT MATERIAL STUDIES

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No. 265010.

MARIE CURIE ACTIONS

Edited by
Vasiliki Kassianidou &
Maria Dikomitou-Eliadou

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LIST OF ABBREVIATIONS

BA	Bronze Age
BE or BSE	Back-scattered Electron mode
BG	Black Glazed Attic pottery
CLODD	Clustering in Ordered Dissimilarity Data
DTA	Differential Thermal Analysis
DTA-TG	Differential Thermal Analysis - Thermogravimetry
DM	Digital Microscopy
EBA	Early Bronze Age
EDS or EDX	Energy Dispersive X-ray Spectrometry
ED-XRF	Energy Dispersive X-ray Fluorescence spectrometry
EM	Early Minoan period
ESD	Equivalent Spherical Diameter
ESR	Electron Spin Resonance
FCM	Fuzzy C-Means clustering algorithm
FN	Final Neolithic period
FORS	Fiber Optic Reflectance Spectrometry
FTIR	Fourier Transform Infrared spectroscopy
GC-MS	Gas Chromatography–Mass Spectrometry
HIT	High Iron Titanium glass
HIMT	High Iron Manganese Titanium glass
HPLC	High-Performance Liquid Chromatography
IC	Ion Chromatography
ICP	Inductively Coupled Plasma spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IR	Infrared signal
IRSL	Infrared Stimulation of feldspar
Km	Kilometres
LA-ICP-MS	Laser Ablation Ion Coupled Plasma Mass Spectrometry
LBA	Late Bronze Age
LC	Late Cypriot Bronze Age
LH	Late Helladic Bronze Age

LI	Lead Isotope analysis
MBA	Middle Bronze Age
MC-ICP-MS	Multi-Collector-Inductively Coupled Plasma -Mass Spectrometry
MIP	Mercury Intrusion Porosimetry
μ-PIXE	Micro Proton-Induced X-ray Emission
μ-XRF	Micro X-Ray Fluorescence spectrometry
NAA	Neutron Activation Analysis
ORO	Firing cycle that includes successive firing stages under Oxidising, Reducing, and Oxidising kiln atmosphere conditions
OSL	Optically Stimulated Luminescence
PCA	Principal Component Analysis
PIGE	Particle Induced γ-ray Emission spectrometry
pIRIR	post-Infrared Infrared-Stimulated luminescence
PIXE	Particle Induced X-ray Emission spectrometry
PLM	Polarised Light Microscopy
pXRF	Portable X-Ray Fluorescence spectroscopy
PWWM	Plain White Wheel-made ware
Redox	Portmanteau of words reduction and oxidation
SAR	Single-Aliquot Regenerative dose
SE	Secondary Electron mode
SEM	Scanning Electron Microscopy
TG	Thermogravimetry
TL	Thermoluminescence
TRS	Transverse Rupture Strength
UV-vis	Ultraviolet Visible spectrophotometry
UV-vis-NIR	Ultra Violet-visible-Near Infra Red
VAT	Visual Assessment Tendency
w%	Weight percentage (mass concentration)
XRD	X-ray Diffraction

THE NARNIA PROJECT: INTEGRATING APPROACHES TO ANCIENT MATERIAL STUDIES

This book introduces the research work conducted in the four-year lifespan of the European Marie Curie Actions Initial Training Network (FP7 – PEOPLE – Marie Curie Actions – ITN – Project no. 265010) *New Archaeological Research Network for Integrating Approaches to ancient material studies*, with the acronym NARNIA. This is currently the largest project to receive funding from the European Commission in the fields of archaeology and archaeological sciences, with a budget over 4.5 million Euros and 20 recruited research fellows.

NARNIA was envisaged and realised on the basis that the most comprehensive archaeological studies are those which combine traditional methods of typological and stylistic classification with analytical techniques deriving from the natural and digital sciences, and that the relationship between fieldwork and laboratory is a critical factor for the successful completion of any project. The ultimate objective of NARNIA, therefore, was the development of a new generation of scholars, who understand the complexities of interdisciplinary projects, and may integrate in their research differing techniques and methodological approaches for a holistic study of ancient material culture, enhancing our knowledge on different aspects of the history and archaeology of the eastern Mediterranean.

NARNIA provided a unique opportunity and a rigorous research platform for the collaboration of nine partners; six academic institutions, one research centre and two private enterprises. These are the University of Cyprus – which was the coordinating institution –,Vrije Universiteit Brussel, Université Paris-Ouest, the Hashemite University, University College London, the University of Sheffield, the National Centre for Scientific Research "Demokritos", G. M EuroCy Innovations Ltd and Thetis Authentics Ltd. The NARNIA partnership was active in six different countries, i.e. Cyprus, Belgium, France, Greece, Jordan, and the United Kingdom.

The success of the NARNIA project was already betokened by the success of the initial application to secure the funding. It can be argued - paraphrasing the Roman philosopher Seneca – that success is what happens when preparation meets opportunity. The application that the NARNIA partnership submitted for funding had to compete with 862 other proposals, from all fields of research, and secured both the highest rating and the largest budget among the 63 applications that were finally selected for funding. This was a promising beginning for a project that became an amazing success story and a great school for all those actively involved for its implementation.

During its four-year lifespan, NARNIA brought together the crème de la crème of the archaeological research community – already friends and colleagues – from various research institutions with the shared ambition to join forces, each one offering their expertise, for the realisation of a training and research agenda that could never have been achieved by a sole academic institution. The NARNIA partnership recruited 16 Early Stage Researchers and four Experienced Researchers that became the core focus of the project and its driving force. The duration of the 16 Early Stage Researcher fellowships was three years; during that time they all embarked on doctoral research, following training courses that would enable them to complete a doctoral thesis. The four Experienced Researchers were recruited for two years, in order to complement the training and research activities of the project and conduct research on a post-doctoral level. It is our belief that among the hundreds of applications that the NARNIA partnership received prior to recruitment, we have succeeded in selecting a multinational group of brilliant young scholars that will continue to contribute to archaeological research, putting into practice everything that they have learnt during their involvement in the NARNIA project.

As NARNIA is a Marie Curie ITN, a significant component of the project was dedicated to the training of the fellows. The *raison d'être* of the network was to improve the career prospects for employment of our 20 fellows by enabling them to develop lab-based skills needed for the study of ancient materials. In order to achieve this aim, the partner institutions organised an impressive series of research and training activities. During its four-year lifespan, NARNIA offered 26 training courses across the six participating countries, on the interdisciplinary study of ancient pottery, glass, metals, architectural decoration and building materials, as well as dating and the palaeo-environment, and the application of portable X-ray fluorescence spectroscopy in the field of archaeology. All NARNIA training courses were open to researchers outside the network, and the 16 Early Stage Researchers and four Experienced Researchers recruited by the NARNIA partnership had the opportunity to communicate and interact with scholars and researchers from different disciplines and research backgrounds.

The training agenda of NARNIA was structured to include both scientific training, and training for the development of complementary skills. This assorted corpus of training courses was designed specifically for the diverse research community of NARNIA, which was composed by archaeologists, conservators, physicists, chemists, engineers, and IT analysts. Furthermore, the generous funding that we had received, allowed us to invite high-profile scholars, specialists in the various topics scrutinised by our training courses, in order to train, exchange and discuss ideas and methodologies with our fellows and scientific staff. The NARNIA training courses attracted the interest of the wider research community, and were, thus, also followed by young and more experienced researchers outside the project network.

In addition to the prime scope of NARNIA, which was to offer our fellows the best possible training on archaeological sciences and the analytical techniques applied to the study of ancient materials, improving their prospects of employment and career development, the NARNIA network has been also contributing to the history and archaeology of the eastern Mediterranean basin, a region of great historical, cultural and geopolitical significance. Ancient technology has had a significant effect on the development of humans and their societies, as both human and social evolution are directly entwined with the materials, which, on the one hand, were accessible at any given time and place, and on the other, had the appropriate properties to lend themselves for making artefacts and serving functions. Therefore, the assessment of ancient materials and their processing for the production of artefacts and the evaluation of ancient techniques and know-how are essential prerequisites in composing the history of science and technology, as well as understanding cultural change, and both local and regional histories.

The core research area of NARNIA was focused on the interdisciplinary study of ancient ceramics, glass, copper and its alloys, architecture and building decoration, as well as on techniques of dating and chemical analysis of ancient materials. This requires the full integration of analytical methodologies from the mainstream fields of chemistry, geosciences and engineering in order to develop a supra-disciplinary area of science and technology applied in archaeology. It is emphasised that the combination of infrastructures and analytical equipment made available within the partnership provided our fellows the means and support to conduct an interdisciplinary study of the materials that they have been assigned to investigate, and to answer key archaeological and cultural questions.

We were very pleased to observe that despite the division of the project into six distinct work packages, our fellows identified areas of research overlap, and developed important synergies among them, integrating different approaches and areas of research, always with the support and guidance of their supervisors and other members of the partnership. This has resulted in a number of joined publications, as well as the establishment of research collaborations that will continue to flourish after the completion of the project.

Towards the end date of the NARNIA project, we have prepared this book as a solid reflection of the individual and collective work that has been conducted for the past four years by all our fellows and members of the NARNIA partnership. The short papers presented by our fellows in the following pages, are only a glimpse of their research, which will be more extensively published in peer-reviewed journals and, hopefully, monographs following the submission of their doctoral theses. We envisage this book to serve as a medium for people outside the network to become acquainted with the research that was undertaken by our fellows under the supervision of the NARNIA scientific staff, but also as a token of the hard work, dedication and passion of all the people that worked hard for NARNIA to become a milestone in archaeological research.

Prof. Vasiliki Kassianidou, NARNIA Project Coordinator
&
Dr Maria Dikomitou-Eliadou, NARNIA Project Manager

Archaeological Research Unit, University of Cyprus
Nicosia, November 2014

THE NARNIA NETWORK

Members of supervisory board, Early Stage Researchers (ESR), Experienced Researchers (ER), and other scientific staff per work package

Work Package	Name	Institution, Country
Work Package 1 **Project management**	Prof. Vasiliki Kassianidou (Project Coordinator)	University of Cyprus, Cyprus
	Dr Maria Dikomitou-Eliadou (Project Manager)	
Work Package 2 **The study of ceramic artefacts from the eastern Mediterranean**	Dr Peter Day (Work Package leader)	University of Sheffield, UK
	Dr Vassilis Kilikoglou	National Centre for Scientific Research “Demokritos”, Greece
	Dr Eleni Aloupi-Siotis	THETIS Authentics Ltd, Greece
	Dr Maria Dikomitou-Eliadou	University of Cyprus, Cyprus
	Dr Anno Hein	National Centre for Scientific Research “Demokritos”, Greece
	Dr Ioannis Karatasios	National Centre for Scientific Research “Demokritos” , Greece
	Prof. Philippe Claeys	Vrije Universiteit Brussel, Belgium
	Dr Noemi Müller (ER)	National Centre for Scientific Research “Demokritos”, Greece
	Christina Makarona (ESR)	Vrije Universiteit Brussel, Belgium
	Roberta Mentesana (ESR)	University of Sheffield, UK
	William Gilstrap (ESR)	University of Sheffield, UK
	Artemi Chaviara (ESR)	THETIS Authentics Ltd, Greece
Work Package 3 **Glass production and trade in the eastern Mediterranean**	Prof. Karin Nys (Work Package leader)	Vrije Universiteit Brussel, Belgium
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	Prof. Philippe Claeys	Vrije Universiteit Brussel, Belgium
	Prof. Wendy Meulebroeck	Vrije Universiteit Brussel, Belgium
	Prof. Herman Terryn	Vrije Universiteit Brussel, Belgium

	Prof. Hugo Thienpont	Vrije Universiteit Brussel, Belgium
	Dr Caroline Jackson	University of Sheffield, UK
	Anastasia Cholakova (ESR)	University College London, UK
	Andrea Ceglia (ESR)	Vrije Universiteit Brussel, Belgium
Work Package 4 Copper metallurgy in the eastern Mediterranean	Prof. Vasiliki Kassianidou (Work Package leader)	University of Cyprus, Cyprus
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	Prof. Thilo Rehren	University College London Qatar
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	Dr Roger C. Doonan	University of Sheffield, UK
	Dr Andreas Charalambous (ER)	University of Cyprus, Cyprus
	Lente Van Brempt (ESR)	University of Cyprus, Cyprus
	Demetrios Ioannides (ESR)	University of Cyprus, Cyprus
	Frederik Rademakers (ESR)	University College London, UK
	Mainardo Gaudenzi Asinelli (ESR)	University College London, UK
Work Package 5 The study of architectural decoration and building materials from the eastern Mediterranean	Prof. Anne Marie Guimier-Sorbets (Work package leader)	Université Paris-Ouest, France
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	Dr Veronique Vassal	Centre national de la recherche scientifique, France
	Dr Fadi Balaawi	Hashemite University, Jordan
	Dr Firas Alawneh	Hashemite University, Jordan
	Dr Yahya AlshawabkehL	Hashemite University, Jordan
	Dr Naif Haddad	Hashemite University, Jordan
	Dr Mohammed El-Khalili	Hashemite University, Jordan
	Dr. Abdulraouf Mayyas	Hashemite University, Jordan

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	Dr Eleni Philippaki	National Centre for Scientific Research "Demokritos", Greece
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Work Package 7 pXRF application in archaeology	Dr Roger C. Doonan (Work package leader)	University of Sheffield, UK
	Dr John Hurley	NITON UK, UK
	Dr Ellery Frahm (ER)	University of Sheffield, UK
Associate partners	Geological Survey Department, Cyprus	
	Department of Antiquities, Cyprus	
	The Jordan Museum, Jordan	
	NITON UK, UK	

WORK PACKAGE 2

The study of ceramic artefacts from the eastern Mediterranean

WORK PACKAGE 2

The study of ceramic artefacts from the eastern Mediterranean

The eastern Mediterranean, especially the area of the Aegean, has led the way in Old World archaeological ceramic analysis over the past 50 years. As such, not only is there a wealth of expertise to draw on across Europe, but also there is a continuing need for the training of young researchers in materials analysis, to answer the key questions asked on a routine basis of archaeological pottery. NARNIA work package 2 aimed to transfer knowledge to a new generation of researchers, whilst developing new insights and procedures, in order to take ceramic studies forward.

This work package was led by Dr Peter Day of the University of Sheffield, with close collaboration of colleagues in N.C.S.R. 'Demokritos' (Dr Vassilis Kilikoglou, Dr Anno Hein and Dr Ioannis Karatasios), Thetis Authentics Ltd (Dr Eleni Aloupi-Siotis), University of Cyprus (Dr Maria Dikomitou-Eliadou) and Vrije Universiteit Brussel (Prof. Philippe Claeys). Our focus was to train and research in both of the key strands of ceramic analysis, technological reconstruction and the ascription of provenance, focussing on the range of choices and practices involved in ceramic manufacture and use. This was achieved not only through dedicated training courses, but also by the conduct of a number of innovative research projects. Perhaps in a reflection of the importance which has been given to pottery within the discipline, and certainly on account of the range of expectations put on archaeological ceramic material, there were a large number of fellows on this work package, one Experienced Researcher and four Early Stage Researchers (ESRs).

Dr. Noémi Müller, hosted by N.C.S.R. 'Demokritos' in Athens, is an experienced post-doctoral researcher and has taken forward pioneering approaches to the modeling of mechanical and thermal properties. She developed new techniques for the modeling of thermal performance of both cooking vessels and technical ceramics, in order to aid in understanding the affordances of different materials and designs. In terms of mechanical performance she researched new methods of assessing ceramic impact resistance, which sees applications notably in the study of the pottery containers so crucial to trade throughout the ancient Mediterranean.

Roberta Mentesana, an ESR at the University of Sheffield, also concentrated on developing an understanding of pottery technology. Her diachronic study of pottery production at the site of Phaistos in southern Crete focused on the transition from the

Neolithic to Early Bronze Age and used an integrated approach involving chemical, mineralogical and microstructural techniques to reveal the *chaîne opératoire* of pottery over this period. She has demonstrated that changes across the operational sequences used in the production of different types of pottery were not simultaneous. Instead, while the Early Bronze Age saw radical transformations in pottery production, some had their roots in practices which had a historical depth going back into the Neolithic.

Artemi Chaviara, an ESR hosted by Thetis Authentics in Athens, examined the detail of materials and techniques used in production of the fine quality 'black glaze' slipped surfaces that Attica was so famous for. Using an explicitly experimental approach, she not only compared Geometric, Archaic and Classical examples of black glaze with modern reproductions, through the application of XRF, PIXE and μ-PIXE, but also in terms of detailed assessment of the macroscopic appearance of the slip layers. She then built on this fundamental understanding of production technology, analysing a number of raw material sources in the study area to match them to ancient black glaze in terms of chemistry and features such as shrinkage and crazing.

Will Gilstrap's research also touched on Attic pottery production, but in his case belonging to the end of the Mycenaean period. Hosted as an ESR by the University of Sheffield, Will carried out a study of pottery production and exchange around the Saronic Gulf, identifying and characterising ceramic centres that manufactured fine and coarse wares. Integrating thin section petrography, neutron activation analysis and scanning electron microscopy, Will has revealed the large-scale movement of ceramic products throughout the areas bordering the Gulf, detailing production at the major production centre at Kontopigado Alimos, characterising products produced in the Corinthia, as well as demonstrating the continued ceramic craft activity on Aegina at this time.

Also concerned with the provenance of pottery, Christina Makarona's project has worked to develop the methods and application of isotope analysis of ceramic materials, specifically of lead and strontium, hosted by VUB in Brussels. Working with raw material and Bronze Age pottery from Cyprus, her research has taken forward our understanding of isotopic compositions of materials from sediments to mudstones. Her insights have led to a more confident appraisal of the role of isotope studies as part of an integrated approach to archaeological ceramics with a clear understanding of the manipulation of raw materials by ancient potters.

All researchers and teams have shown the fundamental nature of an understanding of ceramic technology, not only to archaeological questions which examine technical or social aspects of pottery manufacture, but also in providing a firm basis for provenance determination. The young researchers' backgrounds differ as much in disciplinary training, from chemists to conservators and archaeologists, as they do in terms of nationality and perspectives. Their team-work, not only in their host institutions, but by forming a truly collaborative team within the network, has paid dividends. They have taken forward their own training, but imparted knowledge within and outside their institutions and carried out first class research.

Dr Peter M. Day
Work Package 2 leader
University of Sheffield, UK

THE FINAL NEOLITHIC - EARLY MINOAN TRANSITION IN PHAISTOS, CRETE: CONTINUITY AND CHANGE IN POTTERY MANUFACTURE

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Abstract

The site of Phaistos in southern Crete offers great potential for examining the transition between the FN and the EBA in Crete. Given the completeness and continuity of its stratigraphy as well as the abundance and the sheer quality of the ceramic material, the site provides much information concerning the degree of change in material culture in these phases. This paper adopts a 'bottom-up' approach to explore the dynamics of technological and social change at Phaistos. It starts with an investigation into technological variation within ceramic assemblages across the period under study, which shows the adoption of distinctive surface treatments and paste recipes. However, the paper goes beyond technological reconstruction. The analytical study is intertwined with the contexts of consumption of the site in order to understand their relationship with artefact manufacturing. By examining the significance of technological choices in pottery making, this study demonstrates a complex picture of continuity and change over the period of study, which disproves recent assumptions of a single-phase transformation at the beginning of the EBA.

The Final Neolithic - Early Minoan transition in Crete: A technological and cultural revolution?

The transition from the Neolithic period to BA has been often considered as the boundary between two periods of great contrast. Society in the EBA contrasted to the Neolithic in terms of economic and social structure, settlement arrangement and technological advancements (*cf.* Tomkins 2004). Only in recent years have scholars attempted to bridge the gap in literature regarding this transition from Neolithic to BA by re-examining the nature and pace of change. There has been a notable focus on the phases at the end of the fourth and beginning of the third millennia BC, especially regarding the peculiarities of material culture that introduced some new features while continuing some aspects of the Neolithic traditions.

Two main models have been offered in explanation of such a transition. Some advocate that the migration of people from the eastern Mediterranean to Crete brought about technological change, such as advanced pyro-technology including the widespread practice of metallurgy, and different fashions visible in material culture of the initial stage of BA (*cf.* Hood 1990; Muhly 1973; Warren 1974). Specifically, the appearance of a class of pottery with red painted linear decoration on a pale-firing background, which resembles those found in Palestine, was used to support this position (Hood 1990).

Other scholars have observed signs of change already in the final phase of FN. The occurrence of a different ware, Red Ware, and the foundation of new sites in defensible locations relying on natural defences, have been argued by Nowicki (2002) to be the result of external agents coming to Crete. Furthermore, several authors do not exclude the possibility of new people settling on Crete, but favour a scenario of small group movements, which generate the integration of new and pre-existing cultural elements (Manteli 1993; Papadatos 2012; Vagnetti and Belli 1978).

Most recently, Betancourt (2008) has presented a vision of large-scale technological change on the FN-EBA horizon. He bases his argument on the introduction of calcareous clays for the production of lighter coloured pottery, the introduction of the updraft kiln, which allowed better control of kiln atmospheres, and the achievement of consistent, high firing temperatures. Coupling these technological changes in ceramic production – irrespective of whether these are thought to be an endogenous development or deriving from outside the island – with the necessity to store and transport perishable goods, Betancourt (2008: 99) posits a technological and cultural revolution at the beginning of the BA.

A crucial question for the current research project is whether these changes took place at a single phase horizon or whether there is a pattern of gradual technological and cultural change observed in a long-term view from FN to EM I. Pottery, being the most ubiquitous archaeological material, has always been used to measure change in the archaeological record. While much of similar work in the past was heavily based on the external, macroscopic characteristics of pottery, including pot typology and style, in recent years a shift in research, combining ceramic classification with analytical work, has revealed a more complex and multi-faceted picture of ceramic production and distribution in Crete (Day *et al.* 1998; 2005; 2010; 2012; Nodarou 2011; 2012).

This project is an interdisciplinary study of pottery from the site of Phaistos in the Mesara Plain of southern Crete. Phaistos provides an uninterrupted stratigraphic sequence from FN to MBA, when the 'palace' structure was constructed on the hilltop (Todaro 2010; 2013). This provides a unique opportunity to record technological changes that took place in ceramic material culture across this long sequence of occupation. Furthermore, considering the presence of different contexts of ceramic production and consumption at the site, Phaistos provides an ideal case study for an investigation into the interplay between the manufacture of pottery and its consumption. Preliminary and selected analytical results relating to key questions in this project will be presented in this paper.

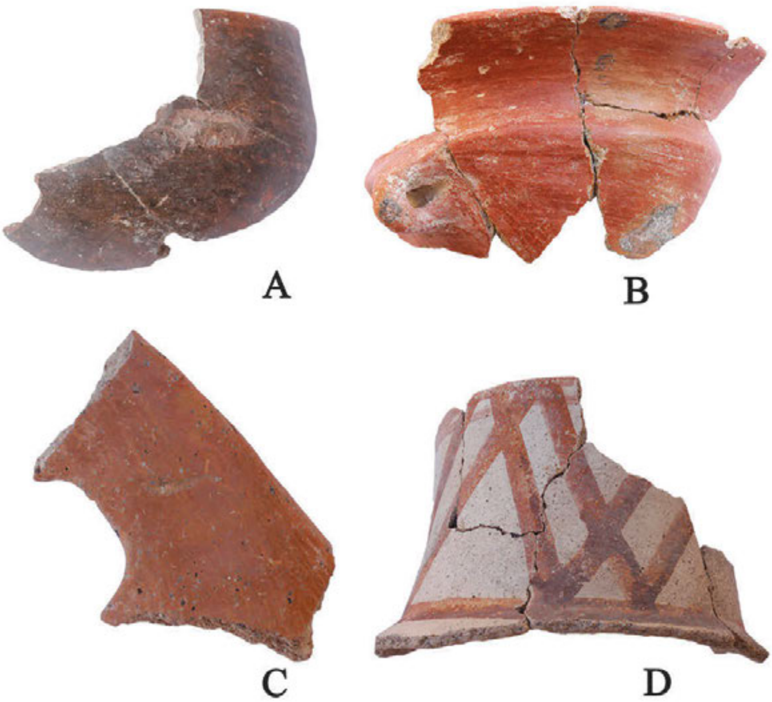


Figure 1. (a) Burnished ware (FNIII); (b) Red slipped and burnished ware (FN IV); (c) Brown Slipped and Polished ware (EM IA); (d) Dark-on-light painted ware (EMIB). Not in scale. Pictures courtesy of S. Todaro and of the Italian School of Archaeology in Athens.

Reconstructing technologies, reconstructing their significance in context

Materials and Methods

A total of 304 ceramic samples have been selected. The pottery under study belongs to the first four phases of occupation at the site, dated to FN III, FN IV, EM IA and EM IB (*ca.* 3600-2650 BC, Todaro 2010; 2013). Pottery has been selected in order to provide the best possible representative view of the entire assemblage for each phase. Therefore, several wares (**Fig. 1**) and different excavated contexts have been selected. In order to reconstruct technological variation in pottery manufacture at Phaistos, the concept of *chaîne opératoire* has been chosen as the most suitable approach.

Reconstructing the *chaîne opératoire* of pottery making involves detailing the sequence of steps required to produce the artefact, including raw materials, tools, energy, time, and the processes required to perform the actions. While some of these aspects might be more difficult to approach than others, it has been demonstrated that even those that involve bodily gesture have their correlates in specific methods of shaping (Todaro 2013: 196-201; Day *et al.* 2006). It is argued that current approaches, those that integrate macroscopic study and analytical investigation, allow the reconstruction of the ancient technology with an acceptable level of detail. A protocol of analytical techniques, the practice of which is now well established, has been chosen in order to identify the variables involved in the manufacture of pottery at Phaistos (**Fig. 2**). The reconstruction of forming techniques and the macroscopic examination of the pottery have been extensively studied by S. Todaro and S. Di Tonto (Di Tonto 2006; Todaro 2010; 2013; Todaro and Di Tonto 2008). Therefore, the outcomes of this project are going to be fully integrated with their results in order to identify tendencies in manufacturing over time. Finally, technological reconstruction has to be inter-woven with the dynamics occurring at the site in each of the four phases in terms of consumption practices. The aim is to investigate the biographies of different technological sequences during the period of study, and those of the vessels *per se* within the consumption patterns on the Phaistos hill. The investigation of technologies in the context of consumption allows us to reconstruct the significance of their adoption, transmission, transformation and abandonment over time.

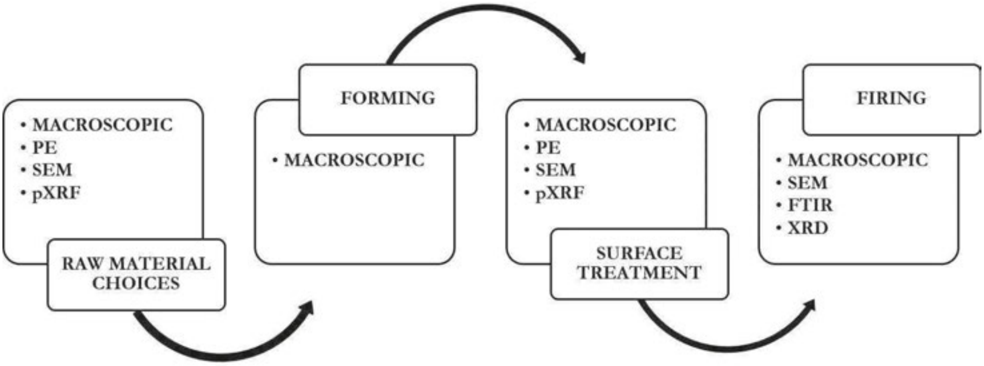
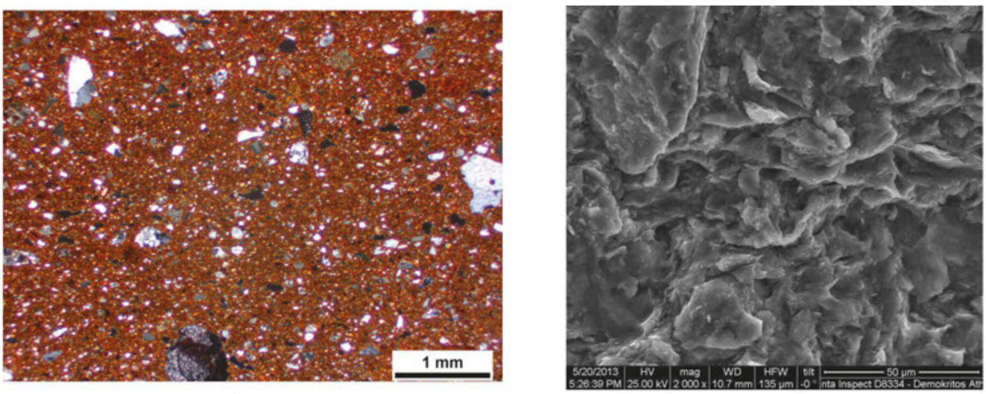
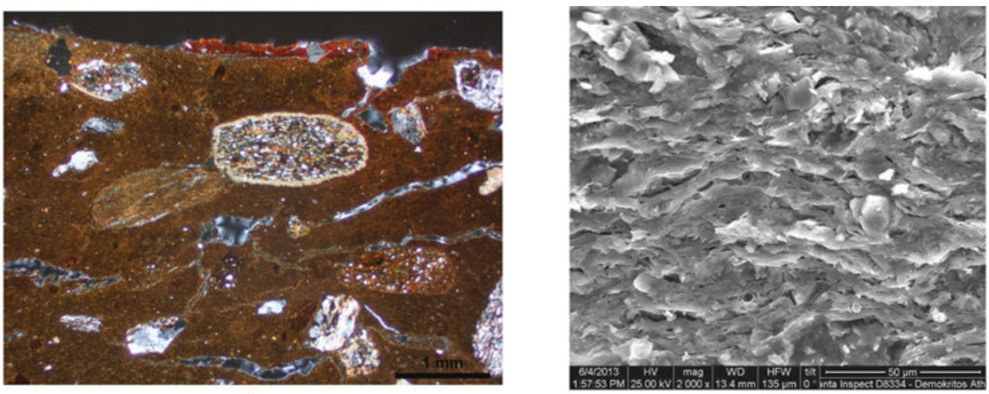


Figure 2. The methods adopted in reconstructing the chaîne opératoire of pottery manufacturing at Phaistos.



A B

Figure 3. Microphotograph (XP, A) and SEM image (B) of terra rossa clay paste.



A B

Figure 4. Microphotograph (XP, A) and SEM image (B) of sand-tempered clay paste.

First results

It has been argued that the adoption of a more calcareous clay, mixed with sand, and fired at a high temperature allowed the production of vessels that were less porous and of higher quality when compared to those of the Neolithic period (Betancourt 2008). The introduction of calcareous clays in pottery manufacturing is indeed a prominent change because this material involves the adoption of different strategies by the potter in terms of manipulation and firing procedures. However, the first results at Phaistos suggest that the introduction of calcareous clay occurred within other main technological transformation in the ceramic manufacturing, involving raw material choice as well as their manipulation, decoration and firing procedures.

Petrographic examination suggests that there were at least two raw material types adopted to make pots during the studied period. One of the two is a red clay, a *terra rossa* densely packed with quartz, feldspar and biotite (**Fig. 3a**). The study of coarse wares shows evidence of the addition of larger inclusions of mixed mineralogy to the base of red clay, which would have been done by the potter to decrease the plasticity of this clay in constructing thicker wall vessels. This paste was mainly adopted for the manufacture of FN III and FN IV burnished (**Fig. 1a**) and coarse wares and, to a lesser extent, later for cooking pots, brown slipped, red burnished and dark burnished wares. In addition to their macroscopic investigation, the SEM analysis of samples coming from the four phases shows that this is a low calcareous paste which was consistently low fired in incomplete oxidised to neutral atmospheres (**Fig. 3b**).

Furthermore, the use of finer red clays with larger rounded inclusions is attested mainly from the FN IV phase onwards. Petrographic examination shows that the samples belonging to this fabric have much variability in terms of size modality, coarseness of the groundmass and texture; they are all, however, characterised by the presence of large rounded inclusions of mixed mineralogy with a prevalence of low-medium grade metamorphic rocks (**Fig. 4a**). This paste was used for coarse ware in FN III and then adopted mainly for red slipped (**Fig. 1b**) and coarse wares in FN IV, and for brown slipped (**Fig. 1c**) and coarse wares in EM IA. In EM IB this was the main paste used for manufacturing dark-on-light painted jug/jars (**Fig. 1d**) and storage jars. SEM investigations of samples from the four phases suggests that, in contrast to the low firing of the other vessels, this group of vessels was always high fired (**Fig. 4b**). Across the four phases, a better control of firing atmosphere is evident from the homogeneous light colour that some vessels show in section from at least FN IV. This paste is the precursor of a common fabric used throughout the BA in the area of the Messara and referred in the literature as the sand-tempered fabric. In contrast to what is thought about this kind of fabric, the clay has not always been highly calcareous.

Chemical investigation indicates that the calcareous content of this clay paste was relatively low during the phases under study. Only in the production of EM IB painted jugs and storage jars is the use of a more calcareous clay attested. The petrographic evidence of clay mixing that could explain this difference is scarce; but the correspondence between specific ware and the clay's calcium content in any case suggests that a specific paste was adopted in EM IB. It is probable that the choice to use a more calcareous clay paste was motivated by the desire to produce a better colour contrast with the red pattern painted on the surface, typical of dark-on-light ware. The use of such linear painted decoration is one of the features considered as novelty in the literature of EM IB (Hood 1990). However, the use of an iron-rich pigment, which becomes red during firing, was a technology already practised from FN IV. In FN IV the entire surface of the vessel was slipped (**Fig. 1b** and **4a**), while in EM IB the paint was applied in linear patterns on the surface of the vessel (**Fig. 1d**). The material and technology involved are likely to have remained unchanged. In addition, the achievement of this red-on-light effect does not necessarily imply the use of an up-draft kiln as commonly thought (*cf.* Vössen and Ebert 1986: 78-80).

Therefore, some tendencies in pottery production during the FN – EM I phases can be observed at Phaistos:

- the coexistence of different paste recipes throughout the period under study; it seems that different firing strategies were used according to the paste recipe;
- the introduction of a sand tempered, fine clay fabric from FN IV; the practice of sand tempering can be found in some *terra rossa* fabric coarse pots;
- the use of a high calcareous clay paste to manufacture dark-on-light painted jug/jar and storage jars;
- the introduction of pre-firing painting technology in FN IV; this practice remained in use during EM IB for the production of the pattern painted motif on jug/jar surfaces.

These preliminary results suggest that specific technological and stylistic changes occurred over a millennium of pottery manufacturing at Phaistos. They did not, however, occur drastically in a single phase, but show aspects of consistency in the long-term. It is worth considering how these technological changes in pottery manufacture correlate with what we know of changes in the nature and extent of settlement at Phaistos. We see substantial changes in FN IV and EM IB and the site contexts of this period are important.

Pottery change and continuity in context at Phaistos

The recent reassessment of the stratigraphic sequence of Phaistos by Todaro (2010; 2013) has indicated intriguing evidence of changes in the use of the site during the phases under study. The first two phases (FN III and FN IV) show evidence of both domestic and ritual activities in the central and western part of the hill site, including the manipulation of human bones and the conspicuous consumption of food in open areas (Todaro and Di Tonto 2008). On the basis of differences in the assemblages, Todaro (2013: 230) suggests that in FN IV diverse ceremonies were performed on the hill and probably by competing households. During this phase other wares were introduced, such as a red slipped ware, together with a dark burnished ware typical of the previous Neolithic phase. As observed above, this last phase sees the extensive adoption of the sand tempered fine clay paste for the newly introduced wares and the practise of painting technology on vessel surfaces.

Later, in EM IA, several buildings characterised by red-plastered walls have been found in the westernmost part of the hill (Todaro 2013: 231). An earthquake and a fire caused the collapse of these structures and little is known about their use. The pottery of this phase is characterised by a notable variability in ceramic classes and has been considered stylistically as transitional between the Neolithic and the BA traditions (Papadatos 2012; Todaro 2013: 171-173). The subsequent phase, EM IB, indicates a significant change in the internal organisation of the settlement, characterised by intense building activity in the central and southern parts of the hill. The deposits are characterised by the discard of many drinking and pouring vessels, along with animal bones. In contrast to EM IA, the pottery of EM IB can be grouped into a few well-defined ware groups and corresponds to the main phase of EM I documented elsewhere on the island (Wilson and Day 2000). Some of these wares, such as the dark-on-light, seem to have been produced with a specific sand tempered and highly calcareous clay paste.

Exploring the FN-EM transition: A few comments from Phaistos

Analysis of the FN – EM I ceramic material from Phaistos has revealed a complex picture of manufacture continuity and change over time from the first phase of occupation. The identification of a single horizon of change, assumed by much of the earlier literature, is still elusive. Moreover, different components of ceramic production at Phaistos, such as raw material choices, surface treatments and firing, change at different times and at different rates. A multi-faceted and dynamic picture seems to emerge; different manufacturing processes coexisted and interacted, probably influencing each other not just in the arena of consumption but also in that of production.

In considering changes in pottery production and consumption, these technological tendencies are suggested to correlate well with architectural changes/construction events that took place at the site, according to Todaro's reconstruction (2013). For instance, major changes in the use of space occurred in both FN IV and EM IB. The significance and meaning of these changes at Phaistos is still to be determined. However, the tendencies outlined here better describe the dynamics occurring at the site in terms of consumption practices and the ways in which they affected manufacturing practices. This research once again demonstrates the subtlety of technological change. While it may be sudden, more often technological change per se is not a drastic event. Paraphrasing a recent paper (Day *et al.* 2010) technological change goes through a continuous negotiation between the old and the new, the producer and the consumer in the arena of practice. Phaistos in this sense therefore illustrates slow and complex technological interactions of prehistoric societies through their pots.

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INDIRECT EVIDENCE FOR POTTERY PRODUCTION ON THE ISLAND OF AEGINA DURING THE TRANSITIONAL LH IIIB-LH IIIC EARLY PERIOD

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Abstract

This project explores ceramic technology and exchange during the transitional LH IIIB - LH IIIC early period in the area of the Saronic Gulf through a multi-technique analysis. Pottery from twelve archaeological sites within the study region has been analysed by combined thin section petrography and chemical analyses, in order to identify and characterise the ceramic fabrics being produced and exchanged in this period. This paper presents a selected case study from the wider research project, in order to highlight how the production origins of three unknown ceramic fabrics were identified through petrographic analysis of complete assemblages in a regional pottery study from a bottom-up perspective.

The results presented in this paper indirectly identify the production of fine tablewares, in addition to coarse cooking pottery and large vessels, including tubs and pithoi, in the northern half of the island of Aegina during the Late Mycenaean period. Tracing the vessels manufactured in these ceramic fabrics from their place of deposition back to the island of Aegina raises several new questions about the island's political centre of Kolonna, a site which presents very little information about the activities that occurred here during this time. Moreover, the patterns reflected through this approach suggest that studies of pottery, be they production technology or provenance, are better used in the investigations of everyday events rather than for reconstructing generalities about political economies in the Mycenaean world.

Introduction

Figure 1. Map of the Saronic Gulf with prominent Mycenaean sites and locations mentioned in the text.

Craft production and exchange during the LBA in Greece and the Aegean are often observed from a binary viewpoint, where palatial and non-palatial politico-economic sectors are mutually exclusive social entities (Aprile 2013; Parkinson *et al.* 2013; Shelmerdine 2013; Galaty *et al.* 2011; Thomas 2005). A large proportion of research has been geared towards understanding the role of the palace, or state, in craft production (Bennet 2008; Nosch 2006; 2000; Voutsaki and Killen 2001; Galaty 1999; Shelmeridine 1985; Shelmerdine and Palaima 1984). In what is effectively a top-down approach, we still have much to learn about the patterns of everyday life. In this light, it was thought beneficial to approach craft production and distribution as a multi-directional continuum of interactions at local, regional and inter-regional scales, as opposed to a division between palatial and non-palatial. In this way Mycenaean economic practice can be afforded a wider lens, through which to observe social interaction among various levels of the socio-political hierarchy. By perceiving social interaction as a continuum, it is possible to observe craft production and other social activities from the bottom-up; moving from commonplace, ordinary or mundane events and material culture into more large scale social organisation, such as state-led activities, where actions and events associated with the social elite are used to characterise power and economic influence of one social faction (e.g. palatial elite) over others (e.g. craft producers, farmers, etc.).

This paper provides a preliminary account of just one of the many results, which are emerging from a regional fabric study of late Mycenaean pottery from the Saronic Gulf (**Fig. 1**). The ceramic fabrics detailed in this paper have been selected to highlight some of the benefits of a large scale scientific study on entire contemporary pottery assemblages of differing character. Here, the indirect evidence gained through a complex understanding of pottery production technology and regional geology of the Saronic Gulf has led to the assignment of production origins for several ceramic fabric groups to different centres within the region, some of which do not currently have extant pottery production remains dated to the period of study. Building on typological work in the study area, it is argued here, through the indirect evidence of ceramic fabric technology recorded at several neighbouring sites from within the Saronic Gulf region, that a pottery production centre on the island of Aegina produced and exported pottery of various Mycenaean types in the transitional LH IIIB - LH IIIC early period of the Late Bronze Age[1]. The evidence is used to briefly demonstrate how this approach is a useful tool for the reconstruction of craft and economic systems in regional Mycenaean studies.

Methods

Sampling of pottery for this study has been guided by typology, defined by morphological and decorative features, and the macroscopic study of ceramic fabrics. The aim of this sampling strategy was to obtain, where possible, a representative sample of fabric types across a broad spectrum of vessel shapes from each site assemblage under study. The samples have been analysed using a combination of ceramic thin section petrography and NAA with a subset selected for analysis with the employment of SEM. This combination of analytical techniques integrates the reconstruction of ceramic technology into the determination of pottery provenance through petrographic, chemical and microstructural observations.

While the reconstruction of the technological process of ceramic production may be considered an aspect worthy of study in its own right, it can also be argued that it comprises a more robust method of assessing provenance than raw material source determination on its own (Day *et al.* 1999). In this project, raw materials are identified and compared to the geology of local and regional locations identified as possible sources, as well as petrographic and chemical comparative material from previous projects. Reconstruction of the production technology offers the added benefit of reconstructing technological practice, in order to examine variability in manufacture both within and between production centres. The information generated through this method is advantageous in unlocking the choices that potters make throughout the manufacture process beyond raw material selection and towards understanding the social forces embedded within (Lemmonier 1993a). In a region where decorative motifs and vessel shapes define chronological phases and act as cultural markers, technological variability

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1 The transitional LH IIIB - LH IIIC early phase is clearly defined in Attica by Mountjoy (1995); at Kanakia by Marabea (2012); and more generally by Vitale (2006).

that lies below the vessel surface has the power to illuminate new information on where, how and on what scale vessels were manufactured. Tracing the movement of pottery from its point of origin, once identified, sheds light onto local, regional and inter-regional patterns of production and consumption, while demonstrating nuances of social and economic interaction in everyday life (*cf.* Day *et al.* 1999; Lemmonier 1993b; Neff 2005; Whitbread 1995).

Results

The first fabric to be discussed was originally, in the case of the wider Saronic Gulf project, identified macroscopically in vessels associated with cooking and general food preparation (tripod pots, one- and two-handled jars, spouted and unspouted basins) at the Mycenaean harbour site of Kanakia, on the island of Salamis (Marabea 2010). Since its identification at Kanakia, this fabric has been observed in Late Mycenaean contexts at the Cave of Euripides on Salamis, at Plaka, Kontopigado and the Mycenaean Fountain deposit on the Athenian Acropolis in Attica, at Ayios Konstantinos on Methana, and Myti Kommeni on the island of Dokos[2]. It is composed of a highly micaceous clay matrix with frequent plagioclase feldspar and hornblende amphibole inclusions (**Fig. 2**). The clay is characterised by very fine grained intermediate porphyroclastic volcanic rock fragments, such as amphibole andesite and rhyodacite. Macroscopically, this fabric is well known in studies of pottery from the MBA and earlier LBA phases in the production of cooking and kitchen pottery at the site of Kolonna, Aegina (*cf.* Gauss and Kiriatzi 2011). Petrographic analysis further indicates that this fabric group is highly compatible to the *Noncalcareous Volcanic Fabric* (Fabric Group 1) defined by Gauss and Kiriatzi (2011: 93-95). At this time there is no way to determine whether this fabric, or any other fabric detailed in this paper, were produced at the Kolonna settlement, however the geological components that make up this fabric can be assigned a decisive provenance in the northern half of the island of Aegina, as detailed in the earlier study by Gauss and Kiriatzi (2011).

The next fabric (Fig. 3) comes in the shape of large tubs (asamanthoi) and pithoid jars that were found at the sites of Ayios Konstantinos on Methana and Kanakia on Salamis and a large tub at Myti Kommeni on Dokos. The raw materials used for the construction

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2 The identification of this fabric has taken place throughout the course of this research project with the exception of Ayios Konstantinos, where the fabric was identified by Lindblom (2001) with respect to potter's marks.

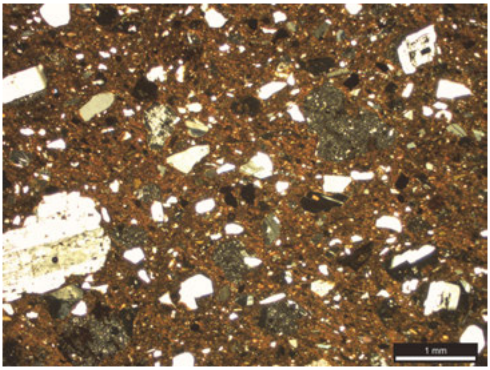

Figure 2. Photomicrograph of Noncalcareous volcanic fabric group in XP.

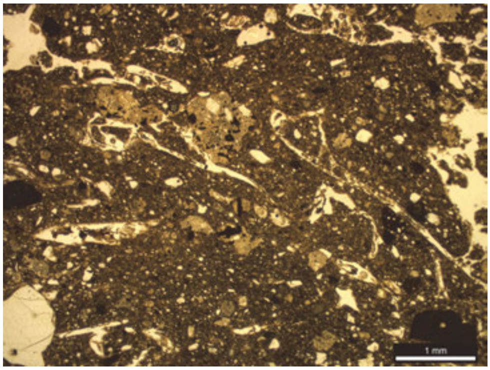

Figure 3. Photomicrograph of Noncalcareous volcanic with organics fabric group in PPL.

of this fabric are the same used to produce the *Noncalcareous Volcanic Fabric* discussed above. The matrix is non-calcareous and micaceous with frequent hornblende amphiboles and plagioclase inclusions. While the matrix is definitively the same as the *Noncalcareous Volcanic Fabric*, it differs significantly in how it was tempered. There are the fragments of the fine intermediate igneous rock that link this fabric to a production on the island of Aegina, but there is a second temper type in the form of organic plant material. Organic tempering of large tubs during the transitional LH IIIB - LH IIIC early phase has been observed at several sites within the study area and in several fabrics of differing production origin. This is a phenomenon that will be further explored at a later date. The pithoid jars are presently the first known exported large storage jars from Aegina during this period.

When we move to other areas represented in the pottery assemblage, another characteristic fabric compatible with an origin on Aegina has been found in vessels associated with the mixing, storing, serving and consumption of liquids. This fabric consists of a fine calcareous matrix with few to very rare inclusions of intermediate rock fragments, andesite and/or rhyodacite, and their constituent materials such as plagioclase feldspar and hornblende amphibole. Carbonates appear in the form of micritic aggregates and foraminifera microfossils. The matrix is high fired as determined by the optical inactivity and the greenish brown colour of the matrix. This fabric is compatible to the *Calcareous Volcanic Fabric* (Fabric Group 2) defined by aggregates and foraminifera microfossils. The matrix is high fired as determined by the optical inactivity and the greenish brown colour of the matrix. This fabric is compatible to the *Calcareous Volcanic Fabric* (Fabric Group 2) defined by Gauss and Kiriatzi (2011: 99-104). Those authors

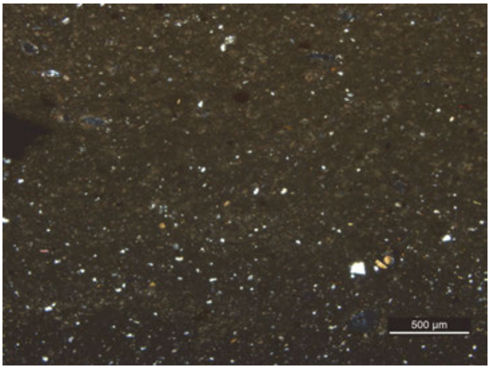

Figure 4. Photomicrograph of Fine calcareous volcanic fabric in XP.

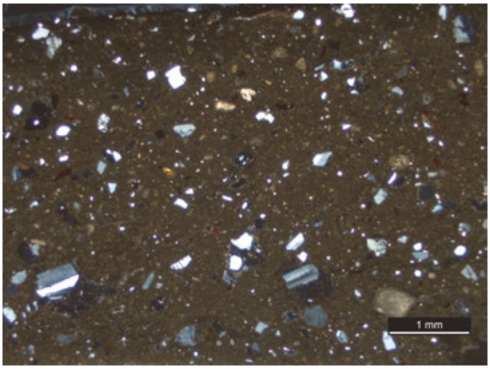

Figure 5. Photomicrograph of Moderately calcareous volcanic fabric in XP.

separate this group into two main subgroups, denoted as Fabric Group 2A and Fabric Group 2B, the latter being defined as having more inclusions and more green amphiboles in comparison to the former. A compatible fabric to the more fine version of Fabric Group 2A, Fabric Group 2Af (**Fig. 4**), has been identified within this study at the Cave of Euripides on Salamis in the form of a fine closed vessel (amphora/hydria/jug). Additionally, a fabric matching the moderately coarse Fabric Group 2Am (**Fig. 5**) has been identified at Kanakia on Salamis, Lazarides on Aegina and at Kalamianos in southwest Corinthia as deep bowls, stemmed bowls, shallow bowls, kylikes and a basin. Finally, a fabric matching Fabric Group 2B (**Fig. 6**) is found at Eleusis in northwest Attica, Ayios Konstantinos on Methana and as the dominant studied fabric at Lazarides on the island of Aegina. This fabric is observed in deep bowls, kraters, kylikes, jars, hydria and amphorae.

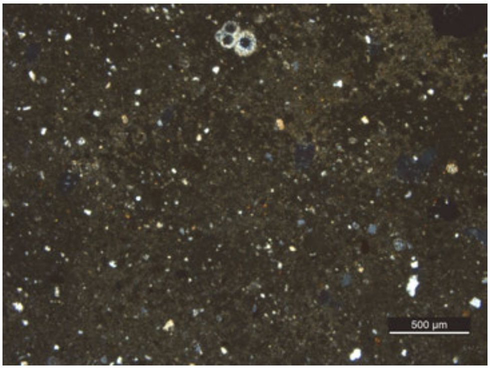

Figure 6. Photomicrograph of Calcareous volcanic fabric in XP.

Discussion and Conclusions

Pottery produced on Aegina is just a fraction of the entire ceramic assemblage that was produced and circulated in and around the Saronic Gulf during the transitional LH IIIB-LH IIIC early period. However, it is interesting to see the continued production and distribution of previously identified, characteristic Aeginetan fabrics during a period which presents few deposits from the site of Kolonna, prompting suggestions of a demise at least in its political power. Through the examination of only a selection of ceramic fabrics, it has been possible to see the variety of vessel types, coarse and fine, that were being exchanged. By considering complete assemblages in this study, new information about the production and dissemination of fineware vessels from the island of Aegina has been added to the often identified cooking vessels. Moreover, it appears that pottery producers on Aegina were also producing large storage jars and large tubs for export in a similar coarse fabric known from the cooking vessels but with the addition of organic tempering.

This case study is a small part of an on-going research and it illustrates some of the main observations made throughout the Saronic Gulf at the end of the BA. The sites in question belong to a short chronological period, thus the resulting data reflect patterns of production and exchange for just a few generations, in several different archaeological contexts. When placed into the wider political and economic context of the Mycenaean world, it is not possible to see whether pottery was produced and exchanged with any political intervention. It is rather unclear if any political organisation influenced either the production or distribution of these ceramic vessels. Ceramic products from Aegina appear in many different archaeological contexts – religious sanctuaries at Agios Konstantinos and Eleusis, settlements at Lazarides, Plaka, Kanakia and Dokos, the Cave of Euripides on Salamis, the harbour at Kalamianos, the production centre at Kontopigado and in the well deposits of the Acropolis at Athens.

The evidence is better considered by trying to determine the kinds of everyday events that brought pottery from Aegina to Attica, Salamis, Corinthia, Methana, Dokos and even further afield. Though political bonds are one means for explaining patterns of product exchange, the evidence presented here may be more readily understood if procurement of pottery is considered based on the availability and utility of particular vessels according to need. By observing the production and exchange of pottery in all shapes and sizes, a foundation has now been constructed to ask if it is even possible to identify political influence from the movement of this type of craft product. While this is only the beginning of reconstructing the everyday transactions of material culture, perhaps the knowledge that Aeginetan products are circulating among many other vessels similar in shape and size with ceramic production in Attica, Corinthia, the Argolid and Crete, one would be less inclined to make an immediate connection between pottery and politics.

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GEOCHEMICAL PROXIES FOR PROVENANCING CYPRIOT POTTERY CLASSES FROM EARLY TO LATE BRONZE AGE CONTEXTS

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Abstract

The project described here has evolved from previous geoarchaeological research undertaken at the Vrije Universiteit Brussel, regarding the application of lead (Pb) isotopic analysis in ceramic provenance (Renson *et al.* 2013). The encouraging results warranted further investigation concerning isotopic provenance, by incorporating an additional system, strontium (Sr). The complex nature of the applied techniques – which are also rather unusual in the field of ceramic provenance – requires the definition of a methodological framework, serving to delineate the cases in which such an approach would be useful for ceramic research and to help with the correct interpretation of the results. Interesting as they are, methodological inquiries such as these can shift the focus away from the true essence of archaeometry, i.e. archaeology. It is for this reason that the project includes a series of relevant archaeological questions.

In this short paper the focus is set on the methodological framework as it has been developed so far. More specifically, we investigate how isotopes relate to petrographic fabric, a most useful descriptor for ceramic provenance research. A short case study from the Cypriot LBA site of Alassa *Pano Mandilaris* is presented to showcase the potential of isotopic analysis in reassessing petrographic fabrics and describing possible sources of clay.

Introduction

Linking ceramic products with raw materials has always been an aspiration of archaeometry. Comparing the elemental compositions of archaeological ceramics and geological clays can be used to this end, but should be interpreted cautiously due to the nature of the materials under investigation (post burial alteration of ceramics, variability of clay sources). Petrography is employed as an alternative or complementary technique, but such attempts can also be compromised (potential subjectivity of the researcher, non-distinctive lithologies in sherds or clays). Therefore, more precise and more diagnostic geochemical techniques, such as isotopic analysis, have recently been considered (Renson *et al.* 2013).

This study investigates the potential of the Sr and Pb isotopic systems to augment elemental, mineralogical and petrographic data in revealing the provenance of ancient ceramics. The ultimate goal is to identify the types of questions isotopic analysis can answer, the archaeological and geological contexts to which this is most applicable and, finally, to provide a guide for the interpretation of isotopic data, in the context of pottery provenance.

For the purposes of this publication, we present a short case study from the LC IIC – LC IIIA site of Alassa *Pano Mandilaris* (Hadjisavvas 1991; 1994). The isotopic results are used to explain the variability in Plain Ware fabrics, to identify potential areas as clay sources, and to investigate the links of Alassa with other settlements in South-West Cyprus.

Methodological framework

Following the thread: from clay to sherds to isotopes

The isotopic composition of clay is dictated by the elemental composition of the source rock, the initial isotopic composition of that lithology, and its age. Isotopes can, therefore, provide a more definitive signature than simple elemental analysis. As with the rock-clay connection, this fingerprint is carried over from clay to pottery and provides a strong link between ceramic groups and geographical regions (Carter *et al.* 2011; Pintér 2005: 25, 42, 128; Renson *et al.* 2013).

This evolution from source lithology to sherd is illustrated in **Figure 1a**. Steps a to c show the geological processes that lead to the creation of a clay bed, the final clay 'source' that a potter would have used. Understanding how these processes affect the isotopic signature of the clay source allows the discrimination of clay sources on a more detailed basis (Clauer and Chaudhuri 2011: 61-83). The second branch (d – f) includes all subsequent processes, both human induced (tempering, firing) and environmental (post burial alterations). Theoretically, the firing of clay (which is essentially low grade metamorphism) should not shift its bulk signature (Faure and Mensing 2005: 89-92). Post burial alterations, depending on their extent, can indeed alter the isotopic signature of a sherd, but their effect can be reasonably modeled using mixing equations (Langmuir *et al.* 1978: 381-383).

The most interesting step is the tempering of the clay by the ancient craftsperson or the presence of inclusions. It is the specific combination of the type of clay matrix with the type and relative quantities of inclusions that leads to the isotopic signature of a sherd (**Fig. 1b**). The bulk isotopic composition of any sherd is a combination of the signatures of these components, based on their individual abundances and their Sr and Pb

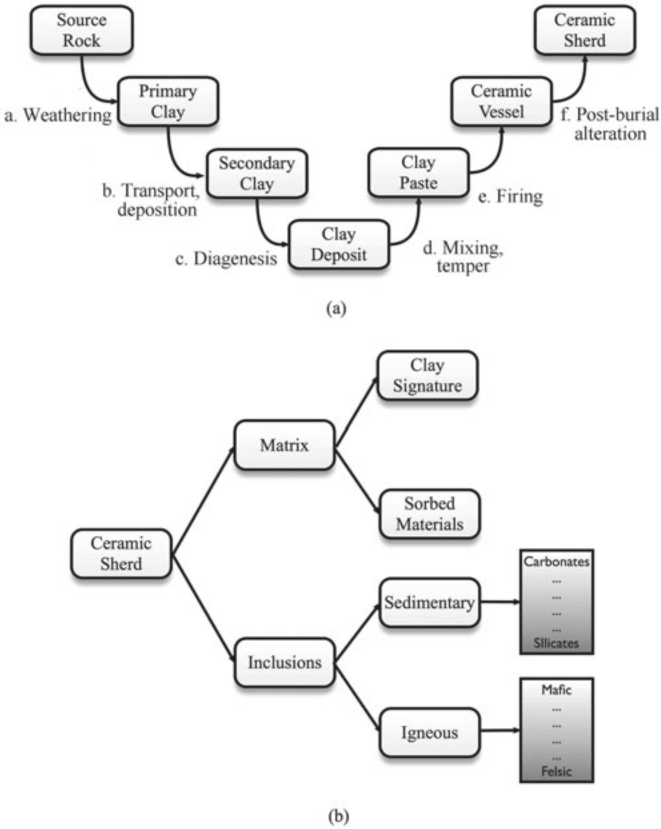

Figure 1. (a) All processes leading from source rock to ceramic sherd should be considered in terms of how they affect its final isotopic composition; (b) The connection between the petrographic fabric and the isotopic signature of a sherd derives from the combination of its components, with different isotopic compositions and Sr and Pb concentrations

concentrations (Faure and Mensing 2005: 76, 215). In a mix such as this, the component with the highest concentration of the relevant element will shift the total isotopic composition towards its own, according to mass balance effects (Langmuir *et al.* 1978: 381-383).

The Sr and Pb isotopic systems

Pb occurs as three radiogenic isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb, daughter products of ^{238}U, ^{235}U and ^{232}Th decay respectively, and one non-radiogenic isotope ^{204}Pb, used as the normalising isotope ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$). The isotopic signatures of Pb, in the form of these ratios, are distinctive for the four main geological terranes of Cyprus but are insufficient for the discrimination of individual sedimentary formations (Renson *et al.* 2013: 521-524). The combination of Pb with a second isotopic system could provide greater certainty. Pb is mostly hosted in the silicate fraction, as Pb^{2+} replaces K^{+} in K-feldspar (Faure and Mensing 2005: 256). Therefore, an isotopic system more sensitive to carbonates, the main fraction in many Cypriot sedimentary units, would be useful. Sr^{2+} replaces Ca^{2+} in Ca-bearing minerals like calcium carbonate, plagioclase and apatite, as well as K^{+} in K-feldspar, although less favourably (Faure and Mensing 2005: 75-76). Sr has one radiogenic isotope, ^{87}Sr, formed by the decay of ^{87}Rb, and three non-radiogenic isotopes, of which ^{86}Sr is used as the normalising isotope ($^{87}Sr/^{86}Sr$). In both the Pb and Sr systems, such radiogenic/non-radiogenic isotopic ratios of a sediment will be a function of the characteristics of its source lithology – initial isotopic composition, parent/daughter element ratios (U/Pb, Th/Pb, and Rb/Sr), age (Faure and Mensing 2005: 76-77, 218) – and any subsequent weathering or mixing.

Comparing petrographic and isotopic signatures

When comparing the petrographic fabrics and isotopic signatures of different sherds, there are only four possibilities to consider:

Case I: Same fabric, same signature

The signatures can be identical either because the isotopic compositions of all constituent materials are the same, or because the materials have such a combination of elemental concentrations and isotopic compositions that produce the same cumulative signature. The second scenario is statistically highly unlikely, since it is the same petrographic fabric that dictates the types and proportions of raw materials. Therefore, if the signatures of all the materials are identical, the sherds have likely originated from the same area or from different areas with the equivalent raw materials.

Case II: Different fabrics, same signature

If the cumulative signature of the raw materials is the same in all fabrics there must be a common component that shifts the signature in its direction because of its dominance in the fabric and/or its higher concentration in the element of interest (Sr or Pb). The following case study of the Alassa assemblage serves as an example for this effect.

Case III: Same fabric, different signatures

Here the fabric is the same so a common technological process was used, but with raw materials from different geological sources, leading to distinct isotopic signatures.

Case IV: Different fabrics, different signatures

The differences in the components of each fabric are significant enough to create distinctively different isotopic signatures.

A case study from Alassa *Pano Mandilaris*

The fabrics of Alassa

Alassa *Pano Mandilaris* (LC IIC - LC IIIA, 1340/1315 - 1125 BC) is located in the Kouris valley, south of the important administrative site Alassa *Paliotaverna*. Even though there is no direct evidence for pottery production at Alassa, the discovery of misfired sherds attests to the practice of pottery manufacture at or near the area (Jacobs *et al.* 2014). The ceramic assemblage from Alassa shows great variety, boasting 16 petrographic fabrics of both calcareous and non-calcareous base clays (Jacobs *et al.* 2014). **Figure 2** shows a visual summary of the characteristics of the 11 Alassa fabrics discussed in this publication. An important question, also the subject of Jacobs *et al.* (2014), is whether or

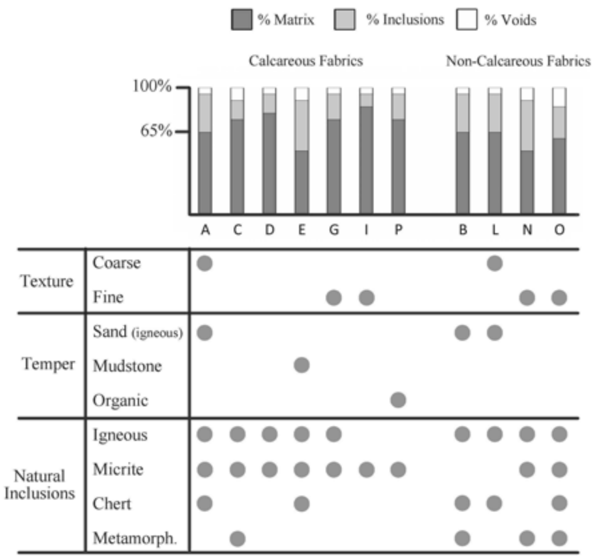

Figure 2. Visual illustration of the petrographic data for the Alassa assemblage

not these fabrics represent an equally large number of clay sources. Moreover, it is crucial to establish which material could have been produced at Alassa, which was imported and from where (Renson *et al.* 2013).

Geological setting

The local and regional geology of Alassa is shown in **Figure 3** (G.S.D. 1995). While the igneous Troodos complex was still submerged as a paleo-seabed, weathering of its igneous materials generated the bentonitic clays of the Perapedhi formation. The Moni mélange also includes bentonitic clays, mixed in this case with an assortment of siliceous sandstones, mudstones and serpentinites. The Kathikas mélange is similar in origin to the Moni formation, but as it developed in the SW Mamonia, it is dominated by those lithologies and not Troodos material. Sedimentation of carbonates began with the Lefkara marls and chalks, which include chert nodules within their lower horizons. The overlying Pakhna formation comprises marls, chalks and calcareous sandstones. The weathering and mixing of all these components led to the gravels, sands and clays of the Pleistocene deposits and the Holocene alluvial covers.

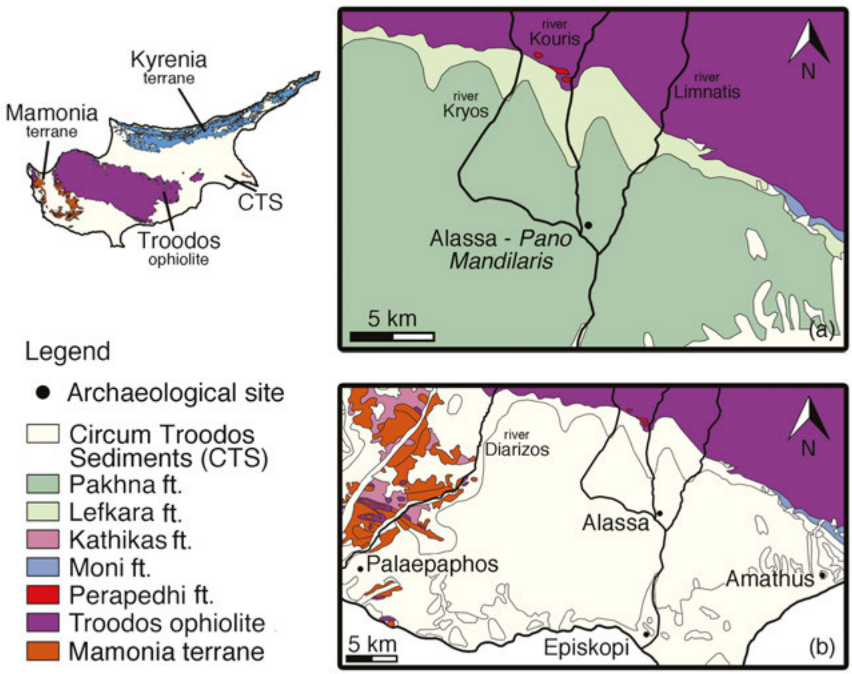

Figure 3. The geological environment of (a) the environs of Alassa *Pano Mandilaris* and (b) the wider region of SW Cyprus.

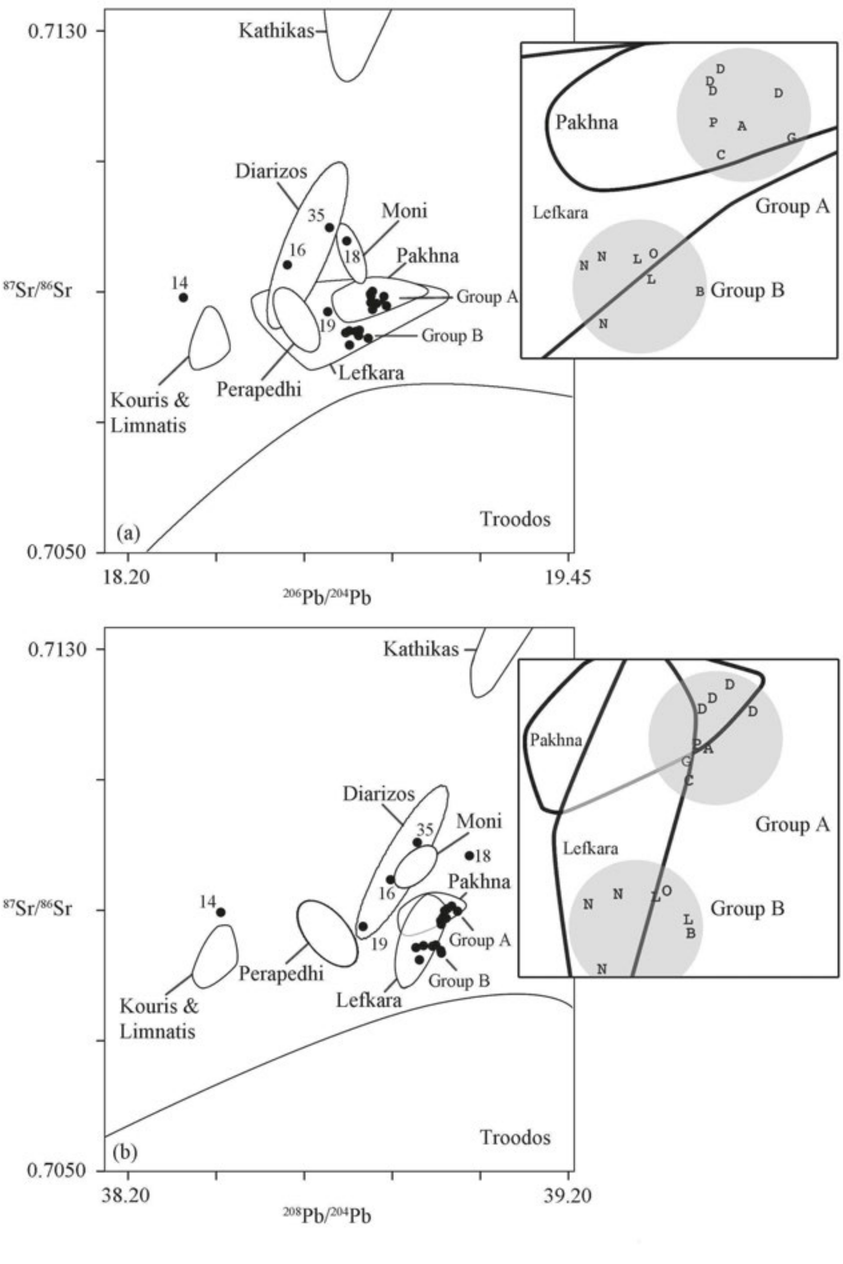

Figure 4. Isotopic biplots of (a) $^{206}Pb/^{204}Pb$ -$^{87}Sr/^{86}Sr$ and (b) $^{208}Pb/^{204}Pb$ -$^{87}Sr/^{86}Sr$ illustrating the relationship of the Alassa sherds to local geological formations. Sherd samples are shown as black dots with a diameter of 2σ (standard deviation values) on both axes. In the subplots letters A-N denote the petrographic fabric of the sherds, replacing the dots.

Isotopic data

Isotopic ratios – $^{87}Sr/^{86}Sr$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ – were measured using MC-ICP-MS, according to procedures described in Makarona *et al.* (2014). The Sr isotopic data used in this study are presented in Jacobs *et al.* (2014) while the Pb isotopic data were obtained from Renson *et al.* (2013). $^{87}Sr/^{86}Sr$ isotopic ratios are plotted versus $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ in **Figure 4**. Two well resolved groups stand out, Group A and Group B, comprising sherds from exclusively calcareous and non-calcareous fabrics respectively. This distinction is statistically significant as the distance between the two groups is well beyond analytical error. The individual sherds belonging in each group are presented in **Table 1**, while outliers are discussed below.

Locating potential clay sources

The petrographic descriptions indicate that the clay matrix is the dominant component in most fabrics, with abundances above 65% (**Fig. 2**). Therefore, the isotopic signatures reflect the matrix's composition, meaning that the two groups actually correspond to two distinct clay sources. The two sources are well defined, with limited internal variability compared to that of related geological formations. This apparent internal variability could be the result of tempering and/or sorting by the ancient potters. For example, the sherds of fabric D (calcareous, untempered) form a slightly distinct subgroup, while the remaining fabrics of Group A plot lower, due to their significant igneous inclusions content.

Group B corresponds to a non-calcareous clay source, which Renson *et al.* (2013: 254) relate to bentonites and weathered gabbros from the Troodos ophiolite. Indeed, weathered products from Troodos would exhibit higher $^{87}Sr/^{86}Sr$ ratios than the respective bedrock, as a result of the weathering process (Clauer and Chaudhuri 2011: 83-86). However, Group B does not correspond to either of the Upper Cretaceous Perapedhi or Moni bentonite deposits and so its source should be considered as the result of more recent weathering processes.

More information about the location of source B can be understood through investigation of the inclusions. Fabric N (non-calcareous, significant marl inclusions) is shifted towards the Lefkara isotopic field. The high Sr concentration of marl and its high abundance in these sherds pull them towards its own composition, hence identifying the micrite of fabric N as Lefkara material. This confines the location of source B near the margin between Troodos and the Lefkara formation. Moreover, the identification of Perapedhi mudstones as temper in AL 19 (see next section) means that the Alassa potters were exploiting this formation. This final clue indicates that the non-calcareous source

Isotopic Group	Sample	Shape	Ware	Fabric
Group A	A 17	large closed	Plain	A
	A 13	jug	WPWM III	C
	A 2	wide bowl	Plain	D
	A 22	basin	Plain	D
	A 27	jug	Plain	D
	A 30	basin	(undefined)	D
	A 20	jug	Black Slip	G
	A 1	basin	Plain	P
Group B	A 33	large closed	Plain	B
	A 11	jug	Coarse-cooking	L
	A 12	jug	Coarse-cooking	L
	A 15	jug	WPWM III	N
	A 23	jug	Plain	N
	A 28	jug	PWWM II	N
	A 26	jug	PWWM II	O
Outliers	A 18	large closed	Plain	E
	A 19	large closed	Plain	E
	A 14	bowl	WPWM III	G
	A 16	jug	WPWM III	I
	A 35	bowl	WPWM III	I

Table 1. Description of the Alassa sherds, after Jacobs *et al.* (2014), categorised according to the groups emerging from isotopic analysis

should be at the interface between Troodos, the Perapedhi outcrops and the Lefkara carbonates, about ten kilometres North of Alassa, along the Kouris River.

The calcareous source for Group A corresponds to the $^{206}Pb/^{204}Pb$ composition of both Lefkara and Pakhna carbonates. However, the $^{208}Pb/^{204}Pb$ signature and the fineness of the natural igneous inclusions of Group A indicate that this source is more likely to be located within the Pakhna formation, which is further away from Troodos than Lefkara. The presence of chert and igneous inclusions in the clay suggest that the source is actually reworked sedimentary material along the Kouris or Limnatis Rivers.

Outliers or interactions?

The majority of the Alassa assemblage examined here (fifteen out of twenty sherds) can be allocated to one of the two isotopic groups described above. In order to provide an explanation for the provenance of the remaining sherds, characterized as 'outliers' (**Table 1**), further investigation is required.

Sherd AL-14 was described as originating outside of Cyprus, based on its very different Pb isotopic composition (Renson *et al.* 2013: 525). Even though it indeed lies well off the main Cyprus field it is still in close proximity to the Kouris and Limnatis river sediments. Therefore, local provenance cannot be ruled out. Extensive chemical weathering may result, under certain conditions, in the loss of radiogenic isotopes ^{206}Pb and ^{208}Pb, leading to lower isotopic ratios (Faure and Mensing 2005: 229). This could explain the low signatures of the river sediments (highly weathered material) and that of AL-14 (described as showing post burial alterations); but further investigation is necessary. This case highlights the ambiguity that may arise during the interpretation of isotopic data.

A more interesting issue is the displacement of the mudstone-tempered sherds, AL-18 and AL-19, in different directions, which has been attributed to different sources of mudstone. Our analysis confirms that the mudstone in sample AL 19 derives from Troodos (Renson *et al.* 2013: 525), and we have identified it more specifically to the Perapedhi formation. The ^{206}Pb/^{204}Pb - ^{87}Sr/^{86}Sr composition of AL 18 initially suggests that it corresponds to the Moni mélange. However, inspection of the ^{208}Pb/^{204}Pb - ^{87}Sr/^{86}Sr data (**Fig. 4b**) shows that instead, AL-18 is a mix of calcareous clay and Kathikas mudstones, definitively relating the sherd to the Mamonia terrane, as noted also by Renson (2013: 525). Sherds AL-16 and AL 35 also have clear Mamonia signatures, connecting fabric I to the Diarizos river sediments. These three sherds are, thus, considered imported material from SW Cyprus.

Discussion

The above assessment supports the hypothesis that the majority of pottery from Alassa *Pano Mandilaris* was produced locally (nine out of the twelve fabrics outlined in Table 1) and describes the possible local clay sources more precisely. The use of a calcareous clay - Group A (fabrics A, C, D, G and P) - is expected, as it is abundant around the site. On the other hand, the systematic use of a less accessible non-calcareous source for the production of wares belonging to Group B (fabrics B, L, N and O) can be attributed to its suitability for manufacturing specialised vessels. Indeed, Group B includes cooking pots and thin-walled PWWM II sherds, representing wares whose long-term use would require specific thermal and / or mechanical properties. This source, however, is simultaneously used for vessel shapes produced with the calcareous clay as well (WPWM III and Plain ware, **Table 1**). This reinforces the argument for the parallel existence of potters /

workshops following different traditions, but producing overlapping sets of commodities, within the same socio-economical context (Jacobs *et al.* 2014). Moreover, the local provenance of AL-19 and the exotic nature of AL-18, AL-16 and AL-35 demonstrate two modes of interaction in SW Cyprus; shared technological know-how (a common mudstone-tempering tradition) at different sites (Jacobs *et al.* 2014) and the exchange of finished products.

Concluding remark

The particularity of isotopic data lies in the multiple layers of information they represent, if interpreted correctly. This is both a gift and a curse; relying on a 'few' isotopic values to describe sources and mixings seems easy but in reality is quite complex and opportunities for mistakes remain behind every data point. Nevertheless, the work that this publication represents is designed to ultimately serve as a guide, identifying these exact issues and providing solutions.

Acknowledgements

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A TECHNICAL APPROACH TO ATTIC-POTTERY PRODUCTION DURING THE HISTORIC PERIOD: RAW MATERIALS AND THE BLACK GLAZE

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Abstract

This study addresses a longstanding archaeological question regarding the clay-sources in Attica used for the clay-paint on BG pottery of the Historic period. The aim is to achieve a direct analytical comparison of archaeological BG ceramic sherds with modern BG specimens, produced in the laboratory following the original process of the iron-reduction technique. The analytical methodology is mainly comprised of μ-PIXE, μXRF/pXRF and SEM-EDS used on selected samples in order to characterise the microstructure of the glaze, related to the particle size and the clay-paint refinement processes. This is the first time that ancient and modern BG ware, produced with the same process, has been compared in terms of the glaze chemical composition at the level of trace elements.

The selected archaeological samples (dated between the 6th and 4th centuries BC) have all been recently excavated and are well-documented fragments from the areas of the Acropolis and Keramikos in Athens, Greece. The laboratory BG specimens were produced from clay-soil samples collected in the region of Attica during geological surveys. The necessary information for these landscape investigations was obtained from readily available contemporary historical, topographical and geological maps, in combination with image-processing software.

The analytical data and the macro/micro examination of the contemporary BG samples indicate a conditional compatibility between archaeological and laboratory specimens that depends on specific properties of the clay-paint. This outcome suggests that both the selection of the clay source and the preparation process of the clay-paint in antiquity required specialised technical knowledge in order to achieve a high quality BG. This hypothesis may contribute to theories on the organisation of pottery production in classical antiquity.

Introduction

The technique for producing black decoration patterns and figures, referred today as the "iron-reduction technique" (Noll *et al.* 1975: 604), dominated the ceramics of the Mediterranean for 2500 years, from the Bronze Age until the 1st century AD, when it was gradually abandoned. However, the best-known pottery to be produced using this technique is that dated to the 6th and 5th centuries BC. The black and red figured pottery produced in Attica and characterised by the deep "blue-black" colour of the "glossy" glaze is widely known for the high quality in production, fineness along with technological innovation. Attic-ware is synonymous with the "iron-reduction technique" that involves three different stages of firing under oxidising, reducing, and oxidising kiln atmosphere conditions. The process followed for the decoration of this pottery uses an illitic colloid clay suspension, low in CaO and rich in iron oxides, for the decoration of the unfired clay-body, which is derived of different clay in terms of the mineralogical and the chemical composition. The ORO firing cycle starts with an oxidising stage up to ~920°C (900°C>Tmax<950°C), during which the body and the clay-paint layer become red due to the formation of hematite (Aloupi-Siotis 2008:118; Aloupi 1993:101). At this stage vitrification of the clay-paint is initiated. In the following reducing stage, the hematite transforms to magnetite, and the body and clay-paint turn to black. During this stage, the clay-paint layer vitrification is accelerated, due to its fine clay particles and low CaO, while the calcareous body retains a spongy-like microstructure. The temperature during reduction decreases due to oxygen absorption and incomplete combustion of the wood. At the final oxidising stage, the well-vitrified clay-paint layer remains black, while the porous body re-oxidises to brick red (Tite *et al.* 1982: 112-120).

This technique has been studied in detail through the application of specialised physico-chemical analytical methods and experimentation (Aloupi 1993: 63-114). Nevertheless, a series of archaeological issues and questions regarding the integration of raw material procurement and processing in the broader social context of pottery production still remain.

Concerning the impact of local availability of natural resources on the choice of the location of workshops, Stissi (2002: 44) notes that the lack of available studies on the location of raw material resources limits the formulation of arguments regarding production locales. Furthermore, he believes that the abundant availability of natural resources has a determining role in the choice of workshop location (Stissi 2002: 43). Attica had numerous clay resources suitable for ceramic production to which the Athenian potters had access (Higgins and Higgins 1986: 26). Several clay-deposits were located near Athens, for instance in the suburb of Amarousi, which was used until recently, and in the ancient Cape Kolias (Higgins and Higgins 1986: 26). The ready availability of clay in the area of Attica is a result of geological changes during the Neogene period leading to the reformation of the land and faulting that produced basins which were then flooded, filled with sandstone, shale, limestone and clay (Papanikolaou *et al* 2004: 816-825; Higgins and Higgins 1986: 26). Although, most clay provenance studies have used elemental analyses (*cf.* Jones 1986: 15-27), Papadopoulos (2003: 20) claims that the mixing of clay practiced by the ancient potters in order to improve consistency may complicate the interpretation of such elemental analyses. Day *et al.* (1999: 1025–1036) also commented on this possibility by comparing the correspondence between the chemical and mineralogical compositions of stylistic and petrographic ceramic groups from the Early Bronze Age of Crete. They highlighted the importance of the geographical scale of analysis and the relationship between provenance and technology when using elemental analyses for pottery provenance studies.

This research addresses a longstanding archaeological question regarding the location of the clay-beds or clay-deposits in Attica, focusing on ferruginous clay-soils the physical properties of which are appropriate for the decoration of BG ceramic production. This question becomes particularly relevant for the reexamination of a longstanding view that the final clay-paint used for the decoration of BG pottery was a result of clay-mixing and the use of additives, such as ash or urea (Noble 1960: 307-318). On the contrary it seems that the clay suspension is derived from a fine illitic clay with the appropriate physicochemical properties (Aloupi-Siotis 2008: 118). This calls for the examination of the local clay sources in Attica and particularly an analytical investigation into the physico-chemical properties of the locally available Attic clays. Aloupi-Siotis (2008: 120) has suggested the use of at least one clay deposit located in the plateau near the borders of Attica and Boeotia (Panakton area), while clay samples from Kalogreza and Pikermi were tested in the past with very poor results (Aloupi 1993: 75-95). Moreover, the difficulties to produce a colloid clay-suspension in water without additives raise several questions, such as: a) was the raw material collected *in situ* from a "readymade" clay-suspension produced naturally in pools of rainwater, and b) was the clay-soil for the production of the clay-paint processed in specialised workshops? The results may contribute to the completion of the puzzle concerning the organisation of ancient pottery workshops, by providing information about the missing technical parts of this ceramic technology in antiquity.

This ongoing work focuses on the detailed analysis of the Attic BG aiming at a comparative technological and compositional study of archaeological BG pottery samples and BG specimens produced in the laboratory, especially concerning trace element composition. Throughout the project, specific efforts were made to apply a non-destructive methodology involving the application of micro-analytical techniques (μ-PIXE and pXRF) for the quantitative and qualitative analysis (major, minor and trace elements) of the BG layer on both archaeological and laboratory specimens. Powder μ-XRF analysis was applied on geological samples in their natural form and different clay fractions, and SEM-EDS for the examination of the BG layer microstructure. Furthermore, the raw materials and the preparation processes of the clay-paint were studied in detail and provided new evidence about the procurement and the processing of the clay-paint used in the production of BG pottery.

Materials and methods

Archaeological specimens

Forty-six archaeological samples dated to the 6th-4th centuries BCE were examined and analysed in the framework of this project. The sample included fragments of Black-figure, Red-figure and BG pottery, including subdivisions such as the Hellenistic west slope style. All selected samples were recovered in Attica; they either come from recent excavations near the Acropolis in view of the construction of the new museum (Eleftheratou 2006:7-21; 2009:6-10) and near Keramikos during the METRO excavation works (Baziotopoulou-Valavani and Tsirigoti-Drakotou 2000: 264-389) or from Pallene and Raphina during the construction of the Attica Tollway (Vargemezis *et al.* 2009: 325-330). Plus, four fragments with strong technological similarities, two BG specimens that are possibly Campanian or Attic imports, and two terra-sigillata sherds from excavations in Badalona, Spain, were included in the study for comparison.

Collection of raw materials

Before proceeding to a detailed study of the clay sources in Attica, it is essential to review the fundamental criteria for the selection of a clay-soil source, suitable for the production of the clay-paint that will eventually lead to a glossy BG, with no cracks or flaking on the surface. In order to achieve this result, the raw material should be a ferruginous, low calcium, illitic clay-soil (Aloupi 1993: 107) for the following reasons:

a) the iron oxides are responsible for the black colour (*cf.* Jones 1986: 798-803);

b) the presence of calcium content especially in the form of calcium-carbonate leads to the production of CaO and carbon-dioxide during the vitrification process. Then, the release of carbon-dioxide creates voids within the glaze that compromise the colour and affect the microstructure of the paint layer (Aloupi 1993: 107);

c) the presence of potassium (K) in illitic clays facilitates the sintering of the clay particles during the vitrification process (*cf.* Jones 1986: 795-809), at the range of temperatures between 850°C-920°C;

d) illite is the only clay mineral whose dispersion in water is not affected by pH (Goldberg *et al.* 1991:378), and may thus allow spontaneous dispersion of a clay-soil in water. In that regard, in this colloidal system no use of deflocculants or dispersing agents is needed.

After carefully examining potential raw material resources using a combination of geological, topographical, archaeological information and Google Earth images, the clay samples were collected at depths of ~15cm from the surface. Moreover, the accumulated personal practical knowledge derived from experiment and observation during the preparation of the clay-paint constituted an equally important factor for targeting clay-areas on the maps.

Raw material sampling was concluded in three individual stages. During the first stage of clay sampling, potential clay resources already known from earlier studies were re-examined; these include the Panakton plateau near the borders between Boeotia and Attica, and a small area in the Mesogea basin. During the second stage of clay sampling, fieldwork was focused on the Mount Parnes and the Mesogea basin, while the third and last part of raw material resource examination took place on Mount Hymettus, and within the city of Athens, in areas adjacent to the banks of the Ilissos River (**Fig. 1**).

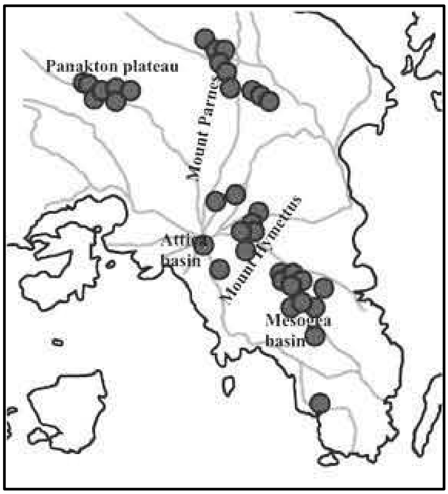

Figure 1. Sampling spots superimposed on the Attica map. The lighter lines indicate the ancient roads - The map is a mix of the contemporary map of Attica and the "Map of Attica 480 B.C" (Adapted from the Historical Atlas by William R. Shepherd (1911), University of Texas).

Laboratory samples

The thirty-five clay-soil samples collected were processed to prepare the colloid clay-suspension in water at the Thetis Authentics preparation laboratory according to the procedure described by Aloupi (1993: 75-113). The refinement process involves the stages a to e (below):

a) Soaking of the clay-soil in distilled water or rainwater, for a prolonged period of time in order to prepare it for the removal of any organic material (S for future reference);

b) Sieving of the clay-soil suspension to remove large aplastic inclusions and the coarse organic material such as plant remains. The remained coarse material was collected for examination (S0 for future reference);

c) Treatment in an ultra-sound bath for 30 mins, in order to reduce particle size;

d) Decantation of the clay-water system and separation of the finest fraction with ESD ($<0.3\mu m$). ESD was estimated according to Stokes' law. The remaining coarser fraction was also collected (S1 for future reference);

e) Concentration of the fine clay-suspension by evaporation to receive a clay paint (S2 for future reference);

The resulting clay-paints were then applied on flat clay briquettes measuring 1cmx1cmx0.5cm in order to assess the resulting BG mechanical and optical properties such as crazing, adhesion and colour. Also, in order to assess their adequacy in vase decoration, the clay-paints were applied on a model clay-body surface, with projections recesses and variable curvature, following the black figure style with incised lines and wide areas covered with clay-paint. The clay used for the formation of all substrates consisted of a single type of commercial clay (Stephanakis, Herakelion Crete), resembling the ceramic body of archaic and classical Athenian ware (*cf.* Jones 1986: 797). Finally, all specimens were fired following the ORO cycle at firing maximum temperatures between 875-950°C at the specially designed electrical kiln at the workshop of Thetis Athentics. The application and firing steps allowed the observation of the clay-paint "behaviour" in terms of the effect of tangential shrinkage coefficient on the background clay, in all the phases of ceramic production and different firing temperatures.

Analytical methodology

The μ-PIXE technique combined with a scanning ion microprobe offers the possibility to analyse the BG layer alone (10-40μm thickness (Aloupi 1993:67)). The analysis was performed at the ATOMKI Accelerator Centre (Institute of Nuclear Research of HAS, Debrecen) in Hungary. Fifty archaeological fragments and thirty-nine laboratory BG specimens were analysed (four BG-specimens from previous THETIS' production were added to the newly produced BG-samples (Aloupi-Siotis 2008: 118). μ-XRF analysis was performed on 120 pressed powder pellets prepared from different clay fractions that separated during the clay-paint refinement process. A customised version of the ARTAX portable μ-XRF spectrometer (BRUKER-AXS) was used for the analysis. An SEM equipped with an EDS microanalysis system (FEI Quanta Inspect D8334) was used for the examination of the microstructure of the laboratory BG samples in polished sections (BE mode) and freshly fractured specimens (SE mode).

Results and discussion

BG laboratory reproductions

The thirty-five laboratory specimens made of different clay-paints have produced dark coloured layers of different quality: two specimens with a glossy black colour and a particularly smooth surface; eleven have a hue colour ranging from black to black-brown; ten have the same hues range with the previous cluster and sporadically developed cracks to a different extent; two specimens are reddish-brown in colour and do not present any indications for vitrification and finally, ten have developed a crazing effect on the entire surface. The last two groups of the clay-paints are considered as not applicable for the decoration of BG pottery due to their optical results after the firing.

SEM-EDS

The final glaze quality of each geological sample after the firing and the changes observed on their surface correspond to the micromorphology of each glaze. SEM analysis on fresh-fractured sections was instrumental in testing the correspondence between macroscopic observations and the microstructural characteristics of the samples. For example, two samples, AGDMT05-BG (**Fig. 2a)** and PRN16-BG (**Fig. 2b**) present a vitrified, dense and uniform layer with few voids or bloating pores. In both samples, a thin glassy layer on the outer surface is visible, which may be responsible for the characteristic glossy appearance of the ware. Similar behaviour has been observed on ancient Attic BG samples (Aloupi 1993: 173; Maniatis *et al.*1993: 26-33), verifying, thus, a successful reproduction of the process. **Figure 2c** shows an SEM photomicrograph of a polished section of DRV04A-BG-sample in BE mode; the bright particles distributed in the entire BG layer

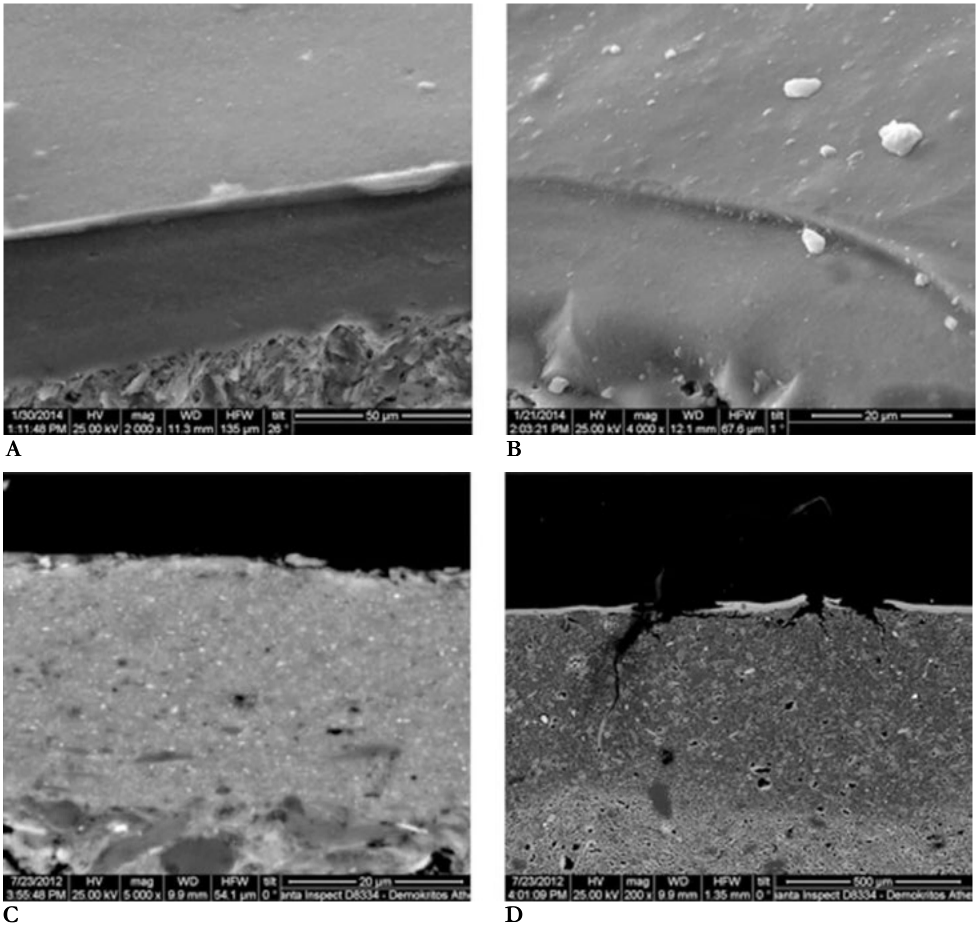

Figure 2. (a-b) SEM photomicrographs of freshly fractured surfaces (SE mode). (c-d) SEM photomicrographs of polished sections (BE mode).

are expected to be the nanoparticles of magnetite formed *in situ* during firing, which are responsible for the glaze colour. The BG layer is again dense with few spherical bloating pores (<1 μm) and elongated voids similar to most archaeological BG samples (Aloupi 1993: 66). However, despite the vitrification of the clay-paint layer and its uniform micromorphology, there are extensive cracks (**Fig. 2d**) on the surface, which were formed during cooling, most probably due to differences in the shrinkage coefficient between the BG and the clay-body. These observations further narrow the criteria for the selection of appropriate clay-soils and suggest extensive experimentation with material testing in antiquity.

μ-XRF

A hundred and twenty specimens of three different clay fractions (S0, S1, S2) have been analysed so far in the framework of this ongoing research[1]. It is interesting to note that although there are some common features amongst the different geological samples, the

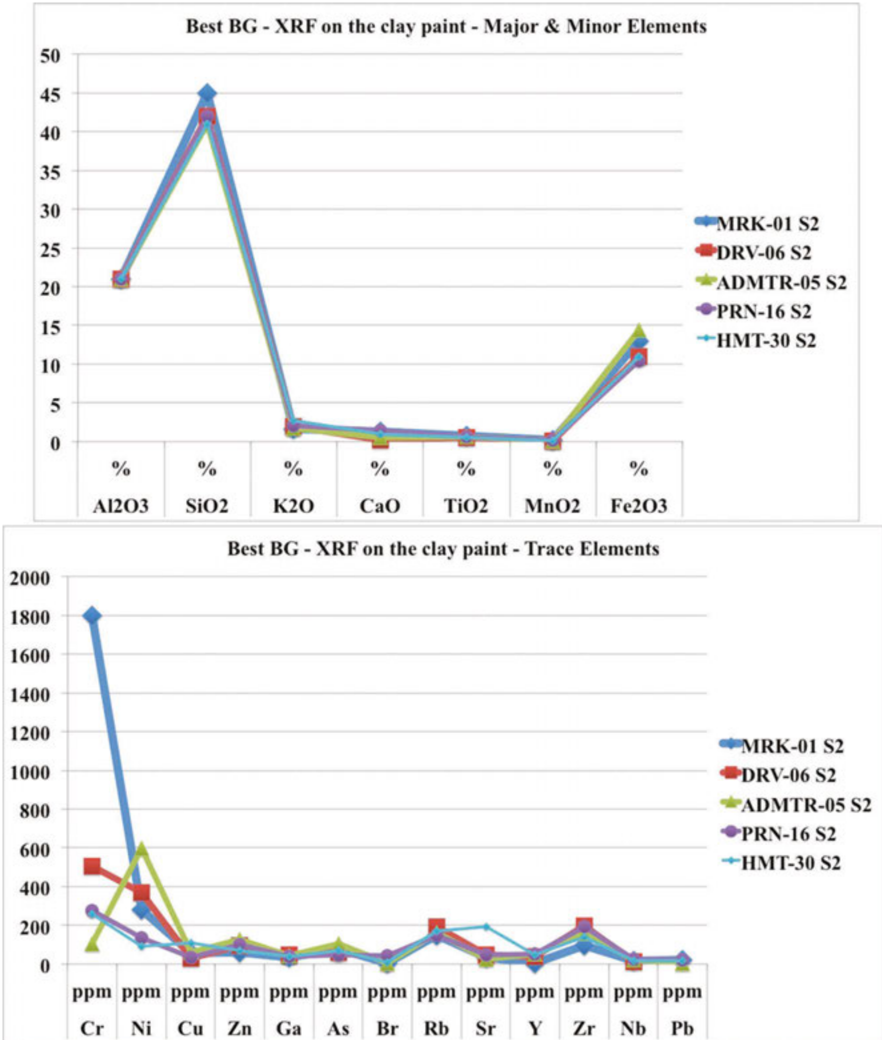

Figure 3. μ-XRF elemental results with respect to major, minor and trace elements.

[1] The analysis of the original geological sample i.e. the clay-soil (S) is still in progress.

compositional patterns of the different fractions-set vary for every element. The comparison of the analysis of the finest clay fraction (S2) however, revealed five samples with similar elemental composition in terms of major, minor and trace elements, while at the same time producing the best quality BG's so far. These clay-paints have been produced from clay-soils originating from four different areas: two are from Panakton plateau (ADMTR05, DRV06), one from Mount Parnes (PRN16), one from the mount Hymettus (HMT30), and one from Mesogea basin (MRK01). The graph of **Figure 3** shows the composition of the finest clay fraction (S2) for the geological samples referred to above. The low value CaO (<1%) in all of them correlates well with the best quality macroscopic characteristics of the BG. Variations appear in some trace elements i.e. Cr, Ni, Sr and Zr but the most interesting observation is that, the only discriminating element is Sr in the composition of the samples from Mounts Parnes and Hymettus.

μ-PIXE

The PCA analysis of the μ-PIXE analytical data revealed several clustering patterns amongst the ancient and laboratory BG samples, with respect to their trace element composition. In the scatter diagram in **Figure 4**, one main group is formed, consisting of fifty archaeological BG samples and thirty-nine laboratory-made BG samples; it is important to note that the three of the best quality laboratory-made BG samples from Panakton plateau and Mesogea basin, are consistently compatible with the Attic BG group in all different combinations of principal components. It is thus reasonable to suggest that the clay-soils from these two areas could have been used in antiquity for the production of the BG clay-paint.

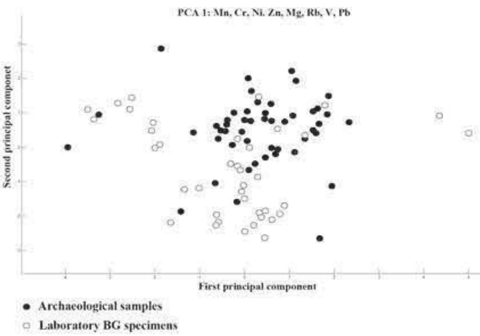

Figure 4. PCA scatter diagram of Mn, Cr, Ni, Zn, Mg, Rb, V, Pb, based on μ-PIXE results.

Conclusions

This work examines several constraints and prerequisites for the procurement of raw materials in the production of the clay-paint used for the production of the black glaze on Attic pottery. In order to compare and assess several competing hypotheses concerning the nature of the raw materials needed to produce Attic BG decoration, this project applies a comparison between BG produced in the laboratory and archaeological BG pottery samples. Raw materials collected from various regions of Attica were prepared here and then analysed alongside actual archaeological examples. Through this approach it was possible to determine the legitimacy of the assumptions being made in previous studies (Aloupi-Sioti 2008: 120) thus eliminating incorrect interpretations. Based on the postulation that the ancient craftsperson was guided by their previous experience, through experimentation, in the selection of raw materials, this research suggests that high quality BG pottery was the result of a combination of careful raw material selection and the subsequent application of known clay processing methods.

Overall, the analytical results have indicated that the production of the clay-paint for the BG requires the use of a clay-soil, which is not the same as the one used for the vessel body. Moreover, it was possible to demonstrate the existence of certain clay-soil deposits in Attica that were suitable for the procurement of the appropriate raw materials for the production of the clay-paint. According to macroscopic results, five different clay-soil locations have been identified as adequate to produce good qualityBG: these correspond to four different areas in Attica and are located at Panakton, Parnes, Hymettus and Mesogea. Furthermore, as determined by μ-PIXE results, four laboratory BG samples from the regions of Panakton and Mesogea group well with several archaeological BG samples. It is plausible that numerous other locations in regions that were not explored could have deposits of clay-soils that can be used for the production of the BG clay-paint. In all cases however, the choice of location would have required experimentation combined with experience accumulated from previous practice. In addition, the subsequent preparation of the clay-paint with the use of these selected clay-soils was proved to be a lengthy and time-consuming process. It should be noted that the quantity of clay-paint produced was very small in comparison to the large quantity of the raw material needed, as well as the human effort, for its production. These observations, when combined with the massive production of the BG Attic ware, suggest that the production and distribution of clay-paint constituted a separate trade that supplied the large number of pottery workshops distributed throughout Attica.

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MECHANICAL AND THERMAL BEHAVIOUR OF FUNCTIONAL CERAMICS: THE INFLUENCE OF FIRING AND TEMPER ON THE IMPACT RESISTANCE OF ARCHAEOLOGICAL CERAMICS

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Abstract

This project focuses on the technology of utilitarian ceramics and includes methodological developments concerning the role of raw material composition on physical properties of archaeological ceramics. The paper presents results of an experimental study which examines the influence of manufacturing parameters on mechanical properties of clay-based ceramics. The influence of firing temperature, amount and grain size of temper on a ceramic's response to dynamic loads and how this compares to static loads are examined. Fracture strength under quasi-static loading increases with increasing vitrification, and decreases with increasing amounts and size of aplastic inclusions. In contrast, while the presence of aplastic inclusions does reduce impact resistance, the amount and grain size of aplastic inclusions do not play a significant role for impact resistance, both in terms of impact strength and fracture energy. The results highlight the importance of carefully considering the potential origins of mechanical stresses when assessing the affordance of a ceramic vessel.

Introduction

Throughout much of antiquity and until very recently, ceramics were employed widely, on an every-day basis, for many different functions. This is due to the widespread availability of raw materials, but also to the material properties of the finished products. Pottery is durable, heat resistant, as well as strong and tough enough to survive frequent handling. The ability of archaeological ceramics to withstand mechanical (or thermal) stresses during use is frequently argued to be important for the selection of particular manufacturing practices. Different demands are placed on storage jars, transport vessels, cooking pots, or pyrotechnical ceramics. Thermal properties are also important for pyrotechnical ceramics or cooking ware, while for transport vessels their ability to resist to mechanical stresses is essential. Mechanical stress can be static stress, arising e.g. from weight loads, but impact stress, arising e.g. from vessels moving against each other during transport, is also important. It is important to note that ceramics gain their characteristic properties during manufacture. Different steps in manufacture (e.g. clay refining, clay mixing, addition of temper material, firing conditions), influence the texture and microstructure of the ceramic material, and consequently the mechanical properties of the finished product. For this reason, one of the main concerns of the study of mechanical properties is the assessment of the influence of ceramic manufacture on the physical properties of clay-based ceramics.

Mechanical (and thermal) properties of clay based ceramics and the investigation of whether they have been the driving force behind potters' technological choices have attracted research interest and debates for quite some time. Shepard (1956) provides probably the first discussion of the potential importance of strength measurements for archaeological ceramics. A paper by Braun (1983), which emphasised that pots are made to be used for certain activities and that their morphology and composition would be constrained by their intended contexts of use, gave the impetus to an increased preoccupation with the subject. Subsequent publications examined how different manufacturing technologies influence the material properties, and explained technical variation in the manufacture of utilitarian ceramics in terms of their impact on material performance (e.g. Steponaitis 1984; Feathers and Scott 1989). However, it has also been noted that the factors affecting potters' choices are many and varied, and the social context of production and consumption must be considered (Sillar and Tite 2000). In this sense, rather than explaining technological choice, the study of physical properties provides a baseline against which the role of cultural and other factors can be examined.

Pottery vessels are exposed to a multitude of stresses in daily use. The ability to retain their contents and to survive loads without losing structural integrity is a prerequisite for functional ceramics. When considering mechanical stresses in archaeological ceramics, their response to static loads is usually examined (e.g. Tite *et al.* 2001). The response of a material to static loads is an indication of its behaviour when exposed, for example, to weight loads, such as those that arise when piling ceramic vessels for transportation. A different case is the response of a material to dynamic loads, when forces are applied over a very short time period and a material is forced to absorb energy very quickly: this is referred to as impact. Fracture occurs - often in a quite spectacular way - if a material is not able to absorb the applied energy.

To assess the behaviour of a material under impact, pendulum or drop weight tests are usually employed. Pendulum impact tests are used, for example, in the quality assessment of modern ceramic tableware (ASTM 2011), using a series of increasing impacts. When using a single blow, the difference in the potential energy of the pendulum, before and after breaking a test specimen, can be used to calculate the so-called impact resistance. When they are instrumented, pendulum tests provide information about the load time history of the sample during the test. Such load-time curves provide information on maximum loads and allow the assessment of fracture energies.

Impact has so far been largely neglected when examining mechanical performance of archaeological ceramics. Exceptions include Bronitsky and Hamer (1986), who used a pendulum type tester to study the influence of temper materials on impact resistance. However, inherent methodological problems in their setup (some of which are addressed in Feathers 1989) resulted in irregular results. Mabry *et al.* (1988) developed a falling weight impact tester to assess impact, but their setup does not provide information on initiation and propagation of fracture. Finally, Pierce (2005) set out to assess the influence of surface topography on what he refers to as 'impact strength' on whole vessels. Although demonstrating some creativity in experimental setup (his 'pendulum test' involves the swinging whole pots with a string against a pillar), no meaningful results are produced both due to flawed experimental setup and inadequate experimental control.

What follows is a presentation of the first results of an experimental study, which examined the influence of manufacturing parameters on mechanical properties of clay-based ceramics, in particular their response to dynamic loads and how they compare to static loads.

Response of ceramics to mechanical stresses

When examining mechanical stresses, both the initiation and propagation of cracks should be considered. Two important terms are strength and fracture energy. Strength is related to the maximum force than can be applied to a material without a crack initiating. This is, however, not necessarily equivalent to overall failure. A vessel will remain intact even if a crack starts, if there are mechanisms that can stop this crack before it propagates through the material. The second term is fracture energy. This is the energy that is required to both initiate and propagate a crack through the material. Much of our knowledge on the mechanical capability of pottery is based on tests performed under slow bending, which are more routinely performed for these materials than impact tests. The former provide information about how a ceramic will react when exposed to a static load, as the material is allowed to absorb the load slowly and over an extended period of time (Tite et al. 2001).

Experimental procedure

Mechanical tests are destructive and require repetition on several samples. Testing of experimental briquettes is preferred over tests on archaeological material, also in view of determining the influence of selected manufacturing parameters. In order to investigate the influence of several parameters on ceramic performance under impact, and to assess how this compares to their response under slow loading, a series of experimental briquettes was manufactured.

Materials and processing

Test briquettes (*c.* 120 x 70 x 10mm) were manufactured with a calcareous clay from Pikermi (Attica, Greece). The fraction with a particle size of <30μm was mixed with water and different amounts of quartz sand to form ceramic briquettes. Quartz sand with an average grain size of 750μm (fraction 0.5-1mm) was added as 10%, 25% and 40% by dry weight. The influence of temper size was also assessed for briquettes with 25% temper fired to 950°C. Additional briquettes were tempered with quartz sand of average size of 94μm (fraction 63 - 125μm), 187μm (fraction 125 - 250μm), and 375μm (fraction 250 - 500μm). Briquettes with 0% and 25% temper material were fired to 800°C, 950°C and 1150°C to examine the influence of firing conditions, while briquettes with 10% and 40% were fired to 950°C. Firing took place with a heating rate of 200°C / h and a soaking time of one hour in air. The large surfaces of the fired briquettes were ground parallel and cut into test bars of *c.* 10 x 10 x 70mm for material tests.

Mechanical testing

A. Fracture strength under slow loading

The TRS was determined by standard methods (BSI 2002) employing three-point bending tests on bars of c. 10 x 10 x 70mm. Measurements were carried out on an INSTRON 1195 universal testing machine, at a constant loading rate of 100μm / min. The load as a function of displacement was recorded for every specimen. For every kind of material (corresponding to a single set of manufacturing parameters) TRS was determined by taking the mean of three measurements. After final fracture, the fracture area was examined visually with the aid of a stereomicroscope. Results from test bars with macroscopically identifiable flaws in the fracture surface were excluded from the determination of the mean.

B. Impact strength

In order to test ceramics for their behaviour under impact, a custom-made instrumented pendulum tester, which had been developed at the Advanced Ceramics Laboratory of the N.C.S.R. "Demokritos", was employed (**Fig. 1**). Loading rates are high under impact, and fracture of the specimens occurs over a very short time. Therefore, the setup was instrumented by equipping the hammer with a nanostructured pressure sensor with enhanced time resolution. After calibration, information was recorded about the load-time history of the sample during the tests, allowing the assessment of both initiation and propagation of cracks. Measurements were carried out with a loading rate of 30m/s.

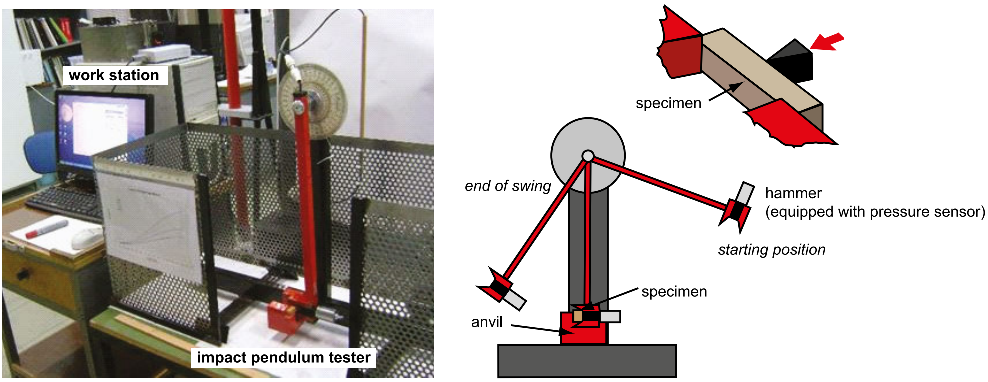

Figure 1. Custom made pendulum impact tester.

Results and discussion

A. Response to quasi-static stresses

Fracture strength initially increases with firing temperatures, and then between 950 and 1100°C it remains stable (**Fig. 2a**). This development is expected and connected to the increasing bonding within the matrix. There is very little vitrification in specimens fired to 800°C, while at higher temperatures vitrification is extensive and typical of calcareous ceramics fired to these temperatures (**Fig. 2b**). For increasing amounts of temper, strength clearly decreases (**Fig. 2c**): the addition of 10% of quartz temper reduces TRS by half; briquettes with 40% temper have a TRS that is less than one tenth of the untempered ceramic. The decrease in strength is due to the increase in flaw density caused by temper particles, which act as stress concentrators (Kilikoglou *et al.* 1998). Finally, an increase in grain size leads to a decrease in fracture strength (**Fig. 2d**). Increasing grain sizes result in an increase in size of preexisting flaws in the material (see also **Fig. 3**); consequently they result in a weaker material.

Moreover, different fracture modes are observed in the ceramic materials tempered with 25% quartz, depending on the size of aplastic inclusions. For small temper sizes, the material shows brittle fractures; once a crack starts it progresses unstably through the material and breaks the specimen in two (**Fig. 3a**). For larger temper particles, load-displacement curves look different, and semi-stable fracture occurs. In this case, the material is able to absorb energy and stop the crack so that additional force needs to be

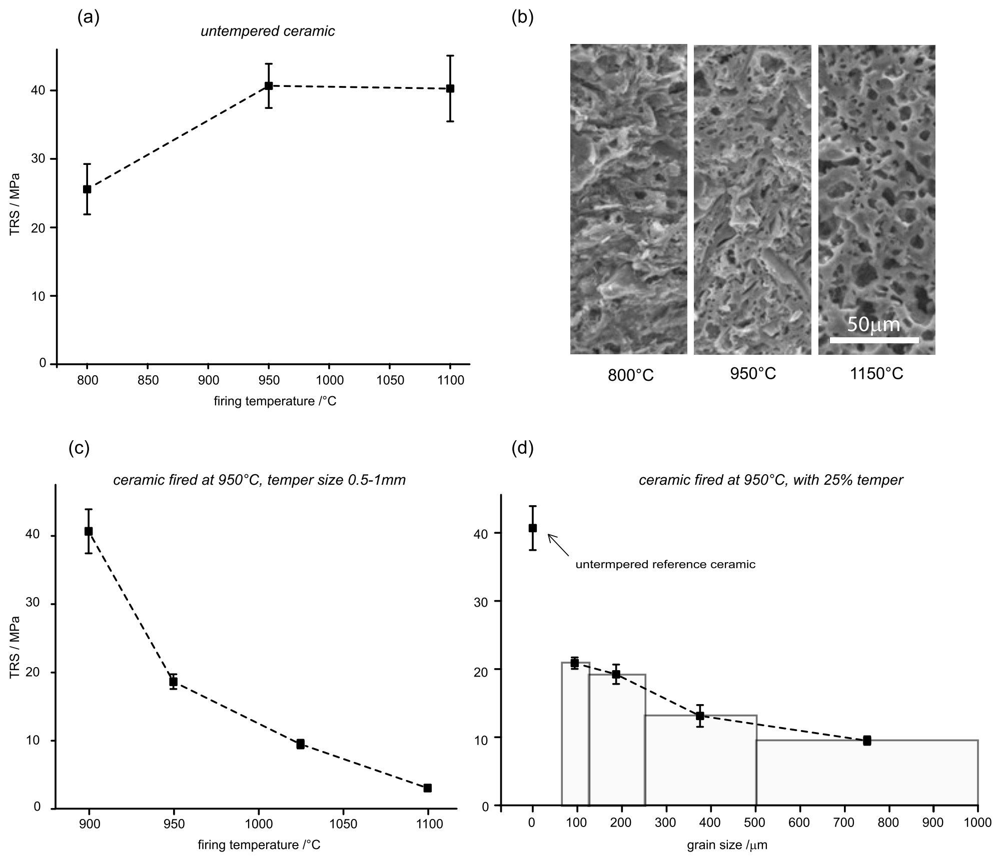

Figure 2. (a) Influence of firing temperature on TRS; (b) Microstructure of untempered ceramic at different firing temperatures; (c) Influence of amount of temper on TRS; (d) Influence of temper size on TRS.

applied to drive the crack through the material and to result in complete fracture. This change in fracture mode is probably, at least partially, connected to the emergence of elongated shrinkage pores, perpendicular to the applied force. These are observed in ceramics with larger temper grains (see also Müller *et al.* 2010) and provide a means for crack arrest (**Fig. 3b**).

(a)

(b)

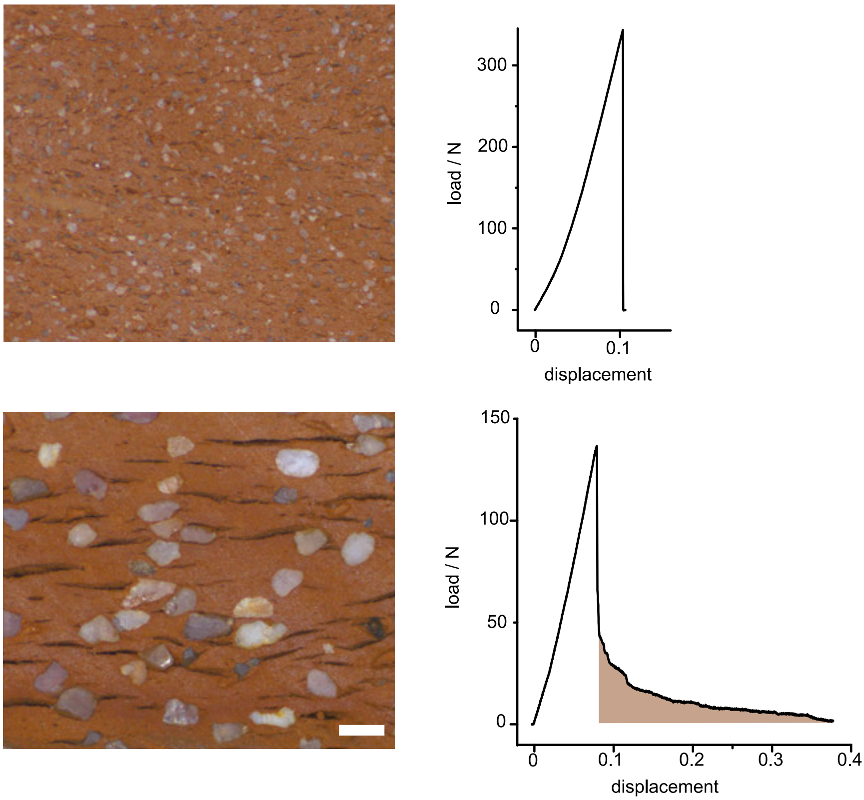

Figure 3. Influence of temper size on fracture mode a. texture and typical load-displacement curve of ceramics with 25% temper fired to 950°C with grain size 125-250µm, and b. texture and typical load-displacement curve of ceramics with 25% temper fired to 950°C with grain size 500-1000 µm (scale: 1mm).

B. Response to impact stresses

Comparing the ceramics' response to impact with their behaviour under static loads, in terms of the materials' ability to resist *crack initiation*, we find comparable values for untempered ceramics exposed to dynamic and static loading, with perhaps a small decrease in impact strength at highest firing temperatures (**Table 1**). Tempering does decrease impact strength compared to untempered ceramics. However, the amount of temper

	Impact loading rate 30m/s	Slow loading loading rate 100 μm/min
Firing temperature	Average (Std dev)	Average (Std dev)
800°C	27 (6) MPa	26 (4) MPa
950°C	45 (4) MPa	41 (3) MPa
1100°C	34 (6) MPa	40 (5) MPa

Table 1. Strength under impact and strength under slow loading for untempered briquettes.

added does not appear to play a role (**Fig. 4a**). In this regard impact strength differs from strength under slow loading, for the latter – as discussed above - the amount of temper is important. This may be explained since under dynamic loading, the stress field does not have the time to expand into the material, and so the bending strength measured depends only on the flaws at the surface which is under tensile stress, opposite the applied impact force (Freund 1998). When the influence of grain size is considered, the situation is similar. While under static load, increasing grain size does reduce bending strength, under impact there is no apparent influence of the grain size (**Fig. 4b**).

As mentioned, an important aspect of the setup employed to assess the materials' behaviour under impact is that of its instrumentation. This allows the generation of load versus time graphs. These show that fracture occurs over a very short time period of only *c.* 50μs. The energy that is absorbed under impact corresponds to the area under the curve, and it can be estimated in this way. The fracture energies under impact show a very similar behaviour to fracture strength under impact. While the fracture energy under impact appears to decrease at very high firing temperatures, probably due to increase in pore size at very high firing temperatures (**Fig. 2d**), it decreases when temper is added. As is the case for fracture strength, the amount of temper does not appear to play a role, and also grain size does not appear to influence the fracture energy under impact (**Figs. 4c** and **4d**). As noted above, fracture occurs over just 50μs, this is very short and there appears not to be enough time for the micro-mechanisms during fracture to act and absorb any energy. Fracture proceeds via the shortest path and the crack wandering is minimal. Therefore, fracture energy appears to be largely governed by intrinsic fracture energy, which correlates to the maximum force that can be applied to initiate fracture (Kilikoglou *et al.* 1995; equation 1 and 2).

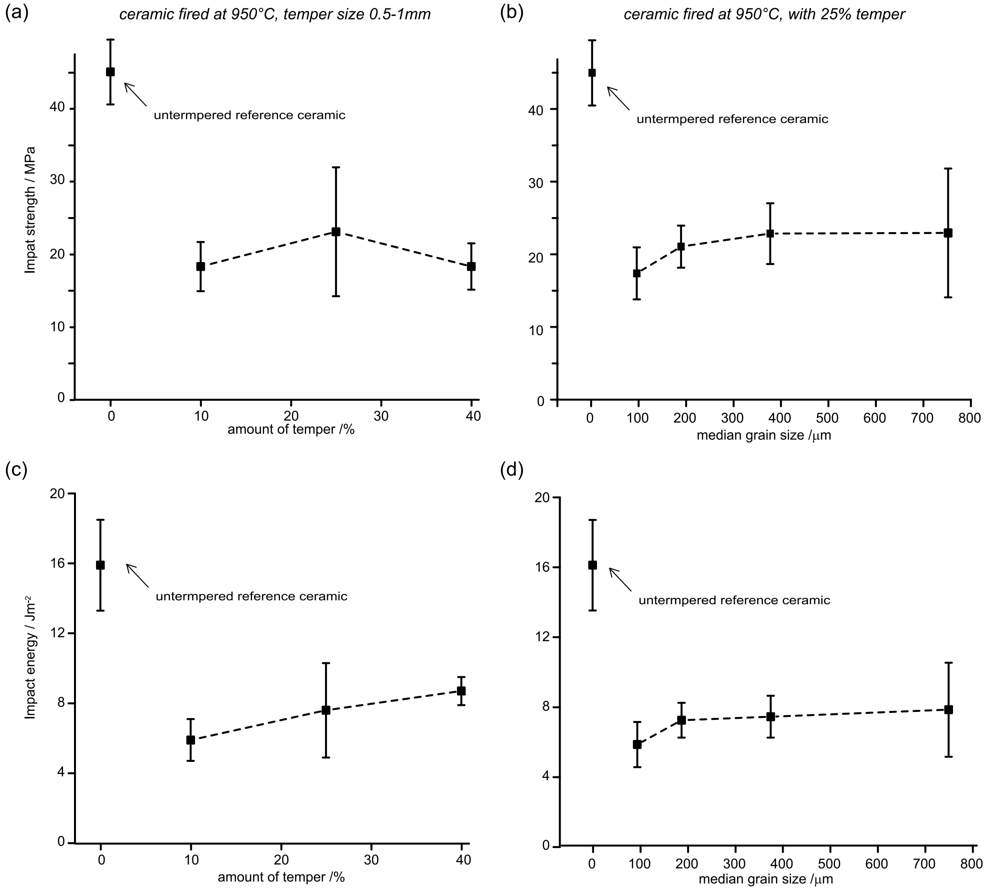

Figure 4. Influence of amount of temper and grain size on impact strength and impact energy.

Conclusions

Under static loads, fracture strength increases with increasing vitrification, decreases with increasing amounts of temper, and decreases with increasing temper size. For dynamic loads, while the presence of aplastic inclusions indeed reduces impact resistance, the amount and grain size of aplastic inclusions do not play a significant role both in terms of impact strength and fracture energy.

For archaeological ceramics, therefore, a fine ceramic with few aplastic inclusions is expected to resist better to stresses arising, for example, from weight-loads, than a vessel with a high amount of large inclusions. On the other hand, both are expected to show a similar response to impact loads. If impact loads are large enough to initiate a crack but do not carry enough energy to result in complete fracture, in subsequent (slow) loading, where crack propagation mechanisms are effective, amount and grain size of temper are important. When assessing the affordance of archaeological pottery, therefore, we must carefully consider the kind of mechanical stresses a vessel was likely exposed to.

Finally, the experiments appear to indicate that only surface flaws on the tensile side influence impact strength. This would imply, however, that the reduction of such surface flaws, - which could be achieved for example through the application of a slip - might increase the impact resistance of a ceramic, and eliminate any difference caused by different ceramic matrices. Further testing of slipped specimens is planned to explore this issue.

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WORK PACKAGE 3

Glass production and trade in the eastern Mediterranean

WORK PACKAGE 3

Glass production and trade in the Eastern Mediterranean

The work package entitled "Glass production and trade in the Eastern Mediterranean" is a collaboration among the scientific teams of the Vrije Universiteit Brussel (VUB), the University College London (UCL) and the University of Sheffield (UNISHEF). Two Early Stage Researchers are connected to this work package: Anastasia Cholakova (UCL) and Andrea Ceglia (VUB).

Within the framework of archaeological enquiries related to glass production and consumption in Late Antiquity, the young researchers were trained in glass analysis techniques like SEM-EDX, LA-ICP-MS, EPMA, optical spectroscopy in the UV-vis-NIR region and Raman spectroscopy. The results of the compositional analyses performed with these techniques have shed light on glass making recipes and furnace conditions, and thus, have enabled the identification of primary and secondary production centres, and the determination of consumption patterns. Moreover, they have provided evidence that can be used to discuss the degree of specialisation of workshops in the production of coloured glass, the identification of routes of social and economic interaction, and the degree of state control over glass production during different periods of the ancient past.

Anastasia Cholakova's research focuses on late 3rd to early 7th centuries AD glass vessels that were found at three sites in present-day Bulgaria. The main aim of her study was to unravel the complexity of the existing distribution networks and to identify the various producer-consumer relationships through time. As such her work contributed to a better understanding of the economic and socio-cultural history of the Balkans in Late Antiquity.

Andrea Ceglia investigated the glass consumption in Late Antique Cyprus based on the material from five early Christian basilicas located at three sites on the south coast of the island. The study of the chemical compositions of an extensive dataset of glass samples from each basilica has allowed us to gain an insight into the various sources of the raw glass procured by each site. In combination with a typological study, these data will thus allow the identification of local consumption patterns and the existence of possible preferential trade routes with either the Levant or Egypt. In addition, the methodological objective of Andrea Ceglia's research was to investigate the usefulness and feasibility of *in-*

situ analysis of UV-vis-NIR transmission spectroscopy for the study of glass finds from archaeological sites.

Prof. Karin Nys
Work Package 3 leader
Vrije Universiteit Brussel, Belgium

SHEDDING LIGHT ON THE GLASS INDUSTRY OF ANCIENT CYPRUS: ARCHAEOLOGICAL QUESTIONS, METHODOLOGY AND PRELIMINARY RESULTS

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Abstract

The aim of the project presented here is to determine the provenance of the raw glass used in Cyprus in Late Antiquity, and to verify the existence of a regional differentiated glass consumption pattern on the island. In order to define the glass compositions used in Cyprus we analysed material from Cypriot ecclesiastical sites as a test case, and compared the results with the known primary glass composition produced in Syria, Palestine and Egypt. The project focuses on the glass material from the Cypriot Early Christian basilicas of Agioi Pente in Yeroskipou, Agios Nikolaos in Maroni *Petrera* and three basilicas at Kalavasos *Kopetra*. The paper presents the methodology followed, in addition to some preliminary results.

Introduction

Since the invention of glass production, sometime in the 3rd millennium BC, the function and economical value of glass changed through history: initially it was considered a very precious commodity mainly used as diplomatic gifts (Pulak 2008, 2010). This changed dramatically with the technological revolution of glassblowing in the 1st century BC (Stern 1999). In the first millennium AD, glass became progressively more accessible and dominated the market of tableware, while it was also used to produce windows. Its properties made it a very competitive product: glass can be transparent, coloured, it can be shaped into a large variety of forms, it can be recycled and it is durable.

During the first millennium AD, glass production shows a multi-levelled structural organisation (Freestone *et al.* 2002). Large production facilities are known in the Levant and in Egypt and are normally called "primary workshops". Glassmakers were able to produce

8-20 tons of glass per batch (Freestone *et al.* 2002). This glass (often referred to as "raw glass") was then broken into rough cut blocks and shipped throughout the Empire in order to supply the secondary workshops where it was re-melted and shaped into consumer goods for the market (Freestone *et al.* 2002).

Major and trace elements of the glass composition help to provenance the raw materials and, therefore, to reconstruct trade routes. Five compositional groups circulated in the Empire between the 4th and the 7th century: Levantine 1, Levantine 2, Egypt 1, Egypt 2 and High Iron Manganese Titanium (HIMT) groups (Freestone and Hughes 2000).

Levantine 1 and Levantine 2 are two compositional groups of glass associated with Palestinian production. The former one represents the primary glass production of four sites: (1) Apollonia, (2) Bet Shean, (3) Dor (Freestone and Hughes 2000), and (4) Jalame (Brill 1988). Brill (1988) showed that this type of glass was made with natron imported from Egypt and sand from the mouth of the River Belus, in the Bay of Haifa close to Akko, which was a famous source for glassmaking in Antiquity. Levantine 2 was a product of the mass-producing glass furnaces at Bet Eli'ezer, in Israel (Freestone and Hughes 2000). The main difference between Levantine 1 and Levantine 2 glass is that the former has lower CaO and Na_2O and higher SiO_2. This is due to the use of sand with a distinctive lime fraction, caused by sand extraction from different layers in the same quarry or mining at different quarries.

Egypt 1 and Egypt 2 are two compositional groups coming from Egypt. They were identified by Gratuze and Barrandon (1990) in their study of Islamic glass weights. Egypt 1 glass has low a CaO concentration (~3-4 wt%) and relatively high Al_2O_3 concentration (~3.5-4.5 wt%). This group is normally believed to have been produced in Wadi Natrun in the 6th and 7th centuries AD (Thirion-Merle *et al.* 2003). Egypt 2 is a high-lime low-alumina group, associated with Egyptian production in the 8th and 9th centuries AD (Freestone and Hughes 2000).

The last group is the so-called HIMT glass, characterised by elevated contents of the oxides of iron, manganese and titanium associated to somewhat high Mg content (Freestone 1994). From the 4th to 7th century AD, HIMT glass was widely traded in the western Mediterranean and in continental Europe, all the way up to Britain (Foster and Jackson 2009; Foy *et al.* 2000; Freestone 1994; Mirti *et al.* 1993).

The current project is focused on the distribution and use of glass in Late Antique Cyprus based on the material from the Cypriot Early Christian basilicas of Agioi Pente in Yeroskipou (Michaelides 2005), Agios Nikolaos in Maroni *Petrera* (Manning 2002) and the three basilicas at Kalavasos *Kopetra* (McClellan 2003). Cyprus owes its strategic position in the eastern Mediterranean due to its proximity to the coast of Syria, Palestine and Egypt and the predominant regional sea currents. The island is therefore an excellent research area from which to gain a deeper insight into glass distribution and consumptions patterns in the eastern Mediterranean in late antiquity. Moreover, focusing on Early Christian basilicas provides a well-defined time window between the 4th century, when ecclesiastical buildings started to flourish systematically over the island, and the mid-7th century, when Cyprus was ravaged by waves of Arab invasions (Tran Tam Tinh 1985).

Nevertheless not much archaeometric research has been carried out on Cypriot glass material. The only published data are the analysis of 19 glass fragments coming from vessels and lamps from the basilica of Maroni *Petrera* (Freestone *et al.* 2002). The authors determined 13 objects of the Levantine 1 group and only four of HIMT glass (2 fragments are of uncertain attribution). The predominance of Levantine glass at Maroni *Petrera* can be explained by its proximity to the Palestinian coast, where Levantine 1 raw glass was produced.

Research questions

The first research objective is to establish new data on the chemical composition of the glass from Cypriot sites dating to the Late Antiquity. The expansion of the dataset will allow more accurate observation of the distribution of glass on the island and to reach stronger conclusions regarding glass suppliers and trade. Therefore, the glass finds from three different sites will be studied extensively. The Yeroskipou material from the south-western area of Cyprus and the material from Maroni and Kalavasos from the central part of southern Cyprus, allow us to verify the possible existence of regional consumption patterns of raw glass. It is possible that different cities traded preferentially with the Levant rather than Egypt or vice versa. Finally, through comparing the compositional data of Cypriot glass with published synchronous material from different geographical areas, we hope to contribute to the reconstruction of glass trade routes in the eastern Mediterranean.

Despite the fact that chemical characterisation is a great aid in investigating raw materials, it cannot reveal all relevant properties of glass. Therefore, the methodological objective of this research project is to investigate the usefulness and feasibility of in situ analysis of UV-vis-NIR transmission spectroscopy to study archaeological glass. Glass colour is an important characteristic and transmission spectroscopy gives a deep insight into the technology behind it. Colour is imparted by several transition metals and both the redox state and the coordination geometry of the metal ions affect the final hue

(Meulebroeck *et al.* 2011). Most Roman / post-Roman glass is unintentionally coloured by iron given that this element is a common sand impurity. Consequently, the redox conditions of the melt are significant for determining the final appearance of a glass artefact (Meulebroeck *et al.* 2012). Therefore, indirect determination of the furnace conditions allows one to understand better the continuously evolving skills of ancient glass making (Ceglia *et al.* 2013). When applying this technique in situ on a large number of fragments, a more accurate view of all the consumed glass of an archaeological site can be determined in an objective way.

Materials

This research focuses on the glass materials of three ecclesiastical sites of Late-Antique Cyprus. The first one is the basilica of *Agioi Pente* in Yeroskipou, located on the western coast of Cyprus, just a few km south of Paphos. The Early Christian basilica came to light following road works in 2002. After a first preliminary excavation campaign by the Department of Antiquities a more systematic excavation programme was undertaken by the University of Cyprus under the direction of Demetrios Michaelides in four consecutive field campaigns from 2003 until 2006. The site was dated between the 4th and the mid-7th century AD (Michaelides 2005).

The second site is Maroni-*Petrera*, situated approximately 3 km from the sea on the southern coast of the island. The basilica of Maroni was discovered during field survey of the locality during 1992. Coins found dated to 643-44 suggest that the site was abandoned sometime in the mid-7th century (Manning 2002).

The site of Kalavasos *Kopetra* was identified in 1978 and excavated in the 80's by Marcus Rautman. Kalavasos is only 4 km away from Maroni. Three ecclesiastical buildings lie in proximity to the settlement of *Kopetra* and are dated between the 4th and mid-7th century (McClellan 2003).

Methodology and preliminary results

One of the unique aspects of this project is the methodological approach that has been used. Up to now, for the archaeometric study of glass, a number of pieces, which were important from an archaeological point of view, were usually selected for analysis. This routine is definitely effective since it directly addresses the archaeological questions. At the same time, it limits the view on the glass assemblage as a whole. How representative could this experimental design be? It is of course strongly biased by the researcher who selects the samples.

In this project the research is based on a two-step process. First, UV-vis-NIR transmission spectra are collected *in situ* with a portable spectrometer. *In situ* optical spectroscopy offers the possibility of analysing virtually all glasses excavated from a site. Spectra from more than 500 glass fragments were collected from the three sites under study; this is a much larger number than one can normally select when taking samples for analysis in the lab. Following *in situ* optical analysis, some fragments per defined spectral/chemical cluster are sampled for chemical analysis in the laboratory. Samples are embedded in resin and analysed for chemical composition by means of EPMA and SEM-EDX for major and minor elements. LA-ICP-MS will be used for the trace elements, which are very useful to determine the origin of the raw materials. The same samples can be reused for other analyses. Raman spectroscopy will be carried out to investigate the structure of the silicate network, while, on a limited number of glass pieces, the redox conditions will be investigated using synchrotron X-rays absorption spectroscopy.

A scheme of the set-up for in situ analysis is reported in **Figure 1**. It consists of a light source connected to an optical fibre, a focusing lens, and an integrating sphere which collects the transmitted light and is connected to the spectrometer by means of an optical fibre. The spectra are recorded on a polished spot between 300-1650nm. The integrating sphere allows the collection of all transmitted light, reducing the effects of the curvature of the glass fragments and eventual polishing defects (Ceglia *et al.* 2013).

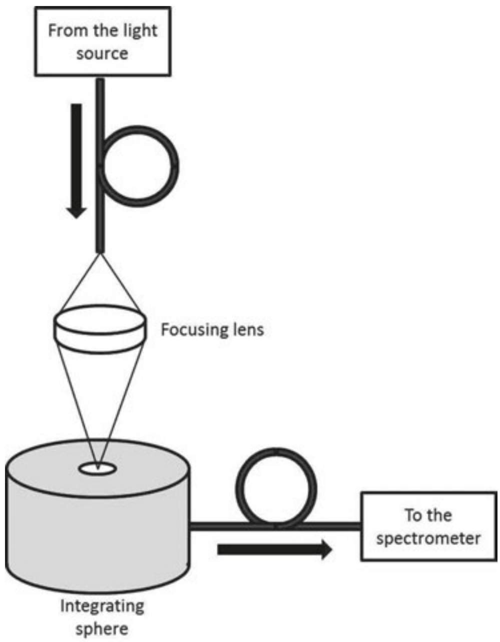

Figure 1. Schematic drawn of the portable set-up for UV-vis-NIR transmission spectroscopy.

Possible obstacles for optical spectroscopy are linked to the fragments' geometry and their state of preservation. The shape of the glass piece might be such that it prevents spectral analysis. While a flat window pane is extremely easy to measure, the analysis of a curved fragment presents a greater number of complications. Lamp bulbs or entire vessels are extremely difficult to analyse. The other obstacle can be caused by the level of preservation of the glass artefact. Weathered glass, e.g. one which exhibits iridescence or has a layered crust, cannot be measured as is. In order to eliminate the corrosion layers that would strongly affect the spectra, we polished an area of few millimetres diameter with a hand-held rotary tool before performing the analysis. Typologically interesting material, which cannot be analysed *in situ* by transmission spectroscopy due to its shape, might also be sampled in order to address specific research questions.

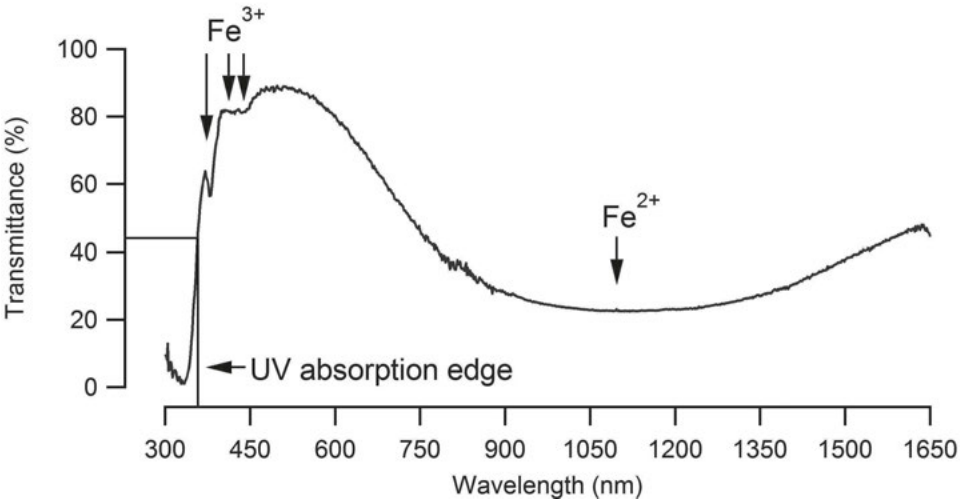

Figure 2. Transmission spectrum of a Roman glass fragment. The main element affecting the final spectral shape is iron, which can coexist in glass in two oxidation states: Fe^{2+} and Fe^{3+}.

Figure 2 shows the spectrum of typical Roman glass. The spectral profile is the result of the individual contributions of several absorbing species. Roman / post-Roman glass has characteristic pale colours due to the presence of iron impurities in the sand. In glass, iron coexists in two oxidation states, the ferrous iron Fe^{2+} and ferric iron Fe^{3+}. Moving from oxidising to neutral to reducing conditions, glass changes its colour from colourless or pale yellow to green-blue. When sulphur is present in the batch and the glassmakers apply very strong reducing conditions, the ferri-sulphide complex can form. This complex gives rise to a range of hues going from olive to olive-green to amber depending on the relative amounts of the ferri-sulphide complex and the ferrous iron (Brill 1988). The optical spectra shape of ancient glass coloured with iron is the result of the iron redox ratio. Nevertheless, the concentration also plays an important role. The absorption at ~1100nm is linearly correlated to the concentration of Fe^{2+}. Since both ions are strongly absorbing in the UV regions, glass is opaque in this region. The UV-absorption edge is defined as the wavelength for which only 50% of incident light is transmitted (**Fig. 2**). The position of the UV absorption edge can be correlated to the iron concentration (Meulebroeck *et al.* 2012), however, other metallic ions such as Mn^{2+}, Mn^{3+}, Ti^{4+} etc may also have an impact.

Conclusions

The different glass compositions circulating during Late Antiquity in the Mediterranean are characterised by different iron concentrations and general chemical composition. As shown above, optical spectra are strongly influenced by both the iron concentration and its redox equilibrium. The undergoing research is showing encouraging results and serves to demonstrate that optical spectroscopy can be used as a very effective tool to distinguish compositional groups. Transmission spectroscopy provides an initial overview of the compositions used and an insight into redox conditions of the batch. Because this technique does not require sampling it allows one to carry out a study on a much wider scale, defining a more accurate view of the entire glass assemblage. The preliminary results on the chemical composition of the glass not only show the main use of Levantine 1 and HIMT raw glass, but also that Egypt 1 (Wadi Natrun) glass found its way to the island. The link between specific shapes and the origin of the glass is also under study.

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The research was conducted as part of the project entitled “Glass production in Antiquity” undertaken by the author under the supervision of Herman Terryn, Hugo Thienpont and Karin Nys, within the framework of the NARNIA (New Archaeological Research Network for Integrating Approaches to ancient material studies) Project. NARNIA is a Marie Curie Initial Training Network which is funded by the FP7 and the European Union (Grant agreement no.: 265010). For more information please visit the NARNIA website: http://narnia-itn.eu/.

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NETWORKS OF DISTRIBUTION AT THE MARGINS OF THE EMPIRE: LATE ANTIQUE GLASS VESSELS FROM THE LOWER DANUBE REGION

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Abstract

The paper summarises some of the main aspects of integrated research on glass vessels from the late 3rd to early 7th centuries AD from three site assemblages in present-day Bulgaria. The historical setting in the region reveals a period of significant transformations. Studying the networks of distribution (in terms of their directions, spatial scale, functional mechanisms, organisation, etc.) within such context can shed light on a variety of economic and socio-cultural phenomena during the turbulent time of Late Antiquity. Taking as a framework the model of division in the Roman and Late Antique glass industry, this study aims not only at tracing the routes of glass supply from the primary production centres but also at reconstructing, as fully as possible, the entire distribution chains of raw glass and finished vessels to consumer sites. Special attention is given to an attempt to distinguish between inter-regional, regional and local networks of distribution, and the stratified production and consumers' needs related to them. From a methodological point of view, the research is based on an integrated classification of the materials constructed from artefact research approaches and scientific techniques for compositional characterisation of glass (EPMA and LA-ICP-MS).

Introduction

The present research aims to explore the distribution of glass in a part of the Balkan territories of the Late Roman and Early Byzantine Empire situated near its northern frontier along the river Danube. Integrating the archaeological evidence for supply, production, and use of glass vessels in the region and the scientific data regarding chemical composition of the finds allows a complex pattern of economic connections, technological and cultural traditions and interactions to emerge, and to be unravelled within the broader framework of dynamics of the eastern Mediterranean in Late Antiquity.

Background of the research

Late Antiquity is seen as a period of very intense changes and an overall process of transformation of earlier Roman traditions toward the realities of the medieval world. In the Balkans (**Fig. 1**), the significance of the administrative reforms of the end of the 3rd century AD is reinforced by the act of establishing in the region the new capital of Constantine the Great, Constantinople (in AD 330), and later, the increased separation between the Western and Eastern Roman Empires (after the death of Theodosius I in AD 395; Blockley 1997). The consolidation of a new political and economic authority during the same period, the Orthodox Church, should also be referred to. The barbarian invasions and the consequences of the migration period have had a major impact in the Balkans as a border region of the Empire along the Lower Danube, whilst at the same time being situated within reach of the new capital. The end of the 4th and the 5th centuries are characterised by intense attacks of Goths and Huns, and even settling of some of their groups to become part of the population in the province of Moesia Secunda. The reign of Emperor Justinian I in the second quarter of the 6th century is marked by certain attempts of the state to stabilise control over the Balkan region (Whitby 2001). An entirely new administrative unit, quaestura exercitus, was established in AD 536 connecting in an exceptional way two Balkan provinces – Scythia and Moesia Secunda, with quite distant East Mediterranean territories i.e. Caria, Cyprus and some of the Cycladic Islands (Jones 1964). The supposed aim of this inter-provincial unit was to ensure the supplies and financial support to the frontier defence along the Lower Danube (Torbatov 1997). However, the increasing raids of Slavs and Avars, and their movement in search for new areas for settling lead finally to substantial ethnic and cultural changes. By the end of the 6th and the first quarter of the 7th centuries most of the Late Antique settlements in the immediate region to the south of the imperial frontier were abandoned (Dinchev *et al.* 2009); furthermore, completely different cultural and political phenomena arose with formation of the Early Medieval Proto-Bulgarian political entity in the last quarter of the 7th century.

The sources outline a very dynamic historical picture of instability, decline, and, presumably, isolation of the northern Balkan region towards the end of Antiquity by the beginning of the 7th century AD, and this, to a certain extent, is confirmed in the

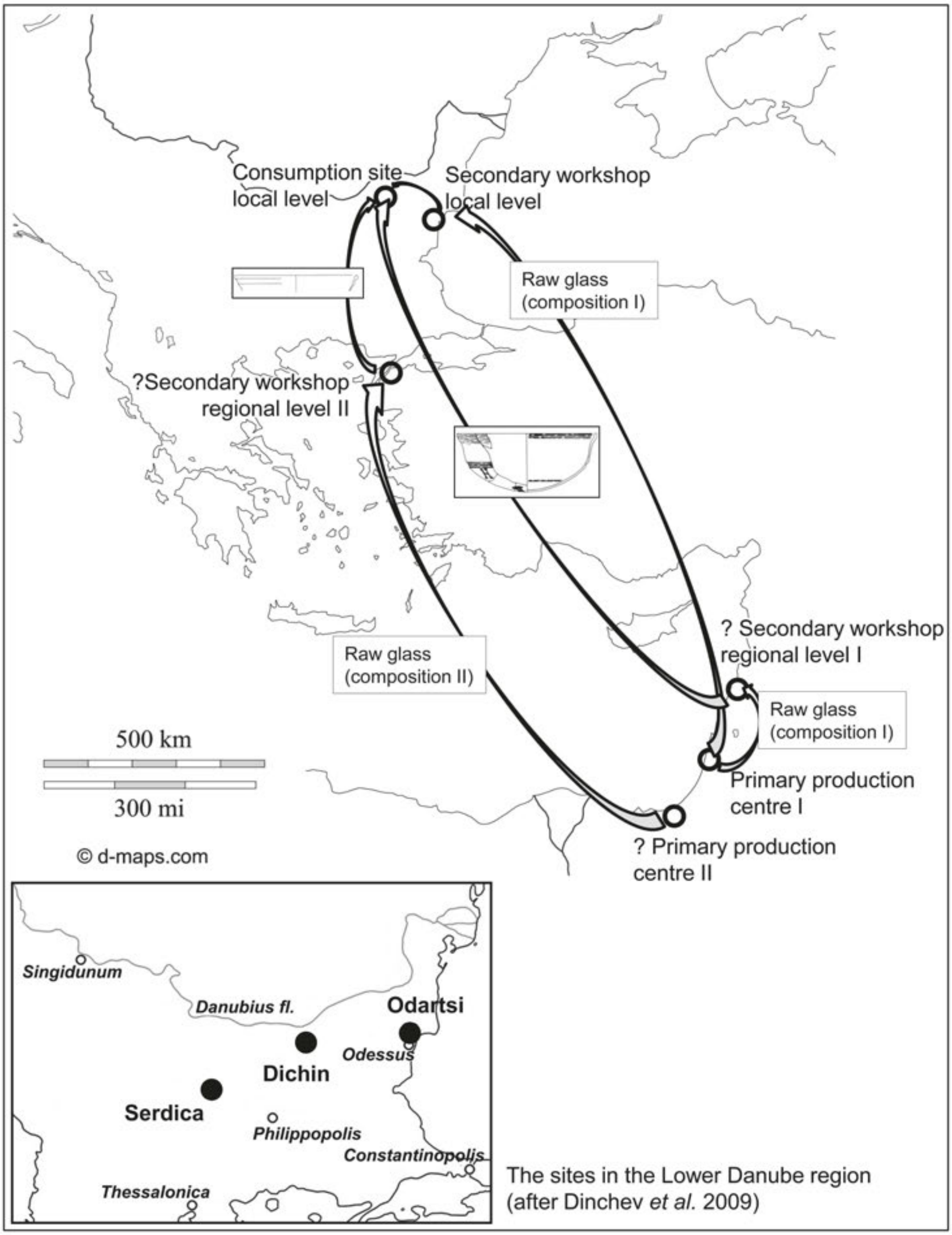

Figure 1. Schematic outline of the spatial scale of the networks of distribution at different levels in the East Mediterranean during Late Antiquity. Map of the Balkans with the sites providing glass assemblages for the present project.

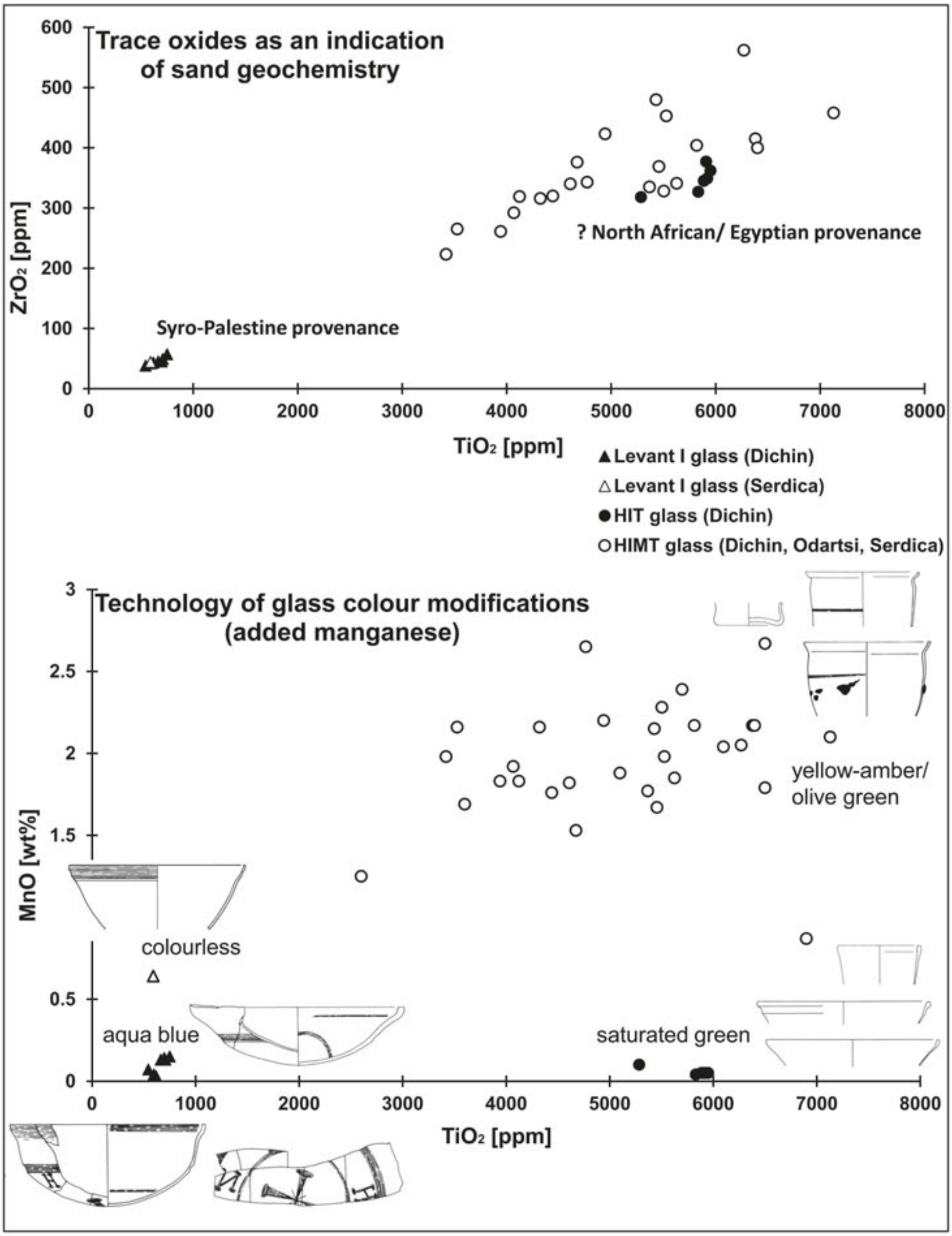

Figure 2. Scattergrams presenting some of the analysed samples: certain trace oxides can reflect the provenance of primary raw glass compositions, while intentionally added manganese (>0.5 wt%) indicates technical choices of the glass makers. Different vessel manufacturing techniques (cold and hot glassworking) and/ or shapes may correspond to particular chemical compositions.

archaeological record. However, much more nuanced processes can be recognised when archaeological materials are studied as primary evidence. The archaeology-based interpretations may highlight phenomena which have escaped written history, or can even shape different narratives about past realities.

The choice of the category of artefacts to be studied in this research, i.e. glass vessels, is deliberate since they provide the opportunity to investigate both their 'archaeology' (in terms of vessel morpho-typology, decoration, manufacturing, etc.) and their 'chemistry' (in terms of chemical composition) as two directions of research that are not unconnected or contrasted but are complementary to each other. Integrating these two approaches in modern glass studies can be seen as essential for a thorough unfolding of the full interpretative potential of such archaeological material.

Glass, as a distinct field of analysis, demonstrates certain peculiarities that stem from the particular method of organisation of the Roman and Late Antique glass industry. Numerous analytical studies and archaeological discoveries of the last two decades have changed the traditional view about glass being made from the constituent raw materials independently in each small glass workshop. Instead, the remarkably consistent chemical compositions throughout the Empire imply a division of the overall glass industry into two stages: (1) primary glass production associated with few large-scale industrial sites, attested so far in Egypt and Syro-Palestine, and, (2) secondary glass working, i.e. manufacturing of finished objects, taking place in a wide range of smaller ateliers across the Roman and Byzantine Empire (Freestone *et al.* 2002; Freestone 2005). This two-stage model presumes the fundamental role of circulation of unworked glass (as raw chunks) from primary centres to secondary workshops where it is only re-melted (and/or recycled cullet is used). At the same time, even if divided into two clearly different stages, glass production should have been functioning as an integral 'hierarchical' and changing system of social, economic, technological interactions, closely related to distribution and supply as the most dynamic sectors of the ancient economy. Surprisingly, the historical sources of that time are rather silent about such a complex phenomenon. It is mostly the combined archaeological and compositional analysis of glass finds that can reveal the direction, scale, and nature of these interactions.

Aims, questions and approaches

The present project strives to integrate conventional archaeological artefact study and scientific analysis using a multidisciplinary range of approaches and techniques whilst taking the functional model of two stage production within the Roman glass industry as a framework. The general objective of the research is to characterise the distribution of glass in the Lower Danube region but not in terms of descriptive, static, detached, and finally, incomplete patterns of vessel typology and chemical glass compositions. Instead, an attempt is made to extend the interpretative value and meaning of glass studies using approaches to technology, exchange, and distribution which have been originally formed in anthropological and economic theory, relating the interpretation to the setting of the historical and archaeological context. In this way, it is hoped that not only a detailed picture of glass supply, production and consumption can be outlined, but it would also contribute to a particular insight into the complex processes of transformations at the edges of political territories and historical periods.

Specifically exploring the distribution networks of glass as the main focus of this research can be justified as such an approach can successfully achieve the main objective of the project as stated above. Glass vessels were certainly only a small part of the perishable and non-perishable goods that travelled along the Late Antique distributional networks but they are probably among the most suitable and responsive archaeological materials for reconstruction and interpreting these networks. As previously mentioned, the supposed division of glass production already indicates the importance of actively used routes of raw glass procurement. At the same time, the specialised nature of secondary glass working, as a commercialised craft, separates it from all other nearly non-exchangeable productions at the domestic level of self-sufficiency, even if it would operate within a closed economic environment of almost full isolation and autarky. Not least, the use of glass vessels, at the consumer end of these networks of distribution, reflects certain other phenomena beyond a mere tracing of trade connections or geographical direction of supplies. Specifics of glass vessels as finished objects and the site glass assemblages as a whole are characteristic for their users' tastes, preferences and everyday habits, providing further means for understanding social and cultural identities and dynamics within the historical context.

A wide range of questions need to be addressed when networks of distribution are identified based on glass vessel site collections, from a 'retrospective' viewpoint, i.e. studying consumption assemblages as the main evidence for distribution. A very simple scheme would assume an essential chain beginning from the primary raw glass production centre, through the secondary glass vessel manufacturing workshop(s), to the consumer end, i.e. the sites of use of final products. Nevertheless, such a general outline has numerous aspects, in which these networks of distribution varied, reflecting economic, technological and socio-cultural differences and changes.

One of the leading criteria for defining the networks of distribution of glass vessels is the spatial scale of these chains. Therefore, as one of the research inquiries, an attempt is made to recognise different networks at inter-regional, regional, and local levels. This spatial stratification is well accepted in studies devoted to ancient trade where distances and time of transit are used as discriminants (Morrisson 2012), and it can be a very efficient tool in glass studies as well. In certain cases inter-regional networks had a decisive role for the glass industry even before the actual transportation of production had begun. One of the main ingredients for glass melting, mineral soda, was procured mostly in Egypt and delivered to other parts of the Mediterranean like Syro-Palestine, where some of the most significant raw glass production centres operated. In the next stage, raw glass chunks from primary centres were distributed along bigger far flung and smaller regional networks to supply different workshops for vessel manufacture (Shortland *et al.* 2006; Freestone 2008). The nature and organisation of this distribution is only vaguely understood so far but certainly such a large-scale circulation belongs to those types of exchange systems which have left very little archaeologically visible evidence. Therefore, the analytical research on glass composition provides a unique opportunity to trace the networks of inter-regional distribution through linking different glass groups attested across the Empire to particular geochemical patterns of glass making sands and hypothetical production locations (**Fig. 2**).

However, the present project is not intended to simply conclude that the Lower Danube territories of the Empire apparently received their glass supplies from the primary East Mediterranean glass-making centres in Egypt and the Levant, as demonstrated by the geochemical sand signatures. Such a picture would overlook many other processes given that the consumption site assemblages are reflections of procurement and usage, not of primary raw glass, but of finished vessels – i.e. artefacts shaped in the secondary manufacturing workshops, with various geographical locations, various ways of provision of glass, and various levels of organisation and craftsmanship. Therefore, a full understanding of distributional networks would ideally imply recognising these intermediate secondary centres as actual places of origin of the glass artefacts found at consumption sites. Addressing such a question only by means of chemical composition cannot be completely productive since a small regional workshop for ordinary vessels in the Balkans may be supplied, at least in theory, with the same primary raw glass as a bigger atelier in the Levant, producing better quality and more elaborate ware for higher consumer demands (**Fig. 1**).

Only through a combined study of shapes, techniques of vessel finishing and decoration, and chemical composition of glass can an intricate pattern of distributional networks (for both raw glass and glass artefacts) be revealed. In terms of spatial scale, this approach would distinguish between imports (and their directions) and locally/ regionally manufactured and distributed vessels found within site collections. Related to this, the use of fresh primary glass versus recycling cullet can be assessed through compositional analysis, providing ways for considering economic connectivity and isolation of the networks. On the other hand, a stratification of consumption which is not equivalent but still linked to the spatial separation can also be explored with this combined approach. Affordable everyday mass-production, more valued and sophisticated, even luxurious items from 'middle class' levels of Late Antique glasswork, up to elite small scale artistic pieces – identifying such an assortment and a range of glass compositions relevant to it within site assemblages is a way for further interpretations of socio-cultural and economic meanings of different distributional chains. Certainly, more aspects need to be investigated regarding the organisation of the networks: commercial market type distribution versus non-commercial factors of economy, the role of state-led mechanisms of the 6th century Justinian's quaestura exercitus, blurring between inter-regional and regional levels, etc.

Materials, techniques and preliminary results

The project is focused on three particular site assemblages from present-day Bulgaria (**Fig. 1**). Dichin is a fortified settlement of semi-urban type in the province of Moesia Secunda dated c. 410-580 AD. It was excavated in 1996-2003 in the framework of a joint British-Bulgarian programme (Dinchev *et al.* 2009; Rehren and Cholakova 2014). Odartsi is comparable to Dichin in its archaeological features but has a more complex stratigraphy and a longer period of occupation, spanning from the early 4th century to c. 610 AD. Similarly to Dichin, it is situated in the frontier province of Scythia, south of the Lower Danube. The site was excavated by a Polish-Bulgarian team in 1969-1991 (Torbatov and Dončeva-Petkova 2001). Serdica is the Roman city preceding the present day Bulgarian capital Sofia. During Late Antiquity Serdica was the capital of the province Dacia Mediterranea. A recent rescue project (2010-2012) in a large area of the centre of the city provided a variety of glass finds (*cf.* Ivanov 2013). Some of them are being studied in the current project.

In general, the aim is to include a wide range of glass fragments which allow the reconstruction of the original vessel shapes, and are representative for the glass repertoire from the late 3rd to early 7th century AD in the region. Materials from well-dated and defined archaeological contexts are preferred. After an initial grouping based on the characteristics of vessel manufacture and typology a selective sampling of the groups was carried out. EPMA and LA-ICP-MS are the techniques used in this study to characterise major, minor, and trace oxides concentrations in the glass. The processing of the analytical data is performed mostly with bivariate statistical techniques.

As a result of the combined research on vessel shapes, manufacture, and glass chemical composition, an integrated classification of the materials is constructed. It is based on complex and even versatile criteria, and assumes that both technology of glassmaking (i.e. recipes) and technology of vessel production (i.e. practices of glassblowing and decoration) are of a major interpretative importance when networks of distribution are investigated. Some well-known compositional glass groups are attested in the studied Balkan assemblages: Levantine I glass which is linked to the production sites in present day Israel, and HIMT glass with a possible Egyptian origin (Freestone 2005). Some other compositions are also recognised including previously not defined HIT and later varieties of manganese decolourised blue-green glass (Rehren and Cholakova 2014). Juxtaposing these compositional groups with evidence for the techniques of vessel manufacture and finishing (**Fig. 2**), and also quantifying their relative presence within the assemblages reveals certain characteristics of the networks. For example, the Levantine I vessels could be interpreted as a limited inter-regional import of good quality finished products, probably distributed by non-commercial mechanisms. Conversely, the HIMT composition may be seen as raw glass import supplying certain workshops in the Balkans which operated to satisfy a particular sector of the local market and consumer tastes. Furthermore, the reliable dating of the finds allows the identification of chronological changes in the overall patterns of distribution. Admittedly, the current project may not be able to provide definite answers alone and, at this stage, some aspects of the distributional networks will probably remain less clear than others. However, it is hoped that the project can demonstrate the effectiveness of its key research approach – to integrate a range of diverse data and tools, from compositional analysis and artefact study to contextual and historical evidence, for reconstructing and interpreting dynamics of the past.

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WORK PACKAGE 4

Copper metallurgy in the eastern Mediterranean

WORK PACKAGE 4

Copper metallurgy in the eastern Mediterranean

The fourth work package of the NARNIA project is dedicated to the study of copper metallurgy. The production and trade of copper was decisive for the formation of the Bronze Age and was one of the guiding forces behind the establishment and transformation of trading networks in the eastern Mediterranean, throughout the long history of the region; the significance of copper and its alloys remained undiminished until Late Antiquity.

The idea of dedicating a work package of the NARNIA project to copper metallurgy should not come as a surprise considering that the project is coordinated by the University of Cyprus. Cyprus was by far the most important copper producer in the eastern Mediterranean until Late Antiquity, and has operated both as a source for raw materials and finished artefacts, but also as stepping stone connecting different parts of the Mediterranean. The principal aim of this work package was the interdisciplinary study of the production and use of copper and bronze across the ancient Mediterranean, with a strategic focus on the entire *chaine opératoire* of the metal. This work package was led by the author, who closely collaborated with Dr George Papasavvas (University of Cyprus), Prof. Marcos Martinón-Torres (University College London) and Prof. Thilo Rehren (University College London Qatar) for the implementation of the various training and research activities organised within its framework. One Experienced Researcher (ER) and four Early Stage Researchers (ESR) were recruited to conduct research on ancient copper metallurgy.

Dr Andreas Charalambous (ER01, University of Cyprus – supervisor: Prof. Vasiliki Kassianidou and Dr George Papasavvas), has undertaken the project entitled *A diachronic study of ancient Cypriot metalwork*. He has analysed a significant number of artefacts made with copper alloys that were produced in Cyprus, in the second and first millennia BC. Surprisingly, only a small number of metallic artefacts from Cyprus had been chemically analysed and published before the commencement for the NARNIA project, therefore the work conducted by Dr Charalambous provided new data on ancient metal production. The employment of pXRF was of great importance for the success of this project, as it provided the possibility for the fast analysis of numerous specimens in a minimum timeframe without prior sampling.

Lente Van Brempt (ESR1, University of Cyprus – supervisor: Prof. Vasiliki Kassianidou) has been conducting research on *The production and trade of Cypriot copper in the Late Bronze Age and Early Iron Age.* Her research is focused on the interdisciplinary study of archaeometallurgical remains from the Late Bronze Age settlements of Kalavasos *Ayios Demetrios,* Maroni *Tsaroukas,* Aredhiou *Vouppes* and Alassa, in an attempt to understand the different production processes and the organisation of the copper industry on both local and regional levels.

Demetrios Ioannides (ESR16, University of Cyprus – supervisor: Prof. Vasiliki Kassianidou) has been involved in the interdisciplinary study of *Bronze Age metallurgical ceramics from Cyprus*, and particularly of the metallurgical ceramics from the ancient urban centre of Kition, in East Cyprus. The material from the site is an ideal case study for the diachronic technological study of metallurgical evidence dating from the Late Bronze Age (14th century BC) to the end of the Classical period (late 4th century BC).

Frederik Rademakers (ESR4, University College London– supervisor: Prof. Thilo Rehren) has been working on a project entitled *Ancient urban metallurgy in the Eastern Mediterranean*. This project focuses on the study of metallurgical crucible assemblages coming from Qantir – Pi-Ramesse (Ramesside Egypt, 13th century BC), Gordion (Achaemenid Phrygia, 6th - 4th century BC) and Serdica/Nicopolis/Philippopolis (Roman Bulgaria, 2nd - 4th century AD). The overarching goal of this research is to evaluate different methodological approaches to the study of crucibles and crucible assemblages by comparing the results deriving from these three examples, not in terms of technology, but by evaluating the influence of varying crucible typology, preservation, abundance, contextual information, and sample availability.

The fourth researcher recruited in the framework of work package 4 is Mainardo Gaudenzi Asinelli (ESR5, University College London – supervisor: Prof. Marcos Martinón-Torres), who has been conducting research on *Copper alloy production and consumption in the Tuscia region during the Middle Ages*. This particular research project aims at the enhancement of our knowledge about copper alloy production and consumption and its broader socio-economic implications during the Middle Ages in the Italian region of Tuscia (current South Tuscany and North Latium, respectively).

Work package 4 has covered a long chronological and geographical spectrum across the Mediterranean and has provided the opportunity to the recruited fellows to be involved with a variety of research approaches, as well as issues of research methodology, material characterisation, ancient technology and differing modes of the organisation of production.

The five fellows have been collaborating with their supervisors, the other members of the NARNIA scientific board involved in this work package, as well as among them for the exchange of ideas, opinions, the interpretation of research results, providing and receiving positive feedback and constructive criticism. It is my belief that all five projects will make significant contributions to the field of archaeometallurgy.

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THE PRODUCTION AND TRADE OF CYPRIOT COPPER IN THE LATE BRONZE AGE

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Abstract

For many decades the provenance of copper oxhide ingots, and hence the Cypriot Late Bronze Age, have received extensive scholarly attention. However, the actual technological process related to the production of copper and its spatial organisation within the island, remain poorly understood. Evidence of large-scale workshops to be expected for a major copper-producing and exporting agent in the eastern Mediterranean are known only from Enkomi, while to date only one primary smelting workshop, that of Politiko *Phorades,* and one mining settlement, namely Apliki *Karamallos*, have been excavated. Nevertheless, small numbers of metallurgical remains have been found in practically all excavated Late Cypriote sites. A systematic and multidisciplinary study of this material by means of a variety of analytical techniques can lead to a better perception of the production and exchange of Cypriot copper. Consequently it can also contribute greatly to the further understanding of the socio-political and economical organisation of ancient Cypriot society. This project, therefore, encompasses a comparative study of the metallurgical remains from a number of important Late Bronze Age sites from Cyprus, mainly located on the southern river valleys, and the neglected copper ingot fragments from the well-known Cape Gelidonya shipwreck.

Introduction

In the Bronze Age metals acquired a high socio-economical significance in the eastern Mediterranean and started to play a primary role in the large-scale trade networks of the 2nd millennium BC. Complete and fragmented copper oxhide ingots, which are generally recognised as a major standardised form, in which pure copper was traded between 1600 and 1100 BC, have been found all over the Mediterranean (Gale 1999: 110). Provenance studies by means of LI analysis have led to the conclusion that the copper used for the ingots dated after c.1400 BC came from Cyprus (Gale and Stos-Gale 2012: 79). Therefore, it is generally assumed that Cyprus became a dominating producer and exporter of copper in the eastern Mediterranean by the 13th century BC (Kassianidou 2013b: 145). This can be explained by the presence of abundant copper ore deposits within the pillow lavas of the Troodos Mountains (**Fig. 1**) (Constantinou 2012: 5).

The growing international interest in Cypriot copper, and consequently the increasing involvement of Cyprus in the eastern Mediterranean trading activity, contributed to the initiation of a range of changes taking place on the island at the beginning of the LBA. It has been argued by some that by the 13th century BC, Cyprus was divided into regional polities within which coastal towns, inland centres, mining settlements and agricultural villages cooperated in intra-regional economic and socio-political networks that may have been put in place for the transshipment of copper from the mining villages on or near the Troodos mountains to primary coastal sites (Catling 1962: 144-145; Keswani 1993: 78-79; Knapp 1997: 156).

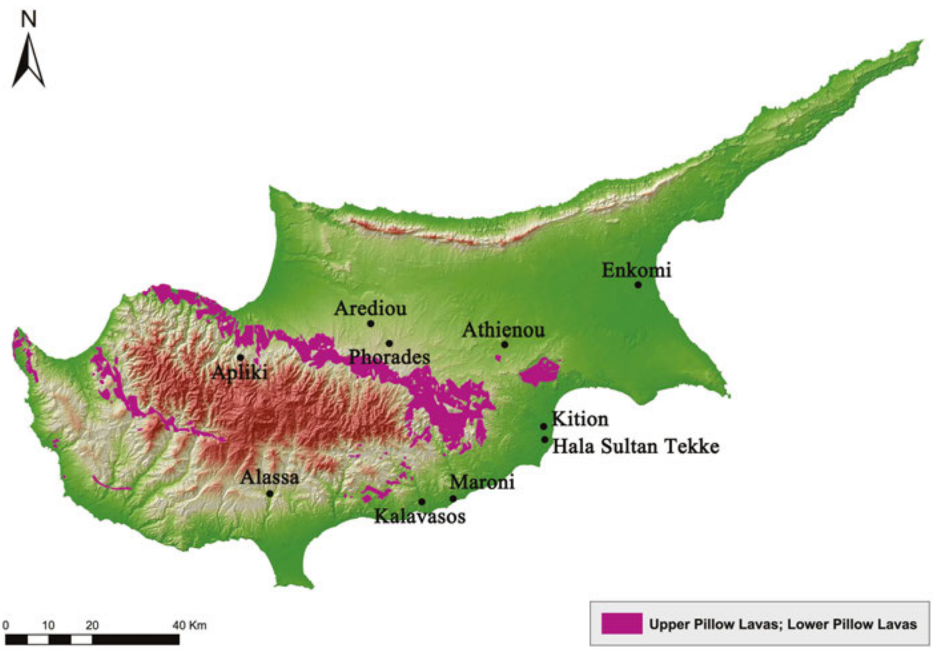

Figure 1. Map of Cyprus showing the pillow lavas and sites mentioned in the text. Digital geological data provided by the Cyprus Geological Survey.

To relate this to archaeometallurgy, metal production is a process of many phases, one of which is the smelting of copper sulphide ores, i.e. the ore-type available on Cyprus, which itself is a multistage process. It has been suggested that the organisation of copper production on the island can be associated with the proposed settlement patterns whereby every stage in the chaine opératoire took place at a different settlement involved in the regional network (Keswani 1993: 78-79).

Surprisingly, not many metallurgical workshops have been excavated on the island. The evidence for large-scale metal production to be expected of a major copper producer is basically missing from Cyprus, with the sole exception of the primary coastal site of Enkomi (Kassianidou 2012; Muhly 1989: 299-301), the LC I primary smelting workshop at Politiko *Phorades* (Knapp and Kassianidou 2008) and LC IIC mining settlement of Apliki *Karamallos* (Kling and Muhly 2007). This may be simply due to the fact that primary metallurgical workshops have not yet been found most probably because of the extensive exploitation of the mining regions, especially in modern times (Kassianidou 2013a: 37). However, at nearly every known LBA site remains of metal production have been found, maybe not of a very large scale but without doubt being an indication that copper must indeed have been an important aspect in LBA Cypriot society (Muhly 1989: 301-302).

The production and trade of Cypriot copper has received much scholarly attention. One of the major objectives has been the identification of the provenance of the oxhide copper ingots; however a thorough understanding of the technology applied in the copper production process and its organisation on the island remains restricted. This is not surprising if one considers the fact that a fair amount of the metallurgical material found in a number of important LC sites has not been thoroughly studied. Even if these metallurgical remains are few in number, they nevertheless do conceal the wide range of technological choices made by the ancient craftsmen during the production process of copper metal. Furthermore, through their study, we may be able to reconstruct not only the technological processes but also its social and spatial organisation (Kassianidou and Knapp 2005: 233). Thus a comparative study of the metallurgical remains from Late Cypriote sites can hopefully contribute to a better understanding of ancient Cypriot society.

Aims of the project

The project presented here consists of two main parts, the aims of which are:

1. To reveal the relationship between the political and technological centres and, hence, to identify how copper metallurgy was organised, intra-site, regionally and island-wide, in

LBA Cyprus. This will be achieved through the characterisation, identification and comparative study of the metallurgical remains from a number of important Late Cypriote sites.

2. To identify the way in which copper was exchanged and, hence, to comprehend the trading activities in the same period, namely the 13th century BC in the eastern Mediterranean. This will be addressed through the primary characterisation of the unstudied copper ingot fragments from the LBA shipwreck of Cape Gelidonya.

Part I: Copper production in Cyprus during the LC IIC

The first part of this project focuses on the Vasilikos, Maroni and Kouris river valleys in southern Cyprus. These regions have recently received much scholarly attention in an attempt to understand the regional settlement organisation by means of geophysical survey and renewed excavations at Kalavasos, Maroni, Moni and their surroundings. Nevertheless the metallurgical debris from these important sites has so far only been studied to a rather limited extent.

In the 13th century BC, two primary centres existed within the Maroni and Vasilikos river valleys at a distance of only 6.5 km from each other (**Fig. 2**). Despite the difference in the geographical situation of the sites within the valleys, the urban centres of Kalavasos *Ayios Dhimitrios* and Maroni *Vournes* do show many similarities (South 2002: 63-64). Both have monumental ashlar buildings that were similar in plan and function, which seems to have been related to administrative activities rather than religious practices (South 2002: 64). Both had access to the same quantity of luxury and imported goods and must, hence, have been to a certain degree involved in international trade (South 2002: 64). Most remarkable is that both valleys appeared to have shared the same copper resources. North of the modern village of Kalavasos, a major copper-mining area is known (South 2002: 65). Unfortunately, whether the copper mines of Kalavasos were actually exploited during the LBA occupation of the valley is uncertain as no archaeological evidence is yet known. Also, LI analysis on the metallurgical remains from Kalavasos *Ayios Dhimitrios* has shown the use of various ore deposits, but not of those from Kalavasos (Gale and Stos-Gale 2012: 79).

As the mining area is located on a reasonable close proximity to the coast, direct exchange contact could be maintained with both primary towns without the need of intermediary centres (Keswani 1993: 79). The exact relation between both valleys and their major sites remains, however, unclear. It has been argued that two individual regional networks may have functioned peacefully side-by-side; one with Kalavasos *Ayios Dhimitrios* as the primary centre in relation to a coastal site which may have existed in the area of Tochni Lakkia, located near the modern village of Zygi, and the other with Maroni Vournes as the primary centre in relation to the nearby coastal town of Maroni Tsaroukkas (South 2002: 64-65). Recently it has also been implied that both areas took part in the same

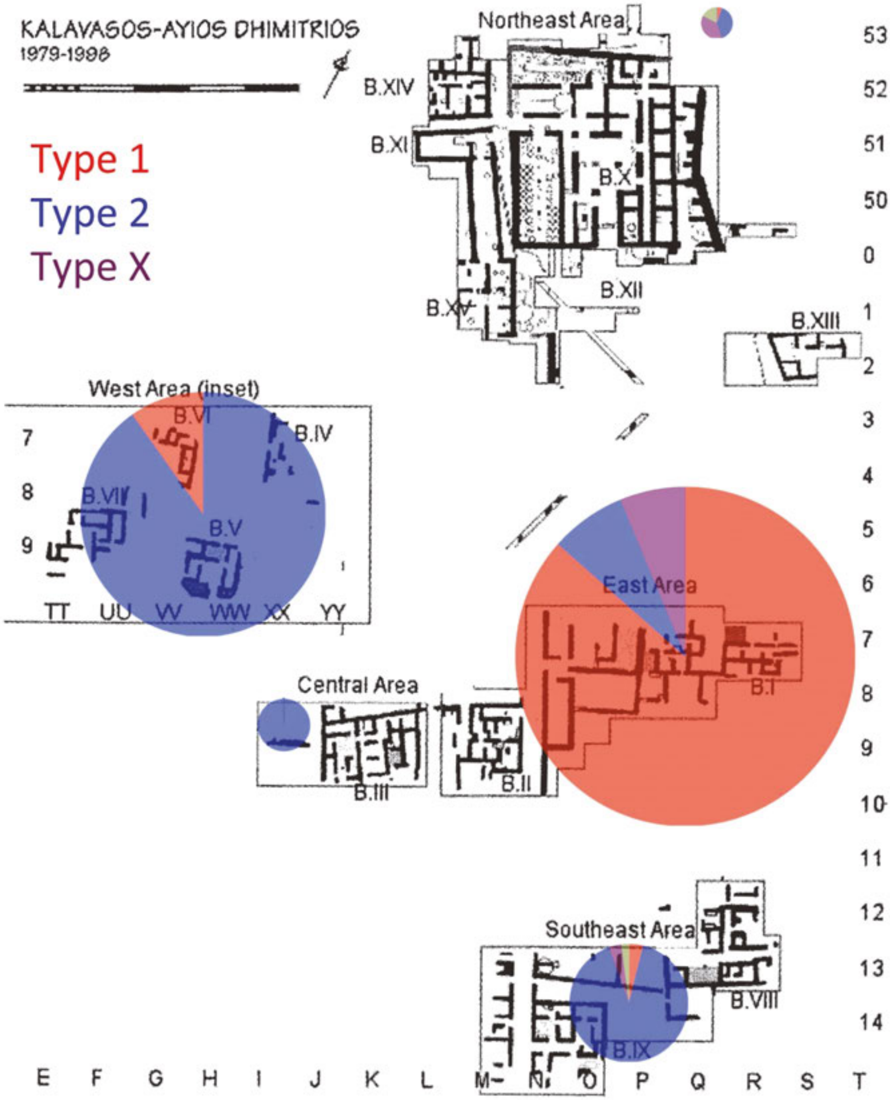

Figure 3. Map of Kalavasos *Ayios Dhimitrios* showing the distribution of the slag assemblage, with a total of 150kg, and the different types on the site. The size of the graphs coincides with the relative proportions by weight % (after South 2012: 36, fig. 5.1, adapted by the author in agreement with A. South).

network within which the site of Kalavasos *Ayios Dhimitrios* might have functioned as a controlling administrative and transsshipment point in relation to the coastal site of Maroni *Tsaroukkas*, which would have carried out the commercial functions (Knapp 2013: 357). What role the site of Maroni *Vournes* may have played herein remains to be clarified.

The project will investigate the production of copper in this region and it will try to identify the different stages in the technological process. Furthermore, it will try to understand how the production of copper was organised, in an effort to gain a better understanding of the socio-political and economic organisation of this part of the island. This will be done primarily by a comparative study of the extensive metallurgical assemblage found at the urban settlement of Kalavasos *Ayios Dhimitrios*. The initial stages of this research project have already revealed the existence of different slag types (**Fig. 3**) which have a different spatial distribution within the site. Furthermore, a very small slag assemblage from Maroni *Tsaroukkas*, and some earlier and later material from the Vasilikos valley recovered by field survey will also be studied and compared and contrasted with the material from Kalavasos *Ayios Dhimitrios* as well as the metallurgical debris from Maroni *Vournes*, which have been analysed and recently published (Doonan *et al.* 2012).

About 35km to the west of Kalavasos, in the Kouris river valley, is the LC site of Alassa, which existed as a dual settlement. In the area of *Paliotaverna* an ashlar Π-shaped monumental building has been excavated which was initially identified by the excavator to be of a religious nature (Hadjisavvas 1989: 41). Nowadays it is believed that Building II functioned as an administrative centre, likely in relation to the coastal site of Episkopi *Bamboula* (Hadjisavvas 2000: 396). A fair amount of metallurgical remains was recovered in the areas of both Alassa *Paliotaverna* and *Pano Mandilaris*, largely including objects, a few pieces of slag, fragments of copper ingots and a pot bellow (Hadjisavvas 2011). This admittedly limited material will also be studied and compared and contrasted with that from the sites of Vasilikos and Maroni valleys.

Finally, the project will also study the metallurgical remains from Arediou *Vouppes* which has only recently been excavated. It is an inland site that has been identified as an agricultural supporting village involved in provisioning one or more smelting sites in the cupriferous region of Politiko and Mitsero, similar to the primary smelting workshop of Politiko *Phorades* which is located at a distance of 10km but is of an earlier date (LC I) (Steel 2009: 138; Knapp and Kassianidou 2008). The fairly small assemblage of metallurgical remains found at the site will be investigated in order to define the metallurgical processes from which the material derived from and where these were taking place.

Methodology

The same methodology is applied on the remains from all the sites. The study will look at all the types of material related to metallurgical processes namely, metallurgical slag, metallurgical ceramics, ingot fragments, metal scrap and finished objects. This technological debris is being recorded and characterised by means of a tiered method. It commences with a macroscopic study of the full assemblage. Through this initial stage, a selection will be made for optical microscopy and chemical analysis through the use of a pXRF. This is followed by the study of a smaller selection of samples with the SEM-EDS. The bulk chemical composition will be determined on powdered samples with the help of an XRF instrument. XRD may be used if it seems to be advantageous. As such the analyses and grouping of the assemblage is being done by a variety of techniques. In addition, we will aim to address the possible use of the local copper mines through time by means of LI analysis on metallurgical remains of different periods within the regions. The final aim of this multidisciplinary analysis will be to identify the technological processes from which the remains may have derived from.

The outcome of the analytical study of this newly investigated material will be compared to similar published studies on metallurgical remains from a variety of LBA, as well as some earlier and later, sites from Cyprus. In a later phase the results will be compared and contrasted with those from other areas in the wider Eastern Mediterranean region.

Part II: The copper ingots from the Cape Gelidonya shipwreck

The second and smaller part of this project will investigate the trade of Cypriot copper through the study of an assemblage of copper ingot fragments from the Cape Gelidonya shipwreck. The largest assemblages of copper ingots (oxhide and bun shaped), were found among the cargo of two LBA shipwrecks discovered along the south coast of Turkey. This is the well-known Uluburun ship, dated to the end of the 14th century BC, and the Cape Gelidonya shipwreck, dated to the late 13th century BC (Bass 1967, 1986). The last one was identified as a possible merchant's or trader's ship with its own metalworker on board (Bass 1991: 73; Muhly 2009: 26).

Past analytical studies have primarily been directed towards the complete, halves and quarters of ingots coming from the Uluburun shipwreck (e.g. Hauptman *et al.* 2002), and to some degree to those from the Cape Gelidonya shipwreck (e.g. Muhly *et al.* 1977).

However, boxes with a large amount of smaller fragments were recently found in the storage rooms of the Museum of Underwater Archaeology in Bodrum, and identified by Dr. Cemal Pulak as copper ingot fragments coming from the Cape Gelidonya excavations (**Fig. 4**). It is remarkable that the excavator has only mentioned these large amount of fragments in the following short sentence: "*Lastly, there were almost seventy-five kilograms of ingot fragments which had been cut or broken away at random from complete ingots*" (Bass 1967: 53).

The many fragments were catalogued by the author at the Institute of Nautical Archaeology in Bodrum under the guidance of Dr. Nicolle Hirschfeld, Associate Professor at Trinity University, San Antonio, Texas. More than 600 pieces with a total weight of

Figure 4. Some of the many copper oxhide and bun ingot fragments from the Cape Gelidonya shipwreck found in the storage rooms of the Museum of Underwater Archaeology in Bodrum (photograph taken by the author).

about 270kg were described and photographed, including the larger fragments which were recorded extensively by the excavator. Amongst the smaller fragments, a fair amount of clear and often well-preserved quarters and edges of bun ingots could be identified, as well as handles and edges from oxhide ingots. Also many of the smaller fragments showed some clear evidence of having been beaten, likely in order to be broken up. Some had fairly straight sides indicating that they had been cut with a sharp instrument such as a chisel. This material is thus extremely important as it can tell us much about the technology used in the production and breaking of these ingots, which would have been difficult to achieve.

Furthermore, in comparison with the metal cargo of the Uluburun shipwreck, the nature of the Cape Gelidonya assemblage, due to the high amount of fragments of ingots, is clearly of a different kind and may guide us towards new thoughts on the metals' trade in the Mediterranean by the end of LBA, a subject that has been discussed by a number of scholars (e.g. Sherratt 2000).

By means of this primary study valuable information may be retrieved, but reliable conclusions can only be drawn by further research. The lack of a profound study of the copper ingots from the Gelidonya shipwreck is striking. The extensive investigation of the copper and tin ingots from the Uluburun shipwreck by Hauptman *et al.* (2002) has proved that microscopic and chemical analysis can offer valuable information regarding the processes involved in the production of these objects. Therefore one of the aims of this project is to offer recommendations for further study and to clarify the value of the assemblage of the Cape Gelidonya shipwreck in the further understanding of ancient metallurgy and related technologies and LBA trade in the eastern Mediterranean.

Conclusions

To conclude, the final aim of this project is to make a contribution towards our current understanding of the technological processes and the way the copper industry was organised in Cyprus by the 13th century BC, a period in which the island acted as the main copper-producer and exporter in the Mediterranean, as well as the metals trade in the eastern Mediterranean. Hopefully this may help develop a better understanding of the socio-political structure of the island during the LBA, and hence ancient Cypriot society.

Acknowledgments

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UNRAVELLING TECHNOLOGICAL ISSUES OF METALLURGICAL CERAMICS FROM CYPRUS: THE CASE OF KITION

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Abstract

Since the 2nd millennium BC and throughout Antiquity, Cyprus is considered to be one of the main sources for copper. Yet we are still far from being able to claim that we fully understand the dynamics that governed the organisation of copper production and distribution. The current study is concerned with the compositional and technological characteristics of the metallurgical ceramics of Kition. Primary issues to be addressed are the processes in which they had been used, their level of refractoriness and raw material procurement patterns. Kition provides an appropriate case study since the metallurgical evidence dates from the Late Bronze Age to the end of Classical period. This enables a multidimensional approach focusing partially on the periods in question using the material record of Kition as an example and on the other hand, on the impact of Kition as an entity in Cypriot society. To answer this, a number of techniques will be employed to investigate various aspects of ceramic production and metallurgical technology.

Introduction

The remains of ancient Kition lie under the modern city of Larnaca, on the southeast coast of Cyprus (**Fig. 1**). The acropolis of Kition was partially excavated in early 20th century, at which time Phoenician and later period strata were unearthed (Karageorghis 1976). Subsequently, four areas were selected for systematic excavations undertaken by the Department of Antiquities, under the direction of Dr. Vassos Karageorghis (2005a; Karageorghis and Demas 1985) between 1959 and 1983.

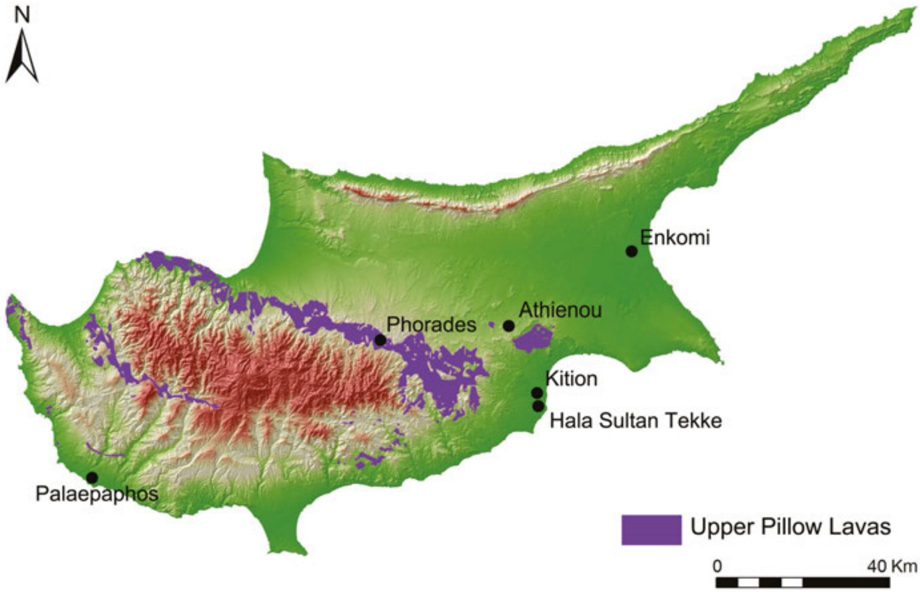

Figure 1. Map of Cyprus showing the location of pillow lavas and sites mentioned in the text.

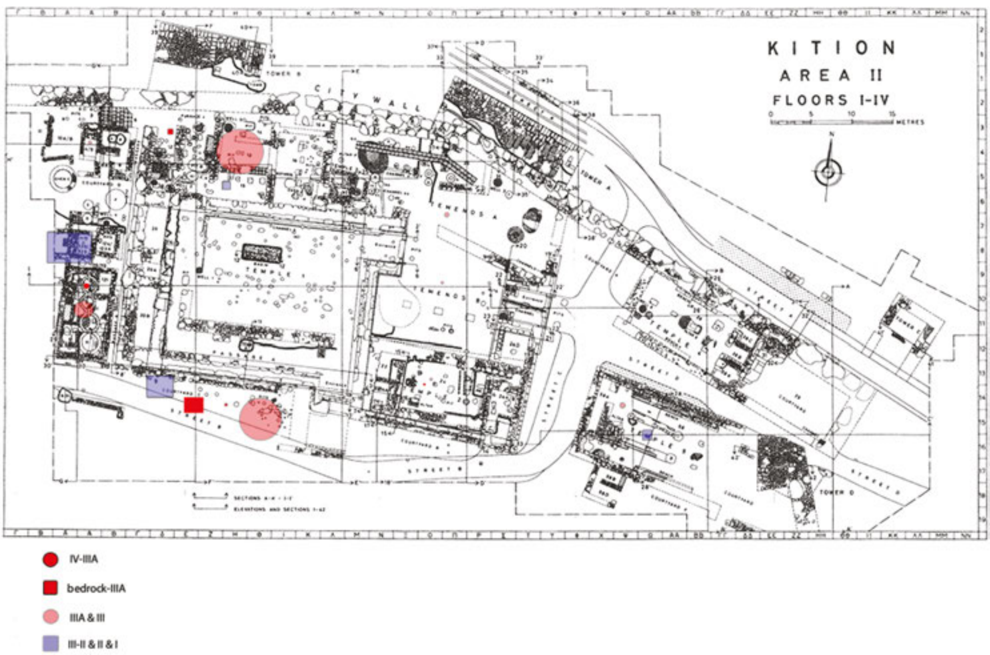

Figure 2. Distribution of metallurgical finds on the LBA floors in Area II of Kition.

All the areas, excluding Area IV, include LBA strata, while only Areas I and II have evidence of metallurgical activity (Karageorghis 1976; Karageorghis 2005a; Karageorghis and Demas 1985). The evidence from Area I is confined in several rooms interpreted as copper workshops on Floor IV, which covers the LC IIC and extends to the transition period of LC IIIA (*c.* 1300 – 1190/1175 BC) (Karageorghis and Demas 1985, 272). The presence of two furnaces, a possible casting pit and some associated metallurgical by-products suggest the processing and working of copper on a small scale (Stech 1982; Stech *et al.* 1985). Further, the non-industrial character of the adjacent rooms and the apparent connection with the tombs found in Area I imply the private nature of the facilities, perhaps within the residence of a local craftsman (Karageorghis and Demas 1985, 10; Stech 1982; Stech *et al.* 1985, 393). Importantly, Area I did not provide any evidence of use during the Phoenician phase although there are architectural remains from the Hellenistic and Roman period (Karageorghis 2005a, 3).

Area II has yielded the best evidence for copper production at Kition, with documented activity ranging from the 13th century BC into the Classical period (Karageorghis 2005a; Karageorghis and Demas 1985) (**Fig. 2**). The earliest metallurgical products date to the period of Floor IV, but no buildings or installations related to metalworking were identified (Karageorghis and Demas 1985, 24-37; Karageorghis and Kassianidou 1999, 174). In the following period, Floor IIIA, which corresponds to the LC IIIA (1190-1125/1100 BC), a grand scale anamorphosis of the sacred precinct of the Area II is attested including the establishment of a set of rooms between the north wall of the Temple 1 and the city wall, which were clearly connected to metalworking (Karageorghis and Demas 1985, 38-103). During the next periods, the so-called "Northern Workshops" were remodeled, until they ceased to exist in the period of Floor I, which corresponds to the Cypro-Geometric I, namely the last half of the 11th century BC (Karageorghis and Demas 1985, 141). The material record and the architectural features demonstrate that intensification of copper production must have taken place during the last half of the 12th century (Floor III), which according to Karageorghis and Demas corresponds to the LC IIIA2.

After a period of abandonment from the late 11th to the late 9th century BC (Karageorghis 2005a), Area II was reconstructed. In the framework of this development, metallurgical activity is evident in the form of copper slag and scrap metal and to a lesser extent technical ceramics. Although the excavator acknowledges the creation of a metallurgical workshop on Floor 2 (*c.* 550-350 BC), which continues to function during Floor 1 (*c.* 350-312 BC), the study of the excavated material, now in the store rooms of the

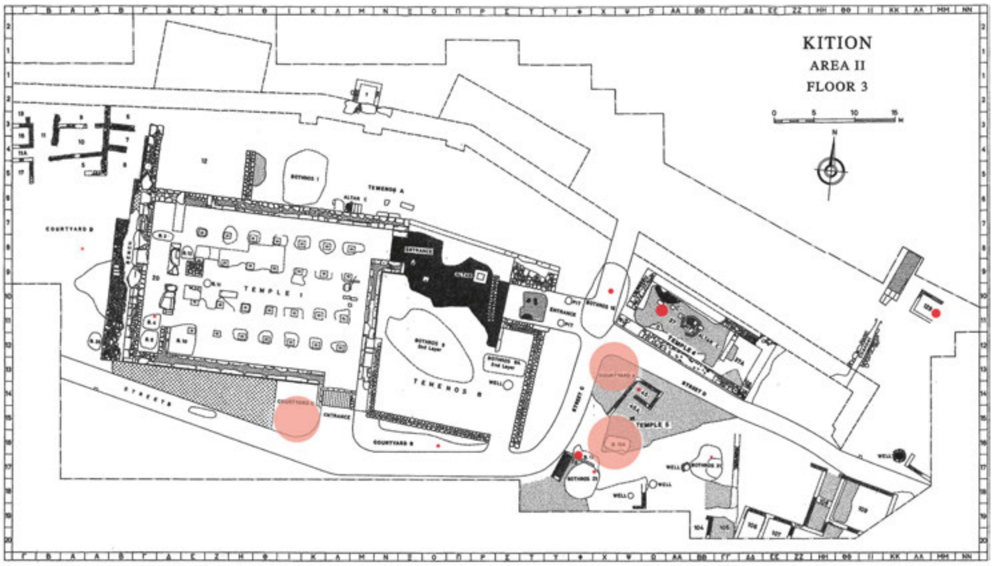

Figure 3. Distribution of metallurgical finds on Floor 3 in Area II of Kition dating to the Cypro-Geometric period.

Department of Antiquities, has revealed that in fact Floor 3 (*c.* 800-725 BC) is the stratum which demonstrates the highest number of sherds from metallurgical ceramics (**Fig. 3**).

The aim of this project is twofold. It will first assess the metallurgical operations that occurred at Kition, and secondly it will attempt to evaluate the complexity of metallurgical production through the analysis of technical ceramics throughout the duration of the settlement. The compositional and mineralogical data obtained will be used to interpret the intra-site diversity patterns reflecting different production models, which may correspond to various technological needs and social choices that changed during the long history of Kition. Similarly, the data will be compared with material from other already studied sites in order to consider inter-site diversity and variation patterns, which may represent different stages of metallurgical processes. A better evaluation of the technological knowledge, and both the raw materials and techniques used in the production and use of metallurgical ceramics will provide an insightful understanding of ancient Cypriot metallurgy and its impact on the social structure of the island.

The material in context

Late Bronze Age

The site of Kition provided a larger assemblage of material evidence than initially expected. Typologically it is similar to the material of Enkomi (Dikaios 1969, 1971; Kassianidou 2012), and the smelting workshop of *Politiko-Phorades* (Knapp and Kassianidou 2008). The furnace fragments are flat or slightly curved deriving from big, cylindrical structures with flat bases and simple and rather flat rims. They were made entirely of coarse, non-refractory, reddish-brown clay mixed with organic and rock inclusions of significant size (**Fig. 4**). In most cases, the interior surface shows traces of the contents of the furnace, slag or corroded metal inclusions. Behind this layer is a zone of reduction-fired gray/black clay, then a larger zone of orange-red oxidation fired clay (see Tylecote 1987: 124). As there are no obvious remains of sediment adhering to the outer surface it can therefore be suggested that the furnace was freestanding.

Figure 4. Furnace rim (Inv. KIT 939) showing evidence of reducing firing conditions and a thin layer of slag.

To increase further their mechanical and thermal strength and decrease heat loss, thick walls were built measuring between 2 and 4cm. The preserved height ranges from 5.2cm to 13.4cm while the diameter can hardly be estimated due to the small size of the fragments. Nonetheless, Tylecote (1985) estimates that the diameter ranges between 20 and 26cm, while Stech (1982) argues for a bigger installation, 30 to 40cm wide. According to Karageorghis and Demas (1985) and Zwicker (1985) a small cavity of about 2.5 cm on the middle part of the wall of one of the furnaces has been interpreted as a tuyère hole as supported by Tylecote (1982; 1985). That led Zwicker to correlate it with the well-known "crucible" from Enkomi identified by Tylecote (1982) as a smelting furnace. However, this is unlikely to be the case for Kition, since any indications for the presence of a tuyère insertion point are confined only to that example. Additionally, the reconstruction model made by Tylecote for the smelting furnace of Enkomi is based on an asymmetric hole that most likely represents a failure of the ceramic fabric where slag was poured out rather than a tuyère hole. Therefore, it is assumed that the tuyères would have been inserted from the upper part towards the charge. That would have been facilitated with the use of elbow tuyères, which have been recovered from Enkomi (Tylecote 1982).

Figure 5. Crucible fragments showing a black inner surface, the result of reducing firing conditions.

Interestingly, a significant number of crucible fragments were also recovered from the same strata at Kition. They are smaller and thinner vessels (with walls measuring between 1 and 2cm), with more curved surfaces ending in pronounced convex bases (**Fig. 5**). This type of vessel was made either from the same clay used for the manufacturing of furnaces or from a coarse gritty orange-brown clay. The interior surface is covered with a gray/black layer bearing evidence of extensive vitrification.

The collection of tuyères from LBA Kition belongs to the straight cylindrical type identified by Tylecote (1982). However, the extremely limited number of a handful of small tip fragments does not permit further investigations. All the examples demonstrate slagged outer surfaces, which often include corroded metal inclusions.

As in the cases of Enkomi and Athienou (Catling 1971; Dothan and Ben-Tor 1983; Karageorghis 1973; Karageorghis 2005a; Karageorghis and Demas 1985), a strong relation of copper production and religion is attested in Kition. The Northern workshops are located in a manner that communicate directly with Temple 1 and Temenos A, while a significant number of technical ceramics occur in Courtyard C, south of Temple 1, scattered throughout the sacred precinct and on a smaller scale inside the temple main rooms.

Iron Age

The material from the Iron Age strata is derived again from Area II but is remarkably decreased in quantity as it corresponds to one third of the material from the previous period. As in the case of Bronze Age strata, fragments were found on successive floors dating from 800 BC to the mid fourth century BC (Floors 3, 2A and 2). Significantly, the largest part of the assemblage came from Floor 3 (*c.* 800-725 BC), the first floor of habitation after a gap of 150-200 years. In contrast to the previous period, the biggest concentration of material from the Iron Age levels was found in bothroi located inside the Temple rooms. Although, one could assume that they represent waste material from previous periods that was collected and deposited in these pits, the contextual evidence confirms an early Iron Age origin for this material.

Furnace, crucible and tuyère fragments form the metallurgical ceramics assemblage. Stylistically and in terms of raw materials they are identical to the ones dating to the LBA, with both slagged and corroded surfaces often with metal inclusions resting above layers fired in reducing conditions.

Sampling strategy

For the purposes of the research, the selection of samples was governed by various considerations. Since Kition demonstrates a continuous application of metallurgy, samples were chosen from all the relevant strata of both LBA and Iron Age in order to examine technological patterns, diversities and changes. In the publication of the site (Karageorghis and Demas 1985; Karageorghis 2005b), the metallurgical ceramics mentioned are too few to conduct a sound archaeological material analysis, thus it was decided to go through all the excavated material from Area II. Complementary to this, a small number of samples analysed by Prof. Ulrich Zwicker in the late 70s and early 80s were chosen. These samples, which are located in the reference collection which Zwicker donated to the Archaeological Research Unit of the University of Cyprus, were given directly to Zwicker by Karageorghis during the excavations; many of these were never published.

Emphasis was given to furnace, crucible and tuyère fragments, which bear signs of usage and of areas demonstrating slag or corroded metal inclusions in an effort to address the nature of production. Another important factor which influenced the sampling procedure was the intention to create a reference collection of samples available for later study. Therefore, two samples were taken from 30 selected fragments, for the preparation of thin and polished sections.

Analytical approach

First, all the fragments were examined macroscopically with the naked eye and described in detail. Then an initial grouping was made according to the type, fabric, and dimensions of the ceramic artefact, as well as characteristics concerning the colour or surface of the fragments. Furthermore, a portable Innov-X Delta, ED-XRF analyser, which belongs to the Archaeological Research Unit of the University of Cyprus, equipped with a 4W, 50kV tantalum anode X-Ray tube and a high performance Silicon Drift Detector (SDD) was used for semi-quantitatively mapping the chemical composition of the clay fabric and the slagged surfaces.

Representative samples from each subgroup were selected for the preparation of thin sections to be studied under the petrographic microscope (Leica DM2500 P) with transmitted light. The aim of the petrographic examination is to determine the provenance of the raw materials particularly in relation to the local geological setting. Furthermore, it will be used to assess mineralogically and technologically the relative refractoriness of the clay fabric. Optical microscopy was also useful in examining the microstructure of slagged and metal-rich surfaces.

Subsequently, the polished sections were studied under a SEM belonging to the department of Civil Engineering of the University of Cyprus, with an Oxford EDS. The analysis with the EDS provided information related to the nature of the metallic inclusions and the major element composition of the ceramic body. The analytical power of SEM and specifically electron imaging was also applied for the study of the degree of vitrification. Although polished sections usually present a less clear picture of the vitrification level in comparison to fresh fractured samples, they offer more accurate determination of the position of the studied area (Evely *et al.* 2012), a key value since a thermal gradient is expected in relation to distance from the internal surface (Hein and Kilikoglou 2007). As the study concerned the use as well as the manufacture of the metallurgical ceramics, slag layers and metal remains were analysed with SEM-EDS to evaluate whether the technical ceramics from Kition regard melting or smelting vessels, the raw materials or alloys used, redox conditions and temperature involved.

Discussion

Although the case of Kition was addressed as early as the 1980s, a comprehensive reconstruction of the metalworking operations and hence the nature and scale of metal production taking place in the northern workshops has not yet been achieved. This phenomenon is essentially because scholarship has been focused exclusively on the analysis of the large masses of metallurgical slag. These enquiries have confirmed that the slag found at Kition concerns a smelting slag of a heterogeneous composition originating from the processing of mixed ores, predominating sulphidic ores (Hauptmann 2011; Stech 1982; Stech *et al.* 1985; Tylecote 1982; 1985, Zwicker 1985).

Nonetheless, the limited amount of slag found at LBA Kition suggests a minor scale production; perhaps for the needs of the sanctuary in the form of bronze votives and offerings (Karageorghis and Kassianidou 1999, Stech *et al.* 1985). This can be explained by the suggested model for the administrative organisation of copper production in Cyprus (Bachmann 1982; Stech 1982; Stech *et al.* 1985; Tylecote 1982; 1985). According to that, the initial treatment of the sulphide ore was performed close to the mines in specific smelting sites producing copper matte or black copper. This is the case for the recently excavated site of Politiko *Phorades* where matte was being produced (Knapp and Kassianidou 2008). Subsequently the by-products of the primary metalworking stage with copper-bearing conglomerates and copper-rich ores would have been sent to the cities for further treatment. It is well-known that the refining of black copper and the smelting of copper-rich ores do not produce large amounts of slag. On the other hand copper may have been mechanically removed from the conglomerate blocks after they had been "re-smelted" (Stech 1982; Stech *et al.* 1985). The latter has been demonstrated by Hauptmann (2011) who recognises in the texture of slag chunks iron and copper sulphides, magnetite and wüstite as being parts of the original slag grains that were re-melted. Another explanation given for the limited number of slag fragments is that the workshops were mostly dedicated to metalworking processes such as casting as well as the practice of recycling metal objects (Karageorghis and Kassianidou 1999). This argument is based on the presence of significant amounts of scrap metal in the environment of Area II and on archaeological and textual evidence from sites contemporary to Kition.

The current study seeks to address the aforementioned considerations from the perspective of the metallurgical ceramics. The analytical data obtained in the framework of this project will be evaluated both independently and complementarily to the slag measurements. In that manner, it is expected to contribute further to the discussion on the socio-political and economical complexity of LBA Cyprus and at the same time to initiate reviewing the role of Cyprus as a copper producer and exporter in the post-Bronze Age period.

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pXRF ANALYSIS OF CYPRIOT COPPER ALLOY ARTEFACTS DATING TO THE LATE BRONZE AND THE IRON AGE

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Abstract

A significant number of copper alloy artefacts coming from two Late Bronze Age sites, Limassol and Pyla *Kokkinokremos*, and two Iron Age sites, the cemetery of Palaepaphos *Skales* and the Necropolis of Salamis, were analysed using a pXRF for the determination of the alloy types used. The results indicate the abundance and the gradual increase of tin in the alloy used to produce weapons in the case of Limassol, the shortage of tin and the use of scrap metal in the case of Pyla *Kokkinokremos*, the abundance of tin in Palaepaphos in the Early Iron Age, and its use in some cases in a high percentage in order to produce objects whose colour imitates that of gold artefacts, and finally, the abundance and use of tin to produce a large number of various types of objects in the case of Salamis. Furthermore, the analysis has shown that lead was added deliberately into the alloys to improve their cast ability. The presence of arsenic in a number of artefacts is interpreted as evidence for the use of recycled metal deriving from artefacts dating to previous periods. Iron and zinc are believed to be non-intentional additions to the alloys, resulting from the smelting process and originating either in the copper ores or in the flux.

Introduction

The LBA (1600-1050 BC) was the era during which bronze, the alloy of copper with tin, predominates in Cypriot metalwork. Bronze replaced arsenical copper, the main alloy used until the end of the MBA. The first bronze objects appeared in Cyprus in the EBA (2500-2000 BC) (Swiny 2003: 369; Webb *et al.* 2006: 266-267), but most of them are believed to have been imported as finished artefacts (Weinstein Balthazar 1990: 161-162). Despite the fact that Cyprus is extremely rich in copper, no tin deposits have been found on the island and therefore this metal had to be imported (Kassianidou 2003: 109). The collapse of the international trade networks of the area caused by the destruction or abandonment of an important number of major cities, in the Aegean and the eastern Mediterranean, during the so-called "Crisis Years" of the 12th century BC (Muhly 1984: 47; Snodgrass 2000: 237-239), must have significantly affected the supply of Cyprus with tin. In order to investigate the assumption of the shortage of tin, a significant number of copper alloy artefacts from four sites on the island (**Fig.1**), which date to the LBA (Limassol and Pyla *Kokkinokremos*) and the Iron Age (Palaepaphos *Skales* and Necropolis of Salamis), were analysed using portable X-ray Fluorescence Spectrometry (pXRF).

The studied artefacts

The first group of 22 copper alloy artefacts comes from tombs excavated in an area of the modern city of Limassol (Karageorghis and Violaris 2012). The assemblage, which dates to the LC I-II (1600-1300 BC), consists of weapons (mainly daggers) and ornaments (rings

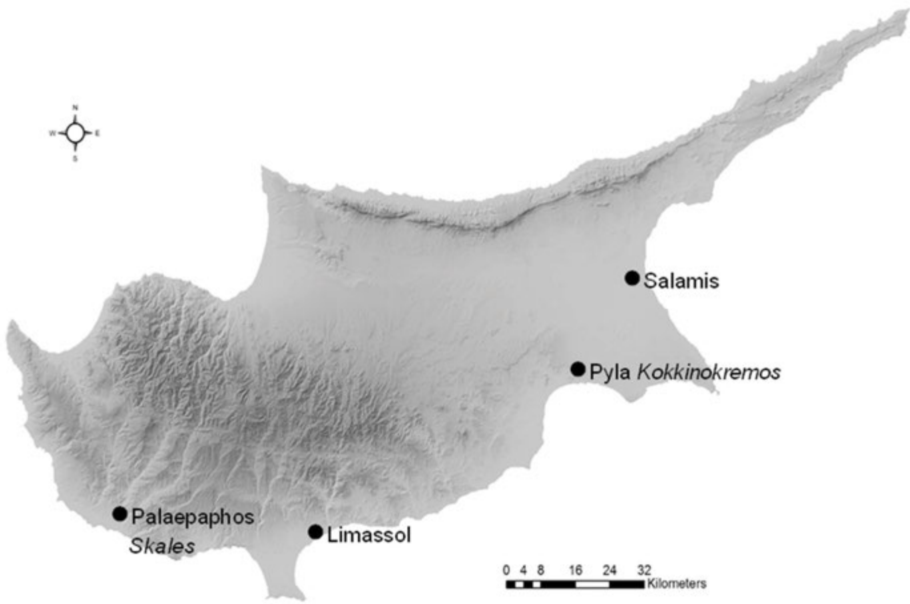

Figure 1. Map of Cyprus showing the location of Limassol, Pyla *Kokkinokremos*, Palaepaphos *Skales* and Salamis (produced by A. Charalambous based on digital geological data provided by the Cyprus Geological Survey).

and pins). The second group of 65 objects comes from the settlement of Pyla *Kokkinokremos*, which dates to the beginning of the 12th century BC (Karageorghis and Demas 1984). Over half of this assemblage consists of various forms of scrap metal, such as wires, sheets and fragmentary artefacts of various categories, such as tools, weapons and ornaments. The third group of 157 artefacts comes from the Early Iron Age necropolis of Palaepaphos *Skales* (Karageorghis 1983) and consists of several types of tools, weapons, vessels, and ornaments. Finally, the fourth and larger group of 563 artefacts comes from the Necropolis of Salamis (9th-3rd century BC). The assemblage contains, along with the usual categories of weapons, tools and jewellery, a significant number of other objects including part of the equipment used for chariots and horses (**Table 1**).

Method of analysis

A portable, handheld Innov-X Delta XRF analyser was used for the non-destructive analysis of the artefacts. The use of the pXRF was requisite since the removal of the objects out of the museum or sampling which would enable the use of other analytical techniques, was not permitted. The specific instrument is equipped with a 4W, 50kV tantalum anode X-Ray tube and a high performance Silicon Drift Detector with a resolution of 155 eV (Mo-*Ka*). The diameter of the X-Ray beam was 3 mm. The final reported composition for each object is the mean value of three to five measurements conducted on corrosion-free areas that were chosen after observation of the objects using a high resolution handheld microscope. The measurement time for each spot analysis was 70 seconds. Certified reference materials like CRM-875 and BCR-691 were used for checking the accuracy of the methods used for material analysis.

Results and discussion

The results of the pXRF analyses indicated that almost all the artefacts are made of copper-tin alloys. Lead, iron, arsenic and zinc are the major metallic impurities. **Figure 2** illustrates the tin content of the artefacts as histograms of the frequency distribution for each assemblage. The addition of tin improves the hardness and corrosion resistance of the alloy and reduces its melting temperature (Tylecote 1987: 192; Klein and Hauptmann 1999: 1080). Tin rarely occurs in concentrations above 0.1% in copper ores so anything above this limit should be considered a deliberate or perhaps an accidental addition (Hall and Steadman 1991: 230; Moorey 1994: 252; Pernicka *et al.* 1990: 272). In some cases, tin levels below 2% may also be the result of mixing copper with recycled bronze.

Site	Weapons		Tools		Jewellery		Table-ware / Utensils		Equipment of Horses / Chariots		Scrap Metal / Copper residues	
Limassol	Daggers	11			Rings	7					Amorphus lumps	9
	Spearhead	1			Pins	3						
											Total: 31	
Pyla *Kokkinokremos*	Arrowheads	2	Needles	7	Earrings	2					Fragments	28
			Handles	2	Bracelet	1					Flat sheets	11
			Spatula	1	Attachments / pendants	2					Wires	2
			Knife	1								
			Nail	1	Pins	2						
			Others	3								
											Total: 65	
Palaepaphos *Skales*	Spearheads	6	Tweezers	3	Fibulae	47	Bowls	32				
	Arrowhead	1	Needles	11	Pins	12	Vessel	1				
			Ladle	1	Rings	12	Obeloi	3				
			Awl	1	Finger-rings	10	Rod tripods	2				
			Saw	1	Earrings	6						
			Spatula	1	Bracelet	1						
			Others	6								
											Total: 157	
Salamis	Arrowheads	28	Rods	19	Earrings	63	Bowls	2	Bands	12		
	Spearhead	1	Needles	4	Pins	18	Cauldron	1	Blinkers	17		
	Shield	1	Chain	1	Attachments	7	Disks	4	Breast-plates	11		
			Scales	1	Finger-rings	3	Belts	5	Attachments	9		
			Rings	10	Rings	51			Standards	11		
			Nails	26	Mirrors	10			Nails	132		
			Spatula	1	Buckle	1			Rings	20		
			Strigils	3	Fibula	1			Sockets	4		
			Mountings	2					Caps	2		
			Handles	2					Tubular objects	17		
			Hooks	2					Loops	10		
			Hinges	3					Bell	1		
			Others	25								
											Total: 563	
											TOTAL: 816	

Table 1. The assemblage of studied copper alloy artefacts.

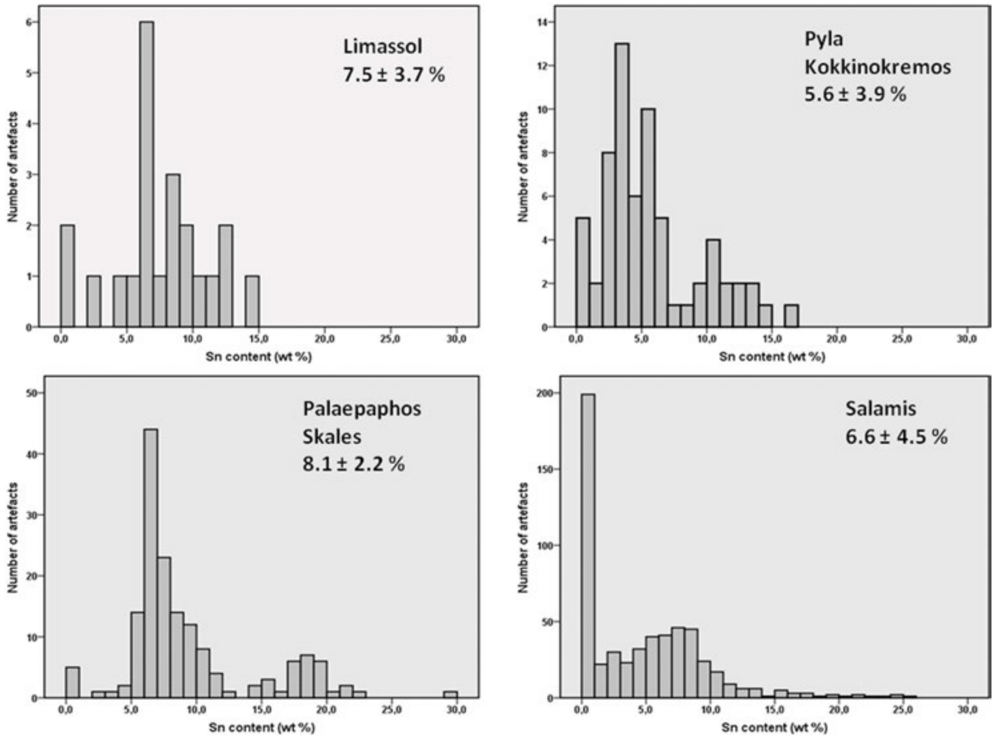

Figure 2. Histograms showing the tin (Sn) content of the studied bronze artefacts.

In the assemblage from Limassol, the average tin content is 7.5 ± 3.7%. More specifically, 18 out of 22 artefacts have a tin concentration ranging between 5.4 and 14.2% (Charalambous and Kassianidou 2012: 301-302). Significantly, all the objects which have a concentration of tin above 10% are daggers. A spearhead and a ring were found to have a very low percentage of tin (0.2% and 0.3% respectively). As Cypriot copper ores do not contain tin (Constantinou 1982: 15; Muhly 1985: 277), this small concentration must have been introduced accidentally and not deliberately, perhaps when copper metal was melted together with recycled bronze (Weinstein Balthazar 1990: 72-73).

The average tin content of the 65 objects from Pyla *Kokkinokremos* is 5.6 ± 3.9% (Charalambous and Kassianidou 2014: 200-203). Because the assemblage consists mostly of scrap metal, it shows a great variability in the tin content. A nail, a thin mass and a sheet, all contain no tin, while an amorphous lump, a small fragment and two sheets, have a tin concentration ranging between 0.5 and 1.5%. Furthermore, 29 objects, mainly scrap metal but also ornaments, tools and weapons have a tin concentration between 5.2 and 9.7 % and only 14 objects, including parts of tools and scrap metal in the form of thin masses and sheets, have a tin concentration higher than 10%.

In the Palaepaphos *Skales* assemblage, the average tin content of the largest categories of artefacts (needles, tweezers, fibulae, pins, rings, finger-rings, ear-rings and spearheads) is 8.1 ± 2.2%. However, there is another group of 32 artefacts, comprised mainly of hemispherical bowls (27 out of the 32), which are made of a high-tin bronze, with an average tin content of 18.9 ± 2.8%. Obviously there was a deliberate choice of alloy with a tin content which is consistently over 10% for this type of artefact. The reason behind the use of this alloy must have been the production of objects with a golden colour, probably in an attempt to create prestigious artefacts that imitate the appearance of similar gold artefacts (Ashkenazi *et al.* 2012: 531-532; Papasavvas 2012: 120). At the other extreme, an obelos and a bowl have a tin content below 1% (0.3 and 0.7%, respectively), and only a pair of tweezers, a pin and a base of a fragmentary vessel, contain no tin at all.

As for Salamis' assemblage, the average tin content is 6.6 ± 4.5%. More specifically, 129 objects have a tin content ranging from 0.1 to 4.9%, 192 objects have a tin content in the range from 5 to 10%, while only 59 artefacts have a tin content over 10%. This high tin group is comprised mainly of chariot standards, horses' breast-plates, rings of various sizes, bracelets, disks and mirrors. At the other extreme there is a large group of 183 artefacts, comprised mainly of nails, which contain no tin.

Lead was a common additive to copper in antiquity. The specific alloying element, when added to copper, lowers the melting point of the alloy and improves the fluidity and by this way the cast ability of the metal (Klein and Hauptmann 1999: 1080). On the other hand, it reduces the alloy's hardness and toughness, when added in an amount higher than a few per cent (Giumlia-Mair 1992: 109). Copper ores are often associated with lead and thus when low amounts of lead are detected in copper alloys they are usually believed to be impurities. However, Cypriot copper ores are unusually free of lead (Constantinou 1982: 15); therefore its presence in the studied artefacts, even at levels lower than 1%, can only be interpreted as a deliberate addition. Lead, in Limassol's assemblage (**Table 2**), is detected in 15 objects (0.1-0.6%), while two pins, have a much higher amount of lead (1.9 and 6.2%). In Pyla *Kokkinokremos*' assemblage, lead is detected in 23 objects (0.1- 0.4%) while in four cases, namely a pendant (1%), a dagger (1.3%), a tool (3.2%) and a small cylindrical fragment (19.9%), the amount of lead is higher. The latter was therefore identified as a possible fragment of a rod tripod stand (Charalambous and Kassianidou 2014: 203) In Palaepaphos *Skales*, lead is detected in all objects, ranging from 0.1 to 2.6%.

Site	Pb (%)	As (%)	Fe (%)	Zn (%)
Limassol	0.1 - 0.6	0.2 - 0.4	0.1 - 1.6	n.d
Pyla *Kokkinokremos*	0.1 - 0.4	0.2 - 0.4	0.1 - 1.5	0.1 - 0.4
Palaepaphos *Skales*	0.1 - 2.6	0.2	0.05 - 1.4	0.1 - 1
Salamis	0.1 - 2	0.2	0.05 - 2	0.1 - 0.8

Table 2. Average concentration of lead (Pb), arsenic (As), iron (Fe) and zinc (Zn) in the studied artefacts.

Four objects have a much higher lead content. They are a hemispherical bowl (5.2%), a fibula (6.7%) and two rod tripods (4.6% and 11.9%). Finally, in the case of Salamis, lead is detected in almost all objects (with the exception of 16 objects) in concentrations ranging from 0.1 to 2%, while 48 objects of various types have a lead concentration higher than 2%.

In the objects with high lead concentrations, it is possible that the results of the surface analysis do not precisely reflect the actual concentration of the metal. Lead, when added in significant amount to molten copper, is not soluble, and has the tendency to produce a dispersion of fine particles on the surface of the object (Giumlia-Mair 1992: 109). In order to avoid this phenomenon, s significantly higher number of areas were analysed in the objects which were found to have a very high concentration of lead. These results are also important for another reason. If lead was being deliberately added to the alloy even in small quantities this will affect the results of any lead isotope analysis used to identify the provenance of the copper metal.

Arsenic, in concentrations higher than 2%, improves the properties of the alloy, resulting in the increase of its ductility and hardness (Pernicka et al. 1990: 268; Hauptmann 2007: 28). In the assemblage from Limassol, arsenic is detected only in six objects (27% of the total number of objects), while in the assemblage from Pyla *Kokkinokremos* it is detected in 30 objects (46% of the total number of objects), ranging from 0.2 to 0.4%. Furthermore, in the assemblages from Palaepaphos *Skales* and Salamis, arsenic is detected only in 25 (16% of the total number of objects) and 21 artefacts (3.7% of the total number of objects), respectively, in a concentration of 0.2%. The low detected concentrations indicate a non-intentional addition of the specific element. Arsenic was normally introduced to the alloy through the smelting of polymetallic copper ores, which contained arsenic in small concentrations (Giumlia-Mair 1992: 113), or through the flux (Tylecote 1982: 97). The only areas in the island with ores having high enough concentrations of arsenic suitable for the production of arsenical copper are Laxia tou Mavrou and Pevkos (Limassol Forest), southwest of the Troodos massif (Gass *et al.* 1994: 183-185). Much more likely is the possibility that these artefacts were partially made of arsenical copper deriving from the recycling of objects dating to the Early and/or Middle Cypriot. This conclusion is based on the fact that almost all objects that contain arsenic also contain tin (Weinstein Balthazar 1990: 78).

Iron was found in all analysed objects in concentrations ranging from 0.05 to 2%. Most of the objects have an iron content below 1%. Iron entered the alloys through the smelting of chalcopyrite (Tylecote 1982: 81), the most common copper ore in Cyprus (Constantinou 1982: 15). Also, the use of iron minerals as a fluxing agent during the smelting procedure, deliberately or accidentally, could have resulted in the introduction of a small quantity of iron in the finished artefacts (Muhly 1984: 36; Ashkenazi et al. 2012: 532).

No zinc was detected in the assemblage from Limassol. In the assemblage from Pyla *Kokkinokremos*, zinc is found only in 15 out of the 157 objects in concentrations ranging from 0.1 to 0.4%. In the assemblage from Palaepaphos *Skales*, zinc is detected in only 20 of the 157 objects in concentrations ranging from 0.2 - 1%. In the assemblage from Salamis, zinc is detected in 110 of the 563 objects (0.1 - 0.8%). Three objects have a much higher concentration of zinc. They are a pin (5.1%), a fibula (8.5%) and a nail (11.2%). The presence of zinc in low concentrations can be justified as a non-intentional addition to the alloy, resulting from the smelting procedure (Hauptmann 2007: 30), due to the occurrence of sphalerite, the zinc sulphide, in association with the Cypriot copper sulphide ores (Constantinou 1982: 15). The three objects which have a high zinc concentration, however, must be seen as examples of the early use of brass, namely the alloy of copper and zinc (Craddock & Eckstein 2003: 216).

Conclusions

The chemical analysis of a large number of copper alloy artefacts from the sites of Limassol, Pyla *Kokkinokremos*, Palaepaphos *Skales* and the Necropolis of Salamis, revealed some interesting results. Even from the earliest phase of the Late Bronze Age (represented by the artefacts from Limassol), bronze was used to produce a variety of objects. The optimum concentration of over 10% however was reserved for the production of daggers.

On the other hand, in the case of Pyla *Kokkinokremos*, the fact that more than half of the assemblage, mainly composed of different categories of scrap metal, has a tin concentration lower than 5% may indicate that tin was not available in abundance in the immediate area during the mid 12th century BC. As for Palaepaphos *Skales*, the analyses of the artefacts showed a generally high tin content, discouraging any suggestions for a shortage in this metal.

The analysis of different categories of artefacts revealed the use of different alloys suitable for the specific type of artefact. Thus, tools and weapons were produced with the optimal amount 8-10% of tin indicating a very good understanding of the properties of this precious additive. A different alloy, with much higher percentage of tin, was used for the group of the hemispherical bowls, in order to produce objects whose colour imitated that of gold.

Finally, in the case of Salamis, the results of the study indicate the abundance and use of tin to produce a large number of various types of objects. However, nails which form a significant part of the assemblage were made only with copper perhaps in order to save up on tin.

Regarding the other detected elements, lead was deliberately added into the alloys to improve their cast ability, although its low concentration in many cases suggests the use of recycled metal with initially higher concentrations of this additive. The presence of arsenic in a number of artefacts is interpreted as evidence for the use of recycled metal deriving from artefacts dating to the Early and Middle Bronze Age. Iron and zinc are believed to be non-intentional additions to the alloys, resulting from the smelting procedure and originating either in the copper ores or in the flux.

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INTO THE CRUCIBLE. METHODOLOGICAL APPROACHES TO RECONSTRUCTING ANCIENT CRUCIBLE METALLURGY, FROM NEW KINGDOM EGYPT TO LATE ROMAN BULGARIA

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Abstract

This research project is devoted to the study of ancient metallurgical crucible assemblages. Three assemblages from sites in distinct historical and cultural areas across the eastern Mediterranean are studied with the aim of reconstructing and contextualising metallurgical activities there. This involves the reconstruction of the technical processes, material use and the organisation of metal production both on the site and on a regional scale. The case studies are Qantir – Pi-Ramesse (New Kingdom Egypt), Gordion (Achaemenid Phrygia) and Serdica/Nicopolis/Philippopolis (Late Roman Bulgaria). No relation exists between these sites and each case study stands on its own: results from the technological reconstruction are interpreted within their particular archaeological and regional/historical context. The main purpose of this research is to evaluate methodological approaches to the study of crucibles and crucible assemblages by comparing the results for these three examples, not in terms of technology, but by evaluating the influence of varying crucible typology, preservation, abundance, contextual information, and sample availability. Contrasting the results of these case studies and comparing them to existing published studies, methodological issues for sampling, studying and interpreting ancient crucibles are discussed. Despite their informative value and common occurrence in (urban) archaeological contexts, crucible assemblages are not often studied in detail and a general approach for researchers has not been defined. Therefore, a final aim is to formulate more general recommendations for examining ancient crucible assemblages.

Introduction

Crucibles are commonly used for secondary metallurgical production processes, such as melting, refining, alloying and casting. Their representation in the archaeological record can vary from a single sherd to thousands of crucibles and from tiny fragments to complete examples. The study of such assemblages can address questions of technological choice and material use within a particular archaeological context, and inform on wider issues such as metals trade and the spread of technological knowledge. However, in-depth examination of crucible assemblages is time-consuming and a methodological framework for best practice is currently absent.

One of the main goals of this research project is to illuminate the methodological issues associated with the examination and interpretation of assemblages of metallurgical crucibles. Therefore, existing metallurgical crucible studies in the literature are reviewed and three metallurgical crucible assemblages from different (urban) sites in the eastern Mediterranean are examined. Their different nature in terms of preservation, abundance and context make these three case studies very suitable for methodological comparison.

However, each case study is of interest in its own regard as it reveals metallurgical practices for three distinct historical/cultural settings. The first case study is Qantir – Pi-Ramesse, the New Kingdom Egyptian capital, with metallurgical remains from the 13th century BC royal workshops. This represents the first full analytical study of metallurgical crucibles from ancient Egypt. The second case study is Late Phrygian (*c.* 540-330 BC) Gordion (Turkey), where crucibles from various dump contexts within the ancient citadel are examined. Again, no comparable studies exist for this area and period. The third and final case study involves crucibles from various emergency excavations in Bulgaria, covering several Late Roman sites from the 2nd - 5th century AD (mainly 2nd century). Though some comparable studies exist for the western Roman Empire, examples from the eastern Roman provinces are few.

For each case study, the crucibles relate to mainly copper-based, secondary metallurgical activity. Their analysis thereby provides a basis for a framework of metallurgical studies for each of their particular historical/cultural settings, but also contributes to secondary copper metallurgy studies in general. Strange as it may seem, very few studies of secondary metallurgical activity exist in the literature, and the production of bronze, for example, is still poorly understood despite its apparently simple nature (Pigott *et al.* 2003; Rovira 2007).

To summarise, the merit of this project is expected to be twofold: on the one hand, each case study will provide a starting point for furthering our understanding of secondary metallurgy for specific areas in the eastern Mediterranean, but also ancient crucible technology in general, while, on the other hand, the methodological approach to the study of crucibles and crucible assemblages should benefit the wider field of archaeometallurgical research.

Research aims

For each of the different sites, the metallurgical assemblage is sampled and studied following methods discussed below. The aim of this analysis is to reconstruct technological choices made by ancient metallurgists. This involves the techniques that were selected to produce a certain metal or alloy and the materials that were chosen for this purpose, which then feeds back into broader issues of trade and technological change. However, the primary goal is to understand each activity within its particular context, and fit the metallurgical results into local, contemporary frameworks of the organisation of metal production. Possible connections to the production of other materials, such as glass, are also considered.

The principal aim of the research is to evaluate existing methodologies for the study of metallurgical crucibles and crucible assemblages. This is achieved by assessing the effects of sampling on both the crucible and assemblage scale, as well as by evaluating the way by which crucible samples are then analysed. Important here is the variability in terms of material remains between the three case studies. For Qantir – Pi-Ramesse, there is an excellent conservation of the abundant remains, coming from a well-preserved workshop context, with high temporal resolution. The Gordion assemblage also consists of fairly abundant, well-preserved material, but comes mainly from dump context, with less constrained dating and only inferred connections to production installations. Finally, the Bulgarian material is far more limited, from various emergency-excavation contexts, covering a broad time period. Here sampling constraints allowed only small or tiny crucible fragments to be obtained.

These case studies provide the opportunity to evaluate the influence of different crucible types and archaeological contexts on methodological choices. This involves questions such as: how many samples are needed to get a representative understanding of a metallurgical crucible assemblage? How large does an individual sample have to be in order to be representative of a crucible? What is the informative value of studying a limited, fragmented assemblage such as the Bulgarian one (which is arguably the most common occurrence in archaeological projects)? What is the best approach and is it actually worth the expenditure of time and money? Which analytical methods are appropriate for answering particular research questions? Can some general recommendations for sampling, analysis and interpretation be defined?

Materials and methods

For each of the three case studies, the main research material consists of crucible remains, with varying degrees of preservation. These crucibles are subjected to macroscopic study by the naked eye in the first stage. All crucibles are analysed using handheld XRF for initial 'screening' and later comparison to more detailed microscopic (chemical) analysis. Following this, a selection of crucibles is sampled for further detailed analysis by optical microscopy and scanning electron microscopy (with energy dispersive spectroscopy). Samples are cut from the crucible using a saw, mounted in resin, ground and finally polished to ¼µm. After study by optical microscopy, the samples are carbon-coated and analysed by SEM-EDS.

Typically, a crucible heated on the interior has three main zones, from the exterior to the interior: a ceramic fabric, a bloated zone and a slag zone. The ceramic zone is simply the fabric of the crucible, usually made up of tempered clay, sometimes pre-fired before use. The bloated zone occurs between the ceramic zone and the slag zone and indicates the point in the crucible profile where temperatures were high enough to disintegrate the ceramic which thereby loses its structure. The slag zone then, marks the complete disintegration of the ceramic and its interaction with the crucible charge, typically consisting of fuel ash and (liquid) metal. This slag zone usually consists of a glassy phase in which remnant quartz (or other ceramic constituents), various oxide phases and metal prills can be found. When crucibles are heated externally, a vitrified layer can also form on the exterior surface of the vessel. In some cases, not all of these zones are present, e.g., when temperatures did not exceed the bloating point of the ceramic and no slag was formed, or when extreme temperatures have completely vitrified the ceramic.

In general, the aim of the microscopic study is to investigate the presence and nature of these different zones. Using SEM-EDS, the chemical composition of the different zones is measured. By comparing changes in bulk composition between the crucible ceramic zone and the slag zone, and the different metal and oxide phases therein, the crucible charge is reconstructed. Looking at the wider assemblage then, variations in the crucibles and their charge are investigated to reconstruct the variability of technology and material use. These results are then interpreted within each particular archaeological context, as well as the wider context of metallurgical and economic activity for the relevant area and period.

Case study: Qantir – Pi-Ramesse

Ancient Pi-Ramesse is located largely underneath modern Qantir, in the eastern Nile delta of Egypt, and was established as pharaoh Ramses II's capital. Under his reign, the city flourished as a Late Bronze Age trade centre, from where Ramses expanded his influence as one of the select rulers engaged in diplomatic exchange in the eastern Mediterranean (Van De Mieroop 2007). During this period, Egypt was at its largest territorial extent in history and actively involved in a complex and changing eastern Mediterranean economic system (Sherratt 2003), exposing it to an expanding cultural diversity. This highlights the importance of Pi-Ramesse as a strategic location, which served as the military basis for the pharaoh's chariot garrison. It is beyond the scope of this paper to fully discuss the history and politics of Ramesside Egypt in its Mediterranean context at this point, but the international nature of Pi-Ramesse is worth highlighting, as does its scale as an urban development project.

A number of high temperature production processes, all involving the use of copper, were carried out at Pi-Ramesse. All of these took place in the area surrounding sites Q I, Q IV and Q V, which should probably be considered as one large high temperature production centre. This encompassed the primary production of red glass (Pusch and Rehren 2007), faience (Hayes 1937; Herrmann 1957), Egyptian Blue (Hamza 1930) and bronze (Pusch 1990, 1994; Rehren and Pusch 2012; for a general background on the excavations at Qantir *cf.* Pusch and Herold 1999).

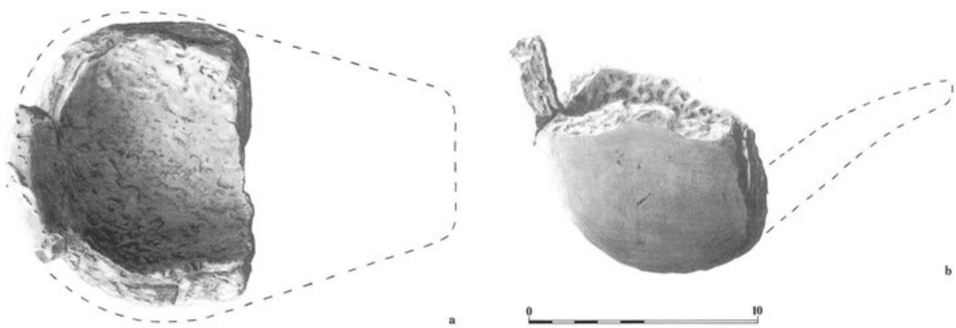

Figure 1. Reconstructed crucible. Left: top view, right: side view (from Pusch 1990).

For this research project, the bronze crucible remains are investigated. Over one thousand crucible fragments have been recovered, all conforming to a highly standardised crucible shape shown in **Figure 1** (though no complete vessel has been recovered). The distinct industrial-like setting of melting batteries and cross-furnaces where the crucibles were found at Qantir, in association with tuyères, pot bellows, a piece of copper ingot, scrap bronze, moulds and bronze objects, immediately allowed them to be identified as part of a high temperature bronze production facility. Macroscopic examination of the crucible fragments shows their consistent thickness (±1.5 cm walls, thickening towards ±3 cm at the bottom of the vessel), porosity from burnt-out organic temper and regular cross-section profile.

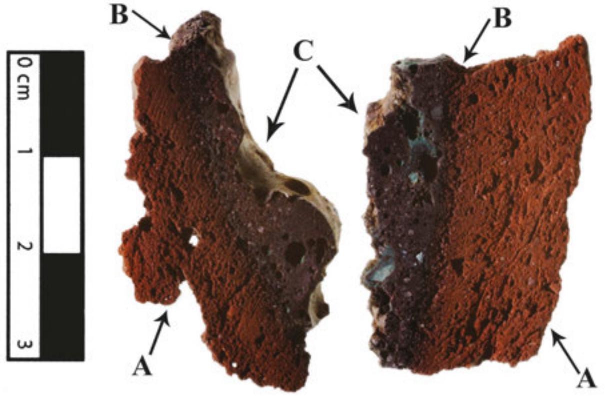

Figure 2. Profile through two fragments of crucible wall: ceramic area (A), bloated transitional area (B) and slagged area (C).

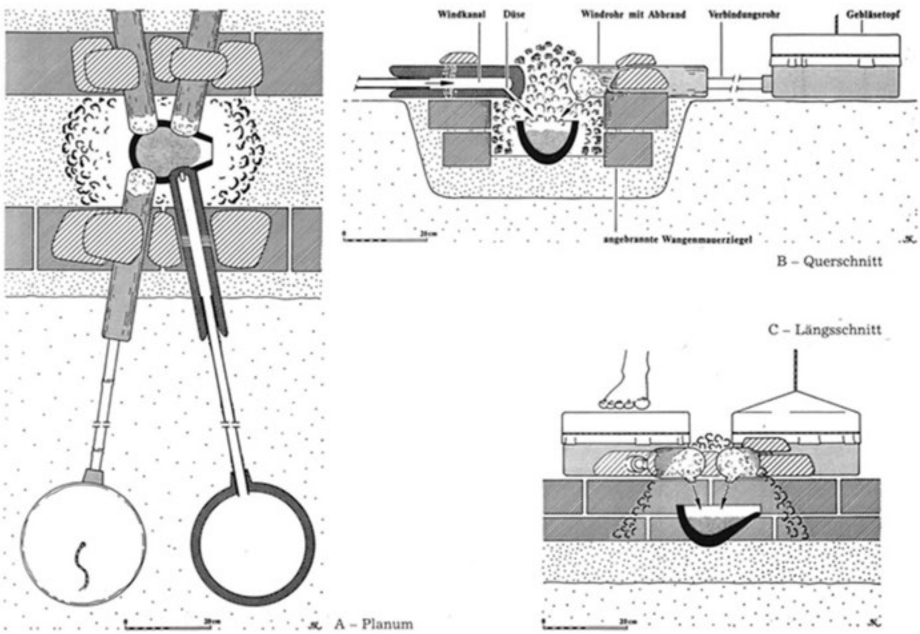

Figure 3. Operation of the industrial melting batteries (from Pusch 1994).

The outside of the crucibles consists of a red-fired ceramic area, the result of pre-firing the crucibles at ±900°C. The ceramic part gradually becomes more porous towards the inside of the crucible wall, up to the point where it loses all its structurally bound water, disintegrates and bloats. Firing experiments performed with local Nile silt indicate that this bloating takes place at temperatures of 1200°C upwards. The inside of the crucible shows the continuation of this bloated zone, which is a (partly) vitrified zone resulting from the further disintegration of the ceramic and its interaction with the crucible charge, which traps metallic residues and other crucible charge remnants. This typical profile, shown in **Figure 2**, is explained by the internal heating of the crucibles, as shown in the reconstruction in **Figure 3**, which exposed the interior of the crucible to the highest temperatures.

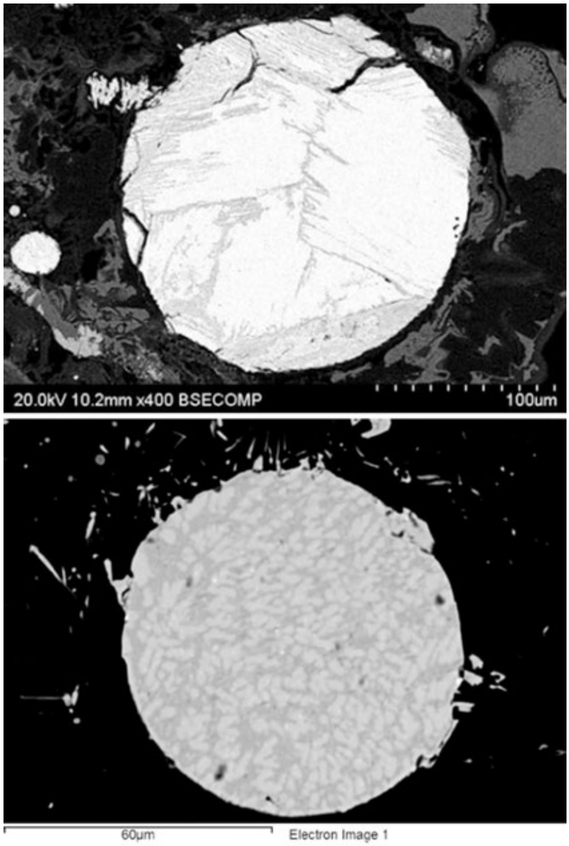

Figure 4. High tin prills. Top: ε-phase (±40wt% Sn, 60wt% Cu). Bottom: δ- and α+δ-phase (±29wt% Sn, 71wt% Cu).

For these crucibles, the chemical composition of the ceramic area and the slag area was compared to reconstruct the crucible charge. The full discussion of how these results are interpreted to reconstruct the technological process behind bronze production at Pi-Ramesse is beyond the scope of this paper (detailed by Rademakers *et al.* forthcoming). In short, the detailed analysis of forty-nine crucible samples has revealed the variability in technology and material use within the bronze production area at ancient Pi-Ramesse. High-tin prills (**Fig. 4**) in several crucibles indicate active alloying. While cassiterite has been tentatively identified in some crucibles, the use of fresh tin could not be excluded as part of the production technology. Therefore, it is suggested that bronze was produced by alternating between the alloying of fresh copper and tin, cementation with cassiterite and recycling of existing bronze. Multiple copper sources seem to have been used in this process. Lead isotope analysis is being undertaken to further elucidate this (Rademakers *et al.* in preparation).

Though a fair understanding has been developed of Late Bronze Age primary copper production and Egypt's probable access to various sources through trade (e.g., oxide ingots), the actual use of metal from these sources has rarely been documented. Only the study of secondary production remains can provide a connection between the trade of metal, its alloying/recycling in a variety of contexts and subsequent use in final objects, again in different settings. These findings show for the first time which materials were accessible for the Ramesside workshops and reveal the technology used to produce bronze there. The range of copper sources (tentatively) attested provides new insights into the nature of metal trade and the probable use of cassiterite for cementation offers an interesting contribution to the long-standing debate on tin use in the Late Bronze Age Mediterranean.

The results also show how, within a very standardised-looking assemblage, large variability can exist both in technology and material use, emphasising the necessity of comprehensive sampling when studying crucible assemblages. They also illustrate how a single technological (crucible) process can yield strongly variable production remains: conditions within a single crucible can vary strongly between different areas of the crucible and throughout the duration of the process. Therefore, a single crucible sample is unlikely to be representative of the entire crucible process, while multiple samples could potentially reveal it in its entirety.

Further work and expected outcome

This case study serves as a condensed example of the intended results for each of the three case studies. A comprehensive overview of metallurgical activity for each of the three sites under investigation will be interpreted within its local context as well as its relevant wider historical and economic framework, and published in relevant journals and/or book chapters. Drawing on the rich variation between them, the results of these case studies will then be used for an overarching discussion of methodological issues concerned with the study of crucibles and crucible assemblages. In conclusion, this project hopes to provide some valuable suggestions for future research in this developing field of ancient technology studies.

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COPPER ALLOY PRODUCTION AND CONSUMPTION IN THE TUSCIA REGION DURING THE MIDDLE AGES

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Abstract

This research aims to make a substantial contribution towards our knowledge of copper alloy production and consumption and its broader socio-economic implications during the Middle Ages in the Italian region of Tuscia (current South Tuscany and North Latium, respectively). The main sites under investigation are Leopoli-Cencelle for South Tuscia and Miranduolo for North Tuscia. These are very similar sites in terms of extent, fortification process, cultural and political influences. Moreover, they are both close to important mining sites, the *Tolfa Hills* and the *Colline Metallifere*, respectively. Everyday life objects, dress accessories, tools, and structural and decorative items are studied, along with scrap metal and a set of metal debris coming from a bell casting pit. The analytical approach includes portable pXRF, optical microscopy and SEM-EDS, so as to acquire information on copper alloy composition and manufacturing process; EPMA and LI analysis with ICP-MS, so as to identify minor and trace elements patterns useful for the determination of the provenance of metal. The data will allow some preliminary discussion not only on technological aspects, but also on how and to what extent Leopoli-Cencelle and Miranduolo were inserted in a wider interregional context. A comparison with regional and interregional contexts and assemblages is anticipated in order to better understand the nature and scale of possible technological, socio-cultural, economic and political relations that occurred during the medieval period between this and other regions.

Introduction

The project focuses on identifying and interpreting patterns in copper alloy production and consumption in the Tuscia region (Central Italy) during the Middle Ages. This research concentrates on the technological and compositional study of copper alloy artefacts and production debris from a range of sites from the 11th to the 14th centuries AD, using a contextual and comparative approach in order to understand aspects of the technological, socio-cultural, economic and political factors affecting the manufacture and use of metal in North and South Tuscia (current South Tuscany and North Latium, respectively).

The main sites under investigation are the town of Leopoli-Cencelle for South Tuscia and the Miranduolo Castle for North Tuscia. These are very similar sites in terms of scale, fortification process, and both cultural and political influences. Furthermore, they are both close to important mining sites involved in the extraction of iron, copper and galena ores during the period under investigation (Calderoni *et al.* 1985; Duchi *et al.* 2001; Valenti 2008).

Applying a comparative approach between these sites, and by comparing these to results available from other regional and interregional archaeological contexts, I am trying to identify patterns in alloying practices as well as in consumption behaviour that may respond to context-specific socio-cultural constraints and, specifically, the nature of the relationships between these neighbouring areas and other regions.

Background

From the 11th century, the Tuscia region played a leading role during the so-called medieval economic revolution (Lopez 1976). Tuscan families, such as the Aldobrandeschi and the Gherardeschi, built their power by controlling strategic activities such as metallurgy thus contributing to the growth and expansion of the influence of towns like Pisa and Siena. As stated by Farinelli and Francovich (1994), the need to control metallurgical activities was one of the main contributing factors to the transformation of villages into fortified settlements in the Southern Tuscia region, a phenomenon known as *incastellamento*. More recently, the same observation has been made with regard to fortified centres built in the Tolfa hills region (Zifferero 2006).

A short overview of the metallurgical activities, including the production and circulation of metals in the region during the period under investigation, is indicative of the general trends of the interconnections between minor and major Tuscia centres. As for copper production and trade, archaeological evidence has shown different approaches by local populations directly derived by the presence or absence of centralised powers. The Tuscia metal ore deposits are the richest in continental Italy, mostly localised in the *Colline Metallifere* area, the island of Elba, the Fiora river territory and the Tolfa hills (**Fig. 1**).

Figure 1. Principal mineralisations of Tuscia, and principal archaeological sites studied (in capital letters), mining districts and main towns (modified from Giardino 2008:74).

The latter were mined at least from the Late Bronze Age (Guidi *et al.* 2005), but there are indications of even earlier exploitation, probably from the Copper Age (Giardino 2005). By contrast, there is little evidence of exploitation of the *Colline Metallifere* during the Bronze Age. Together with the Elba mining district, this coastal area seems to have been extensively mined from the Iron Age onwards, becoming the most important mining district of the Peninsula by Late Antiquity. As with iron production, the collapse of the imperial economic system caused a dramatic downscaling of all sorts of production in this period. Non-ferrous metal mining became a small-scale activity, mostly linked to local needs. As indicated by contemporary Tuscan written sources from the 8th and 9th centuries, specialised metalworkers such as *calderarii* and *aurifices* were very valued and sought after, probably because of the difficulties encountered in the supply of non-ferrous metals (Farinelli and Francovich 1994).

From the 11th century the political and economic situation changed, producing a substantial revitalisation of the metallurgical production and trade mainly led by northern Tuscia families who progressively acquired the right over the principal mining districts of Elba and *Colline Metallifere*. The Miranduolo and Tolfa hills districts seem to have definitively lost their importance, even if small-scale extractive activities possibly continued. By the end of the 12th century all the metallurgical production and trade in the region was subjected to the power of landlords mainly coming from Central and Northern Tuscia, that is from Pisa, Lucca, Siena and Grosseto.

Specific objectives and questions

How the predominant position of Pisacould have affected minor centres in their rights to exploit local mining resources is a matter to be investigated, as well as how these restrictions could have encouraged change in the technologies and metallurgical products. As for the technological exchange and its sociocultural implications, this research is investigating the importance of mobile Pisanworkers, the *fabri pisani*, whose extractive and metalworking activities have been documented along the Tyrrhenian coast from the 11th century (Corretti and Firmati 2011; Gattiglia 2011: 113 and 132). The focus is placed on the Pisan *magistri campanari*, literally 'bell craftsmen', and the possibility that they could have been involved in the bell casting activity of Leopoli-Cencelle, where a furnace structure shows similarities to those recently discovered in the neighbouring Pisan site of Chinzica (Gattiglia and Milanese 2006).

The study also focuses on specific object types categorised by function, taking into account the need to illuminate different aspects of everyday life such as social condition, craft skills, and trade interests. The study of the chemical composition and manufacturing traits enables comparison with medieval sources, as well as an assessment of the number of active workshops, their skill and level of specialisation. Dress accessories and personal ornaments, in particular, are compared in order to establish regional similarities, as suggested for the 12th-13th centuries in a recent work by Belli (2005).

In order to achieve these goals each site is investigated in order to answer the following more specific questions:

1) What are the alloys employed, how do they compare across functional categories and between sites/periods?
2) What are the predominant manufacturing traits and do they suggest specialised techniques that may be related to known technological traditions?
3) What are the main sources of non-ferrous metals? Do patterns suggest centralised exploitation or smaller ventures? Is there evidence of specialisation in the exploitation of copper? What was the role of the Colline Metallifere?
4) What is the nature, scale, skill and technological sequence of copper alloy production and how does it manifest in production remains? How do these compare to what we know for the broader region? Is there any change in organisation of production?
5) Do some specific object types, such as dress accessories and personal ornaments, reflect external cultural influences?
6) Does any local cultural trend emerge from the study of consumption and production assemblages?
7) Do the consumption assemblages reflect a socioeconomic stratification, and during which periods?

Originality and relevance

This project represents the first archaeometallurgical study of medieval copper alloy production and consumption based on comparative analysis between small centres along the border between north Latium and south Tuscany. In addition, it will constitute the first archaeometric study on both Leopoli-Cencelle and Miranduolo copper alloys. As for the Latium town, the only other archaeometallurgical study, by the University of Chieti, focused on the production of iron (Mihok *et al.* 2000; La Salvia and Mihok 2003).

This research takes advantage of the previous works on Tuscan medieval landscapes, perhaps the only geographically structured research conducted in Italy during the last twenty years (Francovich and Valenti 2005; Augenti 2009). The relation of this research with the University of Siena in studying the Miranduolo assemblage provides an important opportunity to add new information on local technology, but in a more effective regional perspective. Thus, this research is placed in the *from local to global* strategy, recently outlined by Brogiolo (2009) as one of the ways to promote a revitalisation of the discipline of Italian medieval archaeology.

As opposed to the Miranduolo project, the work on Leopoli-Cencelle has only recently begun to form part of a wider geographical research project, although the original intention was to define a future archaeological district, with Leopoli-Cencelle and Corneto, the Etruscan *Tarquinia*, representing prominent sites (Nardi and Zifferero 1990; Pani Ermini 2003, 2005). After a long period of a standstill in the research, the Leopoli-Cencelle project finally presents a more structured framework, and this research has been already accepted as a part of the project.

Despite their strong geographical and historical connections over the centuries, the relations between the two investigated territories (north Latium and south Tuscany) have been mainly studied for the Etruscan and Roman period. As for the material and sociocultural interconnection along the borders of these two regions during the Middle Ages there is a substantial gap. Despite the evidence of metallurgical activities both in south and north Tuscia, none of the studies on material culture started during the last decade has focused on copper alloy production and consumption. In fact, the importance of the mining district of *Colline Metallifere* in the economy and social structure of medieval Tuscany seems to have overshadowed minor, but not insignificant, mineral areas such as the ones of the Tolfa hills and the Merna valley (Miranduolo). This research is trying to fill this gap, going from local to regional, and from regional to interregional perspectives. As for the archaeometric approach, one of the aims of this research is to produce new and original data that can be used for metal provenance studies, with information on isotopic and trace element data recovered from mineral deposits from the *Tolfa Hills* and Miranduolo to be added to existing databases.

Analytical methodology

Analysis is focused on technology (style, working techniques, etc.) and composition (alloy selection, provenance, etc.), to provide a reference point for contextualisation and comparison with relevant datasets and studies. The chemical composition of the artefacts, when considered together with the objects' function and style, provides information regarding alloy selection and how these may have varied depending on technical or economic issues such as differential access to resources in different contexts. The impurities detected in the

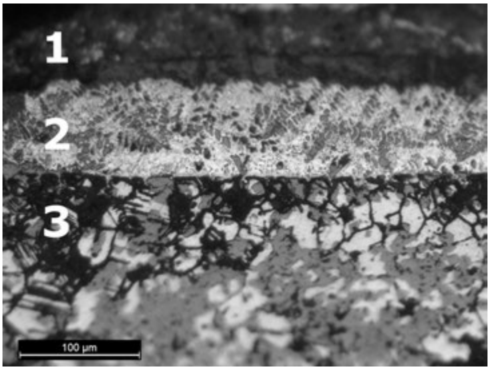

Figure 2. Finger-ring CC-G3/6 from Leopoli-Cencelle. The analysis at the optical microscope allows the understanding of both structure and crystallography and manufacture patterns. 1) Surface relief effect is visible as a result of corrosion; 2) the outer layer presents a two phase structure typical of a cast; 3) one phase structured metal base, highly corroded and showing typical signs of cold-work and annealing. Image under plain polarised Reflected light, magnification 200x.

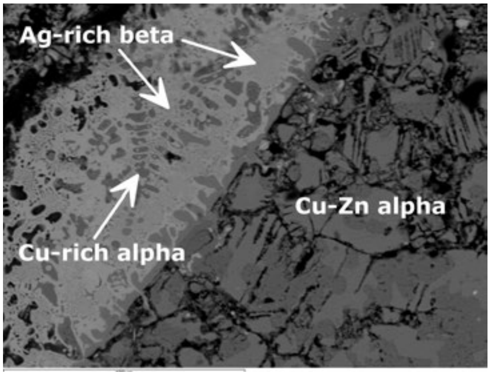

Figure 3. The same finger-ring CC-G3/6 analysed with SEM-EDS. BSE image of the sample, magnification 600x, showing the Ag-Cu coating made of an Ag-rich beta phase (whitish) and a Cu-rich alpha phase (greyish). The base metal is a Cu-Zn single phase alloy.

metal, together with their isotopic signature, help to determine the source(s) of the raw material, thus helping to reveal the extent to which metal production may have been centralised.

The instrumental analyses concentrate on:

- identifying the composition of copper alloys artefacts, so defining compositional groups;
- reconstructing the manufacturing process;
- identifying the geological origin of the metal.

In order to achieve these objectives, artefacts and metallurgical waste materials were analysed at the Wolfson Archaeological Science Laboratories of the Institute of Archaeology UCL with:

1) a pXRF in order to see overall trends in alloy choice and define compositional groups based on semi-qualitative and semi-quantitative chemical composition data; screening data helpful for sub sampling (not at UCL);
2) optical microscopy to understand structure and crystallography of the samples plus manufacture (**Fig. 2**);

3) SEM to perform structural observations and, combined with EDS in order to analyse the major elements composition (**Fig. 3**), and with EPMA in order to identify trace elements in selected samples;

4) LI analysis with ICP-MS in order to identify the provenance of metal (not at UCL).

Conclusions

The data obtained provide some information on both the production and consumption of copper-alloy artefacts in Leopoli-Cencelle and Miranduolo. They can also be used to draft a preliminary discussion based on specific objectives and research questions of this project. Leopoli-Cencelle is marked by the predominance of brass and gunmetal, while Miranduolo shows a predominance of pure copper. As for the former site, three main interrelated aspects seem to have determined the general alloying choices: technological, aesthetic and economic. The first is mainly reflected by the use of lead in brass, with low levels in hammered artefacts, and higher levels in cast objects where it is used to enhance castability. The second is demonstrated by the use of brass in more valuable, decorative objects, and in the use of fire-gilding and mercury silvering techniques to provide valuable coating in clothes fittings such as buttons. The amalgam of gold and mercury is also evident used in the production of jewellery, proof that technological, aesthetic and economic choices can be combined.

The presence of gunmetal as the result of recycling scrap metal, as well as the use of this specific alloy in cheap objects, shows the adaptability of metalworkers in relation to economic constraints, as well as the general awareness of the value to be assigned to different types of alloys in relation to the final product. The small number of pure bronzes in the assemblage could be due to the lack of tin availability in the region. High tin level is almost always associated with gunmetal. Thus, it can be suggested that the large quantities of Etruscan bronzes available in the region influenced both technological and economic choices, leading to an extensive recycling practice. Investigations conducted on scrap metal and by-products confirmed that the two areas identified as workshops were essentially committed to secondary activities such as finishing, repair and recycling of metal artefacts. These workshops functioned at least from the first decades of the 13th century, and were strictly serving local needs.

This small-scale activity matches other similar regional and interregional contexts from the mid-12th century. Both simple scrap metal and fine-worked pieces were recycled by re-melting, or simply by adapting shapes and adding rivets to produce new artefacts. The discovery of fine-worked pieces of different alloy composition, ready to be assembled, suggests a certain manufacturing adaptability of local smiths, as well as the social status of certain customers. Additionally, the study of the technology behind the Leopoli–Cencelle bell casting pit could be related to Pisan *magistri campanari*, or at least by local craftsmen influenced by their works. This is consistent with the documented itinerant activity of one of the most famous Pisan bell founder families, the Bencivenni, which was particularly active in central Italy during the mid-13th century.

The Miranduolo assemblage is characterised by the predominance of pure copper, with few artefacts showing brass or gunmetal composition. The latter are mainly observed in personal ornaments such as finger-rings and brooches, dress accessories, and everyday tools such as thimbles and tweezers. The fact that those types of small and mobile artefacts show a different composition could reflect a certain mobility of goods in order to address specific aesthetic or functional needs. The predominant use of copper, easily available, could be strictly related to the role Miranduolo played in controlling the eastern access to the mineral district of the Colline Metallifere, and the proximity of mineral areas rich in iron, copper and silver. Thus, copper consumption seems to be exclusively related to local exploitation, and not necessarily linked to trade. This does not come as a surprise, as the exploitation of local mineralisation was enhanced by the Gherardeschi, a Tuscan family strongly involved in metallurgical activity, which played a key role also in the Pisan development and exploitation of the south Sardinian silver district of Iglesias.

As for the gilded object typologies analysed in this study, mounts and small decorative objects coming from the Andalusian site of Calatrava la Vieja (Barrio *et al.* 2004) show high similarities in both technological and aesthetical choices. It is worth noting that both Tuscia sites were under the influence of the powerful Tuscan families which were involved in the trade of goods across the Mediterranean, notably with the Iberian Peninsula and the Islamised lands of South Italy. Thus, the high compatibility between gilded artefacts coming from both Andalusian and Tuscia contexts could be consistent with mutual cultural influences that could have occurred across the western Mediterranean.

On both sites, mercury silvering has been found in the form of small hemispherical buttons. This kind of object appeared in Italy and Europe during the 13th century where it was probably introduced from the East Mediterranean by traders. Unfortunately, no other archaeometric studies are reported on this type of artefacts. In the light of the limited evidence available, mercury silvering still seems to have been confined to relatively cheap objects in order to give them a more aesthetic value (Anheuser 1997). The issue concerning a possible local exploitation for both sites is still open but it may be clarified by the results of lead isotope analysis which is currently in progress.

Acknowledgements

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WORK PACKAGE 5

The study and conservation of architectural decoration from the eastern Mediterranean. Issues of material properties and cultural heritage

WORK PACKAGE 5

The study and conservation of architectural decoration from the eastern Mediterranean. Issues of material properties and cultural heritage

Work package 5 is focused on the study of architecture and building decoration from the eastern Mediterranean countries of Cyprus, Greece and Jordan. This work package seeks to develop and employ modern scientific methods of analysis to better understand a series of issues, including the increase in the number of pigments and the consequent enrichment of the colour palette, the use of different binding media, during, for example, the period following the advent of Alexander the Great, or during the transition from the Hellenistic to the Roman period, the composition of the foundation mortar of mosaics made in different techniques (e.g. opus tessellatum, opus vermiculatum, opus signinum, opus sectile, etc.), in order to better understand the evolution of the technique, the identification of regional characteristics and of local workshops, and, eventually, the establishment of a chronological evolution. This work package specifically deals with:

- the identification and analysis of artificial materials used for the making of mosaic tesserrae, such as glass, faience, silver, gold: papers by Francesca Licenziati (University Paris-Ouest, France) about the Hellenistic mosaics from Delos in Greece, and by Olivier Bonnerot (University of Cyprus) about the production of Cypriot wall mosaics;
- the analysis of the constituents, composition and pigments of stucco decoration from the region: paper by Lydia Avlonitou (University Paris-Ouest, France) about the wall paintings of Macedonia (Greece) from the Classical to the Roman period;
- an assessment and quantification of masonry damage at the castle of Azraq, in central Jordan, involving the digital documentation of the masonries and the compositional characterisation of the mortars used in the castle construction, with the ultimate objective to develop a conservation and management plan for the site: paper by Mart Tenconi (Hashemite University, Jordan);
- the application and the development of computational intelligence methods in the analysis of archaeological data: paper of Elisavet Charalambous (G.M EuroCy Innovations Ltd, Cyprus).

Prof. Anne-Marie Guimier-Sorbets
Work Package 5 leader
Université de Paris-Ouest, France

THE TECHNIQUES AND MATERIALS OF HELLENISTIC MOSAICS WITH A SPECIAL FOCUS ON THE VITREOUS MATERIALS OF THE MOSAICS FROM DELOS (GREECE)

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Abstract

This paper presents a research project on the techniques and materials used for the manufacture of the Hellenistic mosaics of the eastern Mediterranean, with a special focus on vitreous *tesserae* used in the mosaics of Delos. The mosaics of Delos comprise one of the most important corpora of mosaics dated to the Hellenistic period; a time of important innovations related to the materials and techniques used for the production of mosaics. The principal aim of this research is the compositional, technological and microstructural study of the glass and faience *tesserae* of the mosaics from Delos, in order to identify the raw materials and the techniques used in their production, and where possible identify the provenance of the raw materials. The analytical agenda of this project comprises two phases. The first phase involves the use of portable non-invasive instruments for an extensive *in situ* compositional and technological study of the vitreous tesserae of the mosaics. In the second stage, isolated *tesserae* have been selected for a more detailed study with the application of laboratory-based analytical instruments. The ultimate objective of this archaeometric investigation is to enhance our knowledge regarding mosaic production in the Hellenistic period, particularly on Delos, and to contribute new data to scholarly discussions about glassmaking in the Hellenistic period.

Introduction

This research focuses on the techniques and materials used in the production of Hellenistic mosaics in the eastern Mediterranean, with a special focus on the vitreous *tesserae* of the mosaics from the Cycladic island of Delos. The Hellenistic corpus of mosaics from Delos is characterised by the use of vitreous materials in a variety of colours which is remarkable for that period, and offers an important opportunity to study mosaic production on the island. An extensive archaeological research on the use of glass and faience in the mosaics of Delos was conducted by Guimier-Sorbets and Nenna (1992; 1995). This current research integrates earlier studies with new analytical data deriving from an archaeometric investigation of vitreous *tesserae*. Finally, this project addresses the growing interest in the study of the materials employed in mosaics production as a complementary tool for understanding the work of mosaicists (*cf.* Boschetti 2011; Neri and Verità 2012; Blanc-Bijon 2012).

The Hellenistic period (4th -1st centuries BC) was a phase of great experimentation in terms of the techniques and materials used in the production of mosaics. A pictorial style in mosaics can be observed starting from the second half of the 4th century BC (Bruneau 1987: 48-86), with Pliny much later describing this as "painting in stone" (Naturalis Historia, XXXV, 3). In fact, from the initial flat and bichrome floor decoration, similar to a "stone carpet" (Bruneau 1987: 54), mosaics began to be characterised by illusionistic three-dimensional representations and a richer polychromy. Mosaicists introduced several innovations to imitate the contemporary paintings and reproduce their naturalistic effects (Bruneau 1972: 34-35; 1987: 55-86; Guimier-Sorbets and Nenna 1992: 607-609).

During the 3rd century BC, the craftspeople started to use small pieces of cut stone, the so-called *tesserae*. The use of regularly cut elements was probably due to both practical and aesthetic reasons. On the one hand, it served as a possible means for overcoming the difficulties related to the availability of pebbles of the right size and colour, and on the other hand it allowed the creation of more elaborate designs, thus enhancing the pictorial effect (Dunbabin 1999: 18-37). Indeed the rectilinear edges of the *tesserae* made the mortar interstices smaller, and as such, consequently reduced the typical discontinuity present in mosaics (Bruneau 1987: 62-64). The intention of the mosaicists to conceal this discontinuity led also to the invention and development of the so-called *opus vermiculatum*; a technique that was first applied by the Alexandrian mosaicists at the beginning of the 2nd century BC. The *opus vermiculatum* technique made use of tiny, irregularly shaped *tesserae* (Guimier-Sorbets 2007) and was particularly employed in the figured decor and in the manufacturing of the *emblemata*, which are small, very fine mosaic panels. They were produced separately in the workshop and then placed on the floor as finished products (Dunbabin 1999: 29).

Another technical trick commonly used by the artisans to enhance the mosaic pictorial character was to paint the mortar the same colour as the surrounding *tesserae*, with the aim to minimise visual discontinuity (Bruneau 1972: 34-35; Guimier-Sorbets and Nenna 1992). The imitation of contemporary paintings, and particularly the achievement of the third dimension *trompe l'œil* effect in mosaic decoration required an extended colour *palette*, not always available in natural materials. For this reason, mosaicists began to use artificial materials such as *terracotta*, faience and glass, to supplement the colours of stones, enrich the mosaic polychromy and play with the light and shadow effects, with the ultimate objective to achieve the illusion of perspective (Guimier-Sorbets and Nenna 1992; Dunbabin 1999: 279-281).

The mosaics of Delos

The mosaics of Delos are one of the most important corpora of mosaics dated to the Hellenistic period. More than 350 pavements have been catalogued by Bruneau (1972), the vast majority of them dated between 130 and 88 BC. It was at the end of 167 BC that Delos was declared a free port and developed into a cosmopolitan island and an important trade centre in the Mediterranean Sea (Bruneau and Decat 2005: 31-48). Between 167 and 88 BC the island witnessed its greatest prosperity.

The mosaic pavements were created using a variety of techniques, including chip and pebble mosaics, *tessellatum* and *vermiculatum*. The majority of them are plain mosaics that were probably produced only for sealing floors. The decorated mosaics are approximately 120 in number (Bruneau 1972: 37) and represent a variety of decorative themes, including geometric and vegetal patterns and figured scenes. In most cases they are found in domestic contexts, with further examples also known in religious and public buildings.

The use of vitreous materials has been reported in nearly fifty mosaics and in a variety of colours (Guimier-Sorbets and Nenna 1992; 1995). Glass *tesserae* were mainly used to achieve blue and green hues, and more seldom red and yellow, whereas faience *tesserae* were used to create lighter shades of blue and green. In addition, the use of grey faience *tesserae* has been reported in one mosaic. These materials were used in the *opus tessellatum* and *vermiculatum,* with only a small proportion of rounded glass elements known in a *scutulatum* mosaic (Fiori and Tolis 2000: 58). A complete and detailed description of colours, decor types and mosaic techniques, in which glass and faience *tesserae* were used, can be found in the publication of Guimier-Sorbets and Nenna (1992). **Figures 1** and **2** show some examples of mosaics containing vitreous *tesserae*.

Figure 1. (a) Detail of a meander pattern from mosaic 25 executed with the use of turquoise, blue and light green glass *tesserae* (scale: 0.5cm); (b) Detail of the vegetal garland from mosaic 68 (Ilot des Bijoux) showing the use of green faience in the leaves and red glass *tesserae*, altered in green.

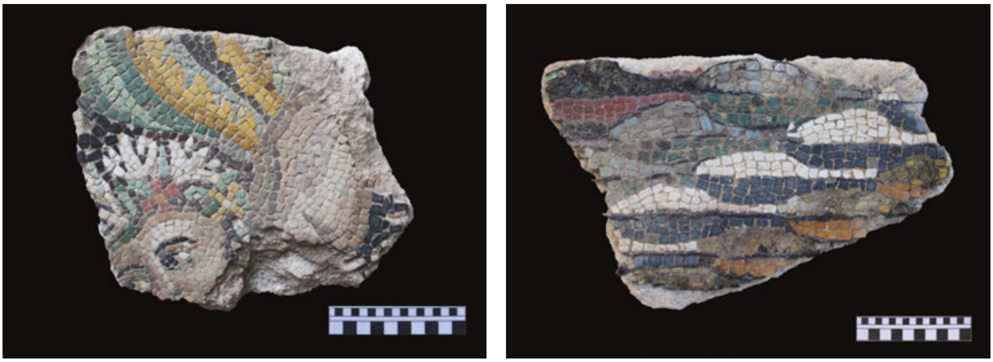

Figure 2. (a) Fragment from mosaic 279 (House IV B, Theatre Quarter) representing Eros, showing the use of light blue, light and dark green faience *tesserae*; (b) Fragment from mosaic 157 (House of Hermes) representing a polychrome overlapping leaves pattern and showing the use of dark green, light blue, yellow and red (almost completely covered by a black crust) glass *tesserae* (double scale: 0.5 and 0.3 cm).

The aim of the research

The principal aim of the present study is to identify the raw materials and the glassmaking technologies used in the production of the vitreous *tesserae* of the Delos mosaics. As glass *tesserae* are generally coloured and opaque or translucent, this study is mostly focused on the characterisation of the colouring and opacifying agents used in their production. In the study of the faience *tesserae*, beyond the chromophores identification, the aim is to determine the glazing methods, following the classification made by Lucas and Harris (1962), and subsequently completed by Kaczmarczyk and Hedges (1983). Special attention is paid to the study of vitreous *tesserae* manufacture in an attempt to identify the semi-products used to obtain them (e.g. rods, cakes, ingots).

The application of archaeometric techniques in the study of vitreous *tesserae* also aims at addressing relevant archaeological issues concerning the production of mosaics in Delos, including the technical processes involved in the mosaic manufacture, the supply of glass and faience, and if possible, the identification of different mosaic workshops operating on the island. Moreover, the physicochemical characterisation of glass *tesserae* can enhance our knowledge about Hellenistic glassmaking, especially the manufacture of opaque glass, which, in this period, was less common than translucent glass (Nenna 1993: 15). Finally, the study of the vitreous *tesserae* provenance is crucial for tracing ancient trade routes given the importance of Delos as an exchange centre in the Mediterranean.

Methodology

The analytical methodology to be used was established in relation to the archaeological questions to be answered and also, significantly, given that sampling for laboratory analysis was prohibited. Therefore a two-step archaeometric approach has been planned; one that involves non-invasive analysis performed *in situ* on the mosaics, followed by the physicochemical analysis in the laboratory of selected *tesserae* of unknown provenance. These *tesserae* were conserved in the store rooms of the archaeological museum of Delos.

The non-invasive analysis involved the use of three complementary instruments: a DM, a pXRF and a FORS. DM allows the assessment of the *tesserae* surface microstructure and weathering state; it allows also the observation of crystalline phases possibly present within the vitreous *tesserae*. FORS is a useful tool for the fast and easy identification of the main chromophores used for glass and faience colouration, such as iron, cobalt, copper and manganese (Weyl 1976; Meulbroeck *et al.* 2010). In addition, the CIELAB colour coordinates, given by the instrument, can provide an objective and quantitative measurement of *tesserae* colour, contributing to the reconstruction of the palette used by the mosaicists.

The pXRF technique allows the measurement of all chemical elements from Al to Pb. This technique cannot detect Na and encounters some limitations concerning the quantification of light elements (e.g. Mg, Al, P, Si), which are the main components of a glassy matrix. Nevertheless, it shows good accuracy and sensitivity for transition metals (e.g. Fe, Co, Mn, Ni, Cu, Zn) and other heavier elements (e.g. Sb, Sn, Pb) which generally enter in the glass composition as colouring and opacifying agents.

While this analytical approach only allows a partial characterisation of the vitreous materials, it provides useful data to make reliable hypotheses about the raw materials and the technologies employed. The main benefit of this kind of fast and non-invasive method is to provide a large number of measurements allowing an extensive analysis of *tesserae*. Larger datasets support the application of statistical methods that compensate their relative inaccuracy and allow the comparative study of samples from different mosaics and/or buildings, highlighting similarities or differences. Finally, it is anticipated that the integration of analytical data, microscopic and macroscopic observations related to the techniques of the *tesserae* manufacture, stylistic considerations and archaeological evidence can be used to contribute to the identification of different mosaic workshops and the process and policies related to the procurement of vitreous materials.

The analytical examination using laboratory-based instruments, which will be used in the second phase of this project, will be conducted on a restricted set of selected isolated *tesserae*; their results will integrate the analytical outcomes of the earlier non-destructive work implemented on Delos and both will be comparatively studied. The complementary compositional and microstructural analyses are expected to enhance the general knowledge regarding the production of vitreous materials in the Hellenistic period. For example, two relevant issues would be the determination of the type of glass by measuring the Na content and the certain identification of the opacifiers used. The complementary analytical techniques to be used in the framework of this project include PIXE and PIGE, LA-ICP-MS, SEM-EDS, XRD and Raman spectrometry (Mass 1999: 15-41).

A more exhaustive and accurate elemental analysis will be achieved with the use of PIXE-PIGE and LA-ICP-MS. The high resolution imaging obtained using SEM will permit the study of morphology, size and distribution of particles possibly present in the glass, while the coupled X-ray microanalysis will provide the chemical composition of both the glass matrix and the crystalline phases, allowing the identification of the base glass type and the colouring and/or opacifying agents respectively (Verità 2000). Moreover, the observation of the morphology of crystals can be useful to distinguish different colouring and opacification processes (Verità 2000; Lahlil *et. al.* 2008). Concerning the study of faience, as shown by earlier studies (e.g. Tite *et al.* 1983; Mao 2000), the examination of cross-sections with the use of optical microscopy and SEM is important for the identification of the glazing techniques. XRD and Raman spectroscopy are fundamental for the mineralogical identification of the crystalline phases possibly present in glass and faience. Finally, all the data (photos, spectra and elemental datasets) collected during this work will be systematically organised in a database to facilitate data management and interpretation, making them accessible to other researchers working on the mosaics of Delos.

First results of the *in situ* analyses

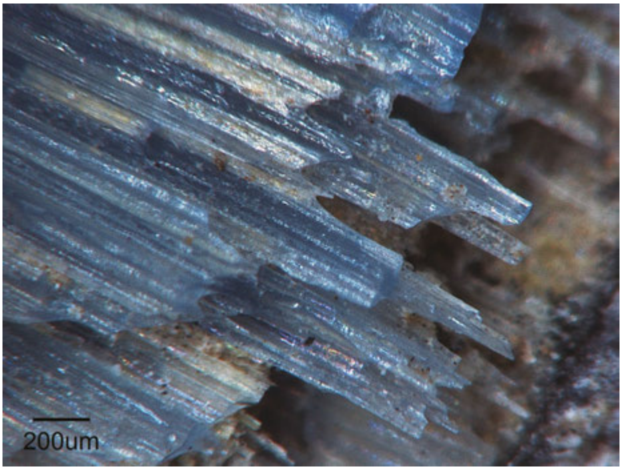

Figure 3. Digital photomicrograph (magnification x140) of a blue glass *tessera* exhibiting a peculiar fibrous microstructure © C2RMF.

Twenty six mosaics, along with some fragments of unknown provenance, were studied during the *in situ* non-destructive analytical study. Nearly three hundred and fifty vitreous *tesserae* were analysed using FORS and pXRF. For around half of these tesserae, digital photomicrographs, at different magnifications, were recorded. The microscopic examination of glass *tesserae* has indicated a peculiar fibrous microstructure (**Fig. 3**) in the majority of the analysed mosaics, which was related to the technology used for their manufacture. As it was first argued by Guimier-Sorbets and Nenna (1992), most of the glass *tesserae* were probably cut from glass rods. The working of these semi-products on the island for the production of certain types of beads has been documented by Nenna (1993, 1999).

The compositional analysis of the mosaics using pXRF has suggested the use of common chromophores in the Hellenistic period, such as Co, Cu, Fe and allowed the building of justifiable arguments about the type of opacifiers used in the glass *tesserae*. Moreover, the combined use of pXRF and FORS allowed to exclude the use of Egyptian blue *tesserae* in the analysed mosaics, which instead has been reported in a Hellenistic pavement in Egypt (Guimier-Sorbets and Nenna 1995), and after 50 BC in the early wall mosaics in Italy (Boschetti 2011).

The elemental analysis of the mosaics has indicated that red glass *tesserae* had high concentrations of Pb and Cu in their composition. These results are consistent with the composition of *sealing wax red glass,* which owes its colouration and opacification to cuprite (Cu_2O) crystals dispersed in a lead-rich matrix (Freestone *et al.* 2003). This type of glass had been produced since the first millennium BC, and the particular difficulties encountered during its production indicative of manufacture in specialised workshops. Its use has been also reported in the Hellenistic mosaics from Italy (Boschetti 2011).

Another striking observation about the analysed glass *tesserae* is the presence of considerable concentrations of Pb in almost all the blue and turquoise glass samples. The highly variable Pb content suggests that this element was not intentionally added to the glass batch, as it happens for instance when the craftsperson intentionally aims to modify the glassworking properties. On the contrary, it seems that the presence of Pb in blue and turquoise glass was probably a result of the use of specific raw materials, such as chromophores and/or opacifiers. This observation needs to be further considered using statistical analysis, and comparatively with published data on glass of the considered period.

Conclusions and research perspectives

The first results deriving from the *in situ* non-invasive analysis have provided important information about the techniques and the raw materials used in the production of the vitreous *tesserae* of the mosaics from Delos. Furthermore, the application of statistical analysis on the whole set of data collected during the *in situ* analytical work will allow the identification of similarities and/or differences among the vitreous *tesserae* coming from different mosaics. The ultimate objective is to contribute to the assessment of important archaeological issues regarding the production of mosaics on Delos in the Hellenistic period. Finally, the integration of the results of the analyses conducted *in situ* and in the laboratory, as well as their comparative study, are expected to provide a better-informed compositional and microstructural characterisation of vitreous *tesserae*, enhancing the general knowledge about glassmaking in the Hellenistic period.

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TECHNIQUES AND MATERIALS USED IN WALL PAINTINGS FROM THE CLASSICAL TO THE ROMAN PERIOD IN THE EASTERN MEDITERRANEAN

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Abstract

The funerary monuments located in the area of ancient Macedonia (northern Greece), namely the monumental Macedonian tombs, as well as the decorated chamber and cist tombs, form a remarkable source of evidence about Late Classical and Hellenistic painting, since they preserve simple or more elaborate compositions executed with the employment of techniques developed at the end of the 5th and during the 4th centuries BC.

In the framework of the NARNIA research project, an interdisciplinary approach to the study of the painted decoration of these tombs was applied; one that combines archaeological and archaeometric techniques of material study and characterisation. The primary research aim was to determine the techniques and materials used and identify the different artistic trends, as well as the reciprocal influences in the ancient world, with a focus on the vegetal and geometric motifs that form part of the decoration of these tombs.

Different analytical techniques are applied for the identification of the various components of the wall paintings in order to identify the pigments and the binding media, and also to suggest the techniques used for the creation of the painting. Specifically, the morphology and the stratigraphy of the paintings were examined with PLM and SEM. The inorganic materials were identified with the combinational application of μ-XRF, EDS, XRD and FTIR spectroscopy. The next step will be the analysis of the remaining organic matter using methods such as HPLC or GC-MS. Statistical methods will then be used for data processing and the interpretation of the information obtained both by the analysis and the review of the literature.

Introduction

This is a study on the techniques and materials used in wall paintings in the eastern Mediterranean, with a focus on the funerary monuments of northern Greece, in particular the region of ancient Macedonia. The research focuses especially on the vegetal and geometric patterns as they appear in the painting decoration of these monuments.

The region under study corresponds to a major economic and cultural centre of the Hellenistic period, where numerous funerary monuments have come to light, with well-preserved, painted compositions, executed with the techniques formulated at the end of the 5th and in the 4th centuries BC (Tsimbidou-Avloniti 2005: 166-171), the so called "Golden Era of painting" (Robertson 1975: 168 *ff.*).

The painted funerary monuments of ancient Macedonia

The monuments under study are located in the area between the modern city of Makrygialos, Pieria in the south-west and the borders of the modern cities of Drama and Kavala in the north-east, covering, thus, a large part of the region of ancient Macedonia. This study is focused on the decorated tombs that date to the period between the second half of the 4th century BC and the 1st century BC, while the majority of them date to the last quarter of the 4th and the beginning of the 3rd century BC.

The funerary monuments under study can be divided into four major categories. In the first category belong the Macedonian tombs. They may be described as underground buildings comprising one or two chambers, which after their construction and the end of the burial ceremonies were covered with earth in the shape of a conical tumulus. Their structure includes characteristic architectural features, namely a vaulted roof and/or a façade, the latter usually resembling the façade of Doric or Ionic temples (or combining features from both orders). Coarse ashlars were almost always used in their construction, covered with layers of white plaster in order to give the impression of marble. Many times the architectural features on the façade and the interior are emphasised with various colours; in some exceptional cases impressive painted compositions decorate the tombs (e.g. the Philip's Tomb in Vergina (Andronikos 1984: 96-116) or the tomb of Aghios Athanassios (Tsimbidou-Avlonitou 2005: 89-171, 173)).

The second category includes chamber tombs (single or double), that may share similarities in structure with the Macedonian tombs, but they lack specific features, mainly the vaulted roof or the elongated "dromos", i.e. the passageway leading to the tomb. These tombs have often been decorated internally (e.g. the chamber tomb of Katerini (Despini 1980)).

Another type of funerary monument that is often recorded in the region of Macedonia is the cist tomb, which consists of large stone blocks that form the receptacle of the dead. Their interior is often decorated with motifs that vary from simple leaf garlands to elegant scroll friezes (e.g. the monumental cist tombs at ancient Pella (Lilimpaki-Akamati 2007)).

Finally, even the most modest funerary structure, a pit opened in the ground, was occasionally decorated, although in a much simpler way (the internal surfaces of the pit "walls" were covered with coloured plaster, mostly white but also red, yellow and black. This category of tombs has been ignored until now, but their study undoubtedly adds to our knowledge about painted funerary decoration.

All the above comprise a remarkable source of evidence on Late Classical and Hellenistic architecture and painting (Andronikos 1988). The particularity of their decoration has rendered these tombs a popular subject, not only in the fields of archaeology and conservation, but also in architecture and the history of art. A database has been created for the management of the vast corpus of information regarding the funerary monuments under study. The database includes both archaeological (i.e. excavation data, architectural characteristics and descriptions of the painted decoration) and archaeometric information (i.e. the analytical data). All the above are accompanied by relevant published references.

The vegetal and geometric ornamentation

As mentioned, specific focus is given to the geometrical and vegetal motifs of tomb decoration. Despite their frequency in funerary monuments, these motifs tend to be rather neglected in comparison with the narrative scenes, which offer more material for iconographical analysis. Apart from a few exceptions (e.g. the intricate scrolls in the cist tomb II from Aineia (Vocotopoulou 1990), or the leaf garlands in the tomb of Lysson and Kallikles (Miller 1993)), little has been written for this type of decoration in wall paintings, and even less in terms of comparative studies (Valeva 2006). On the other hand, the study of similar motifs appearing in ancient mosaics is more popular (*cf.* Balmelle *et al.* 2002).

Nevertheless, the motifs are only literally static ornaments since they change and evolve in time. Characteristic examples constitute the dentils or the cymae that started as architectural features and ornaments of cornices and capitals but gradually lost their third

Figure 1. The Macedonian Tomb II of Korinos. Details of the swastika meander in the antechamber and the floral frieze in the funerary chamber. Above the frieze, a series of dentils and a band with the egg-and-dart motif.

dimension. The fully sculpted moulding became smoother until there were only painted motifs on flat surfaces, often enhanced with shadows, to imitate the depth of a true relief (trompe-l'oeil). To achieve the main archaeological objective of this research, palmettes and lotus flowers, polychrome meanders and scroll ornaments have been thoroughly archived, described and compared. These themes can provide information concerning the artistic and technical progress in this area and suggest reciprocal influences in the ancient world.

In order to gather the different decoration patterns, photographs have been collected representing the astonishing variety in vegetal and geometric motifs. In addition to the descriptions and images found in the literature, this project aimed at the assessment of more recent research that was conducted on some of the known monuments, but more importantly, to enable unpublished material to come to light. Hence, famous monuments such as tomb I in Dion (Sotiriadis 1930), the Macedonian tomb II in Korinos, Pieria (Bessios 1991: 177), the cist tomb II in ancient Aineia, Nea Michaniona (Vocotopoulou 1990: 22-34 and 35-49) were photographed anew (**Fig. 1**), while lesser known monuments, such as the stone sarcophagus from the region of Aghios Mamas, Chalcidiki (Moschonisiotou 1989) and the tomb of Aggista, Serres (Koukouli 1968) were documented *in situ* in detail (**Fig. 2**).

Figure 2. The Macedonian Tomb of Aggista. A general view and details of the pediment presenting a variety of motifs: a series of lotus flowers and palmettes, the egg-and-dart and heart-and-dart motifs and a swastika meander.

The Archaeometric analysis

Wall paintings are not flat, two-dimensional images, but, on the contrary, they are composite, stratified works of art consisting of different colour layers and plaster substrates that contain various colourants, pigments and binding media of inorganic and organic nature. Moreover, the technique employed by the painter is of great importance. It is characterised by the preparation of the painting surface with successive plaster layers and the incision and/or the design of a preparatory sketch to facilitate the painting, but also the individual style of the artist (brush strokes, use of line and colour, rendering of shades and volumes) (Brecoulaki 2006: 395-462). The analytical research of the morphology and the stratigraphy of the paintings is an indispensable tool for the investigation into their technology which can provide information regarding the artistic trends of the time, or the social and economic status of the dead.

This research therefore has a twofold objective; in addition to the study of the decorative patterns, an investigation into the materials and the techniques employed has been conducted in parallel. In order to decrypt the synthesis of a wall painting, various optical, physicochemical and instrumental methods of examination can be applied (cf. Kakoulli 2009: 17-25). The technique is selected depending on the question that the researcher seeks to answer but also on the materials under study. Issues of access to the monuments, the state of conservation and the archaeological importance of the artwork can set various obstacles or limitations in research. In

Greece sampling from painted surfaces is generally prohibited but fortunately, sampling can be permitted on already detached fragments that are considered less important for the restoration of the painting.

The monuments selected for analysis provide painted decoration relevant to the themes under study, while no previous physicochemical examination has been conducted. Thus, twenty-two monuments that vary in terms of structure and decoration have been chosen, representing as many areas as possible within the region of interest. The sampling was limited to miniscule parts of the paintings, from fragments already detached from the wall surface, which were either found in the interior of the tombs or in the storage rooms of the various archaeological ephorates.

Fragments, from which sampling was prohibited, were taken to the Chemistry Laboratory of the Archaeological Museum of Thessaloniki to be examined with the optical microscope and analysed non-destructively using μ-XRF which provided qualitative results regarding the pigments and the plaster underneath. In those cases, in which sampling was possible, several analytical methods were applied at the N.C.S.R. "Demokritos" in Athens. Polished sections incorporating the stratigraphy of the painting were examined with optical microscopy, PLM and SEM. The use of EDS with the SEM allowed the elemental analysis of the different colour layers and the various substrates. In addition, μ-XRF has been used for the analysis of a large number of samples and XRD for a targeted mineralogical analysis. Lastly, pellets containing grains of colour were the subject of FTIR analysis, which can detect not only inorganic but also organic materials in the sample. The archaeometric methodology along with the results obtained via the physicochemical study was recorded in detail and were accompanied by photographs acquired with the use of the different microscopes.

Two indicative analytical examples

Case study 1: The Macedonian tomb of Aghia Paraskevi

A fragment of the sima from the façade of the Macedonian tomb of Aghia Paraskevi (Sismanidis 1986) located in the Archaeological Museum of Thessaloniki was transferred to the laboratory for analysis. It presents the egg-and-dart motif (**Fig. 3**), and a part of the lotus flowers and palmettes band. According to the μ -XRF results, the white background is of calcareous nature (calcite), the red has been produced with a ferrous oxide (probably hematite), the blue is the Egyptian blue, while the black, judging by the lack of other elements apart from calcium, is most probably carbon black.

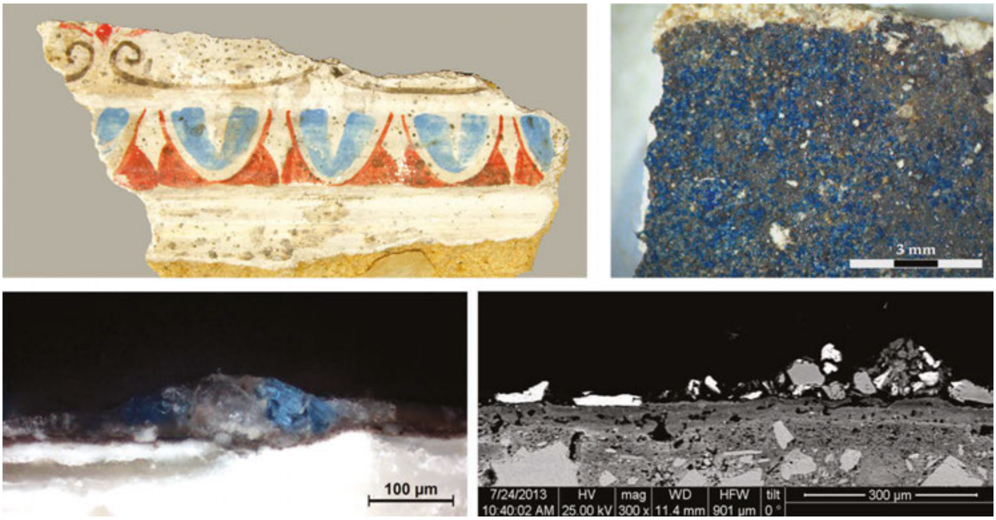

Figure 3. Case Study 1: The part of the sima with the egg-and-dart motif and a fragment from the blue triglyphs. The PLM and SEM images of the cross section show the Egyptian blue grains and the layer of carbon black underneath.

Figure 4. Case Study 2: Fragments of the decoration comprising a part of the dentils series and the floral frieze. Microscopic images emphasising the light pink and yellow details.

The façade had also coloured architectural features, such as dark blue triglyphs and red bands. A sample from the triglyphs was analysed with PLM and SEM-EDS (**Fig. 3**). In this case, a layer of carbon black is overlapped by Egyptian blue mixed with quartz. Underneath there is a substrate of calcite and two layers of lime mortar, the upper with clay minerals and quartz as aggregates, the lower with calcareous aggregates. One can observe the different use of Egyptian blue in order to achieve the desired optical effect. On the sima the motif is painted freely and the pigment is applied in a thin layer, creating a vivid blue on a white background. On the triglyphs, the blue is used as an overlay on a black ground creating a dark blue to cover the large surface, according to the artistic demands of the time.

Case Study 2: The cist tomb 4, area of Phoinikas, Thessaloniki

The internal walls of tomb 4 in the area of Phoinikas in Thessaloniki (Tsimbidou-Avloniti 2009), dating to the last quarter of the 4th century BC, were decorated with a series of dentils and a polychrome flower scroll frieze, painted on a dark background (**Fig. 4**). The μ-XRF analysis has attributed the red of the dentils to an iron oxide (hematite), the white (and the preparation substrate) to calcite and the black to carbon black. The ground is also carbon black with an overlay of Egyptian blue. However, there is another type of white with a slight yellow tint that presented characteristic peaks of lead, an indication of the use of lead white. The details in pink colour contained high levels of mercury, suggesting the use of cinnabar. Lastly, the ochre-yellow details presented peaks of lead and arsenic, an effect caused probably by a mixture of a yellow arsenic compound, such as orpiment or pararealgar, with lead white.

In this case the painter used a ferrous pigment, namely a cheaper material, in order to fill large areas and less important details, like the red part of the dentils and then, he used the more expensive cinnabar to create the striking pink hues. A similar argument applies for the whites, where the familiar calcite is used extensively and the more elaborate lead white is applied to give a different optical effect, where needed.

The next step

The next step will be the analysis of selected samples for the detection and identification of the remaining organic matter that can verify the use of a certain binder, and thus suggest the pictorial technique employed. The contribution of HPLC, or GC-MS, is expected to be crucial in the development of this project.

Statistical methods, such as PCA, will be used for the processing and interpretation of the analytical data, in addition to the information obtained after the review of the literature. The ultimate objective of this project is the integration of all accumulated information, archaeological and archaeometric, which will become the basis for the publication of a corpus on the vegetal and geometric decorative motifs of the Macedonian tombs. This will include a list of the patterns present in the funerary monuments, along with their characteristic features and their occurrence, a comparative, stylistic study that focuses on the vegetal garlands and scroll friezes, and a study of the pigments and binders used, emphasising the less common materials found in these paintings.

Conclusions

The preliminary results of this archaeometric research cover almost the entire palette of the ancient Macedonian painter. The ferrous compounds provide the majority of the reds, yellows and browns, but more rare materials such as cinnabar or orpiment were used, mainly to emphasise the details of the decoration. The blue, namely the Egyptian blue, is almost always a synthesis of silica, copper and calcium. When mixed with yellow ochre or a ferrous red created respectively vivid greens and violets. Green earths are also present in the samples. Moreover, all the above could be mixed with carbon black or calcite for the darker or lighter hues. Lead white is also recorded, although much less often than the usual white of calcite.

The assessment of all archaeological and analytical information is anticipated to develop arguments about certain artistic and technical rules and patterns applied in the region during the Hellenistic period. For example, an important question is whether the choice of the materials is associated with the different decorative themes or with a certain know-how that could circulate amongst the painters and defines their artistic steps. Also, do the pigments or the preparatory steps follow certain rules according to the tomb type or the region? As the research continues, new questions emerge, adding to the main objective: a meaningful contribution to the overall corpus of the Macedonian funerary monuments and their painted decoration.

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ARTIFICIAL MATERIALS USED IN THE PRODUCTION OF CYPRIOT WALL MOSAICS

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Abstract

A number of monuments in Cyprus are well known for their magnificent floor mosaics. Indeed, Cyprus is home to spectacular mosaics from the Hellenistic, Roman and Byzantine periods. Cypriot wall mosaics have often survived in poorer condition than the floor mosaics and are almost always very fragmentary. Such condition may explain why less attention has been drawn to them so far. Nevertheless, the analytical study of the mosaic fragments and the detached tesserae (especially the glassy materials and plasters) can provide valuable information about their manufacture, i.e. the techniques and materials used, as well as raw material provenance. Recent developments in the field of analytical techniques allow scientists to better characterise the materials used to make such wall decoration with minimum sampling. Multidisciplinary research on the materials used in the production of mosaics for the Early Christian Cypriot basilicas is under way at the University of Cyprus, as part of the NARNIA project. Five sites have been chosen for this study: the seaside basilica of Kourion, the basilica of the former Aphrodite Sanctuary in Amathous, the basilicas of Polis Chrysochous, the basilica of Yeroskipou *Ayioi Pente*, and the basilica of Kalavassos *Kopetra*. Both the glass tesserae and the plasters of the preparatory layers have been studied using a range of complementary analytical techniques.

Introduction

A number of monuments in Cyprus are well known for their magnificent floor mosaics. Indeed, Nea Paphos is listed among the UNESCO World Heritage Sites primarily due to the magnificent mosaics that are known at the site (UNESCO 2014; Michaelides 1987). The most famous pavements date back to the Roman Imperial period (particularly to the

2nd and 3rd centuries AD), but mosaics dating back to the Hellenistic period (late 4th to 1st century BC) and to the Early Byzantine (5th to 7th centuries AD) periods have been found not only at Nea Paphos, but also in other regions on the island. The vast majority of the best preserved mosaics are from floor pavements. However, fragments of wall mosaics have also been found across the island, especially in Early Christian churches.

With the exception of a few examples (such as in the apse of Panagia Angeloktistos at Kiti), most of the wall mosaics across the island are in a bad state of preservation, their remains mostly found in the form of loose tesserae and detached fragments (**Fig. 1**). The bad state of their preservation was perhaps the main reason why until very recently the wall mosaics in Cyprus received less attention than the floor mosaics, despite their rare and fragile nature.

Material considerations

Mortars

The mortar (or plaster) allows the placement of the tesserae on the wall, by creating a smooth and even surface which holds the tesserae when dry. It is typically composed of inorganic or sometimes organic binders, mixed with water and a number of additives. The binder is usually

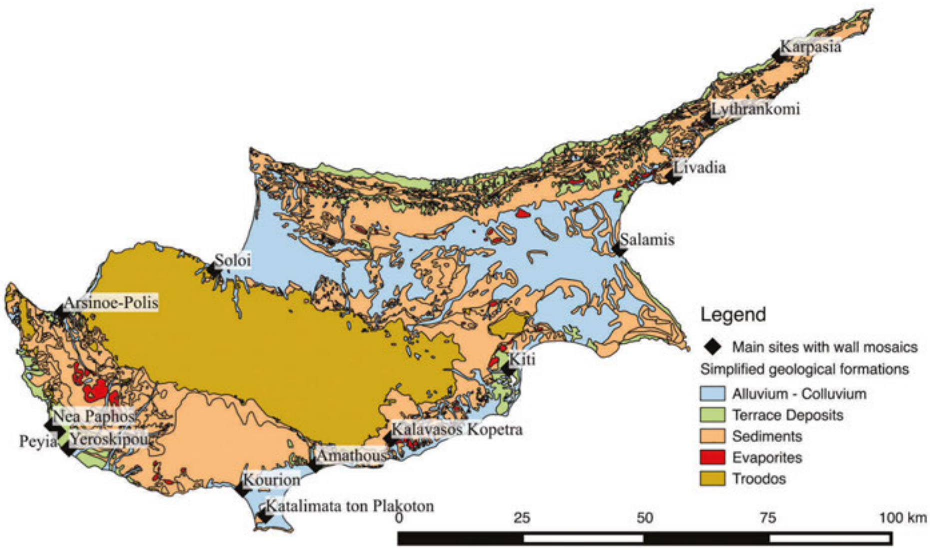

Figure 1. Map showing sites with wall mosaics mentioned in the text. Original map from Geological Survey Department (1995).

lime or gypsum, while additives are most often sand with or without pozzolanic materials, such as fragments of ceramics or volcanic ashes. These pozzolanic materials react with lime and make the mortar hydraulic (i.e. the property of the mortars to harden in contact with water; Fiori 1995). The stratigraphy is not described in ancient sources, and the nature and number of layers can vary. However, the technology is rather similar to that of frescoes, and the same typology is used to describe the different layers (Ciliberto *et al.* 2008; Zizola 2008).

The different layers composing the wall mosaic **(Fig.2)** include:

1. The arricio, which is the layer attached to the wall. It is made of coarse slaked lime with sand or pozzolana, sometimes with straw.
2. One or more intermediate layers are made with finer lime mortars.
3. The external layer on which the tesserae are placed: it is typically made of very fine mortar with slaked and/or dolomitic lime.

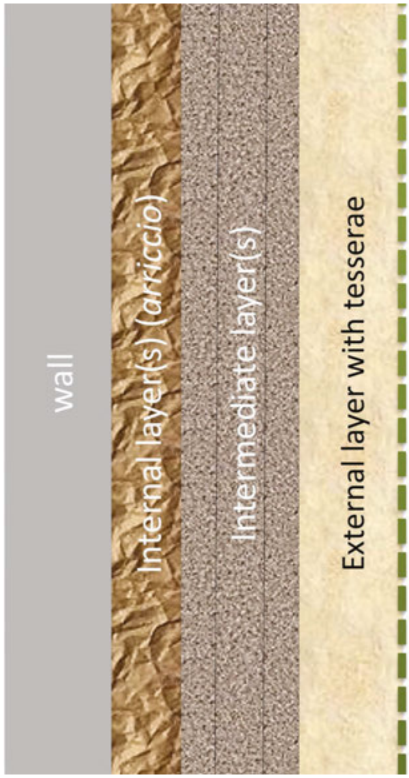

Figure 2. The different layers composing the wall mosaic.

When fresh, the mortar is easily workable, whilst when hardened, it provides the mosaic with several physical and mechanical properties, such as permeability to water, porosity, hardness, compressibility and adhesion, which are crucial for the durability of the mosaic in time. Therefore, the compositional and technological characterisation of the mortar is critical for conservation purposes but also for understanding the technology of mosaic manufacture (Starinieri 2009).

Glass tesserae

Glass is an amorphous (i.e. non-crystalline) solid material composed of a network former (usually silica) and various additives (Zarzicky 1982). Although it is possible to form glass from pure silica, this requires very high temperatures (>1700°C), which could not be achieved in antiquity (Freestone 1991). An additive called a fuse needs to be added in order to allow silica to melt and form the glass. Melted with the matrix, the fuse will replace some of the strong Si-Si covalent bonds with weaker ionic bonds (Cochain 2009). Because of the formation of the ionic bonds, however, the obtained glass is water soluble and gets easily weathered. To address this issue, another additive called a stabiliser, usually lime, needs to be added to the glass matrix: its typical composition is around 20 w% soda or potash and 5-10 w% lime, which gives adequate durability and decreases the required firing temperature to about 1000°C (Freestone 1991).

In the Early Byzantine period, the source of silica in eastern Mediterranean was a specific type of sand, such as that from the Belus River in modern Israel (James 2006). The advantage of this type of sand in comparison to mineral quartz is that it was ready for use without any prior processing. In contrast, quartz pebbles must be crushed prior to melting. In addition, the preferred sand type contained the required lime component (Freestone 2006). The fuse in use was alkali obtained either from natron, in the form of evaporitic salts containing high quantity of soda (Na_2O), and low quantities of magnesium and potassium, or ashes from halophytic plants (i.e. plants which grow in saline water), containing a high quantity of potash (K_2O), and magnesium. The second type begins to slowly replace the first during the 4th century AD (Freestone 2006; Henderson 2002).

It is believed that during the Early Byzantine period (4th-7th century AD), coloured glass for the production of tesserae was made in two separate steps. Raw glass was produced on an industrial scale in a small number of primary workshops (most plausibly in Egypt and the Levant). The raw glass was then exported to various secondary workshops closer to the churches and basilicas, and was further processed *in situ*. It is in these secondary workshops that the glass was reworked and, in the case of tesserae, that colourants and/or opacifiers were introduced to the glass, which was then cut into tesserae (Schibille *et al.* 2012; Freestone *et al.* 2002).

Transition metals from the 3d column of the periodic table of elements dissolved in the glass matrix, in particular iron, manganese, copper and cobalt, are responsible for the colour of the glass tesserae, in association with the opacifiers (calcium / lead stannate or antimonates) (Fiori 1995; James 2006; Mirti *et al.* 2002). Iron, normally introduced in the glass matrix as an impurity of the sand used for glass making, is present in the glass either in its strongly colouring blue Fe(II) form or in its pale yellow Fe(III) form. By controlling the ratio Fe(III)/ Fe(II), a range of hues can therefore be obtained. This was generally achieved by controlling the furnace conditions and / or by adding manganese ions in the form of pyrolusite (MnO_2) (Freestone 2006). Manganese is also used in excess to produce purple glass tesserae (Arletti *et al.* 2012). Copper and cobalt are other common colouring agents. Dispersed in its Cu(II) form, copper produces turquoise blue glass, while cobalt in its Co(II) form produces dark blue glass (Fiori 1995).

Opacifiers, i.e. particles whose size is bigger enough than the visible wavelength to prevent a coloration process by selective absorption of incoming light, were dispersed in the vitreous matrix. As the number of these particles increase in the glass, the refractive index of the material increases as inhomogeneities scatter the incoming light and prevent it to be transmitted, thus rendering the glass opaque (Fredrickx 2004; Lahlil 2010). Up to the 4th century AD, most opaque glass was opacified with the use of calcium (for white opaque) and lead (for yellow opaque) antimonates. Furthermore, tin oxides (for white opaque) and lead stannates (for yellow opaque) began to be used as opacifiers during the second century AD but started to really replace antimony based opacifiers only from the 4th century onwards (Foster and Jackson 2005). The joint effect of iron, copper, manganese and cobalt ions with opacifiers was used to achieve a high number of colours.

Finally, red tesserae were obtained using a different technique. Elemental copper or copper (I) oxide particles dispersed in the glass matrix induce the red colour from light scattering. A perfect understanding of the making of such glass has yet to be achieved (Silvestri *et al.* 2011; Barber *et al.* 2009).

Sampling strategy

Five sites (**Fig. 1**) distributed along Cyprus have been selected in order to see if the technology used was the same across the island or not. These sites are the Early Christian basilicas of *Ayioi Pente* at Yeroskipou, Polis Chrysochous (sector EF2), Kalavasos Kopetra *Sirmata*, the acropolis of Amathous, and the coastal area of Kourion. The mosaics at all the sites under study are no longer *in situ* and the preserved material includes only fragments of plaster (with or without tesserae) and detached tesserae. For each site, a number of samples were selected for analysis, taking into account the availability of the material for analysis. Most importantly, the samples were carefully selected with the aim to represent in the overall sample the range of different textures, colours and techniques at each site and between sites.

The overall collection includes fifteen mortar samples from Kourion, with nine from Kalavasos, seven from Yeroskipou, and five from Amathous. These samples were chosen for analysis primarily using SEM-EDX to detect major and minor chemical elements. The mineral content of the mortar was evaluated with the use of XRD and with DTA-TG. The structure of the mortar is studied with the stereoscopic microscope, and its porosity with MIP.

In addition to the mortar samples, 45 detached tesserae were selected from Kourion, 337 from Amathous, 123 from Kalavasos, and 61from Yeroskipou. All the selected detached tesserae were studied with UV-vis spectrophotometry for colorimetry. A selection of 80 tesserae from the different sites was then selected to be embedded in acrylic resin for complementary analysis with SEM-EDX for major and minor chemical elements analysis and Raman spectroscopy for the identification of colouring agents and opacifiers.

Data analysis

Mortars

SEM-EDX was employed for the characterisation of the elemental composition of each sample. As expected for lime and gypsum mortars, which are the most common kinds used in the period of interest, the main element was calcium (present in both calcite and gypsum) with other major elements present being silicium, aluminium, and magnesium.

DTA-TG allowed the identification and quantification of the different crystalline phases, as the endothermic or exothermic transitions are characteristic of particular minerals (Moropoulou 1995) and the detection of organic materials. The main transitions observed were:

- an endothermic peak characteristic of the loss of adsorbed water at *c.* 60°-100°C
- another endothermic peak corresponding to gypsum at *c.* 150°C
- another endothermic peak corresponding to calcite at *c.* 800°C
- a generally smaller exothermic band which corresponds to the burning of organic materials at *c.* 300°C.

These peaks correspond to the breakdown of crystalline structures and the evacuation of various gases such as H_2O, O_2, CO and CO_2. The mechanism depends on a lot of factors and can differ depending on the temperature, at which the peak is observed. The ultimate aim in the context of this study is to recognize the phases according to the position and direction of the peaks. The weight loss due to these transitions can be quantitatively estimated with the use of thermogravimetry (**Fig. 3**; Middendorf 2005).

The XRD spectra complement the DTA-TG analysis well by providing more accurate quantification. In addition to testing the correspondence with the results of thermal analyses, the employment of XRD is also useful for the detection of some minor mineral

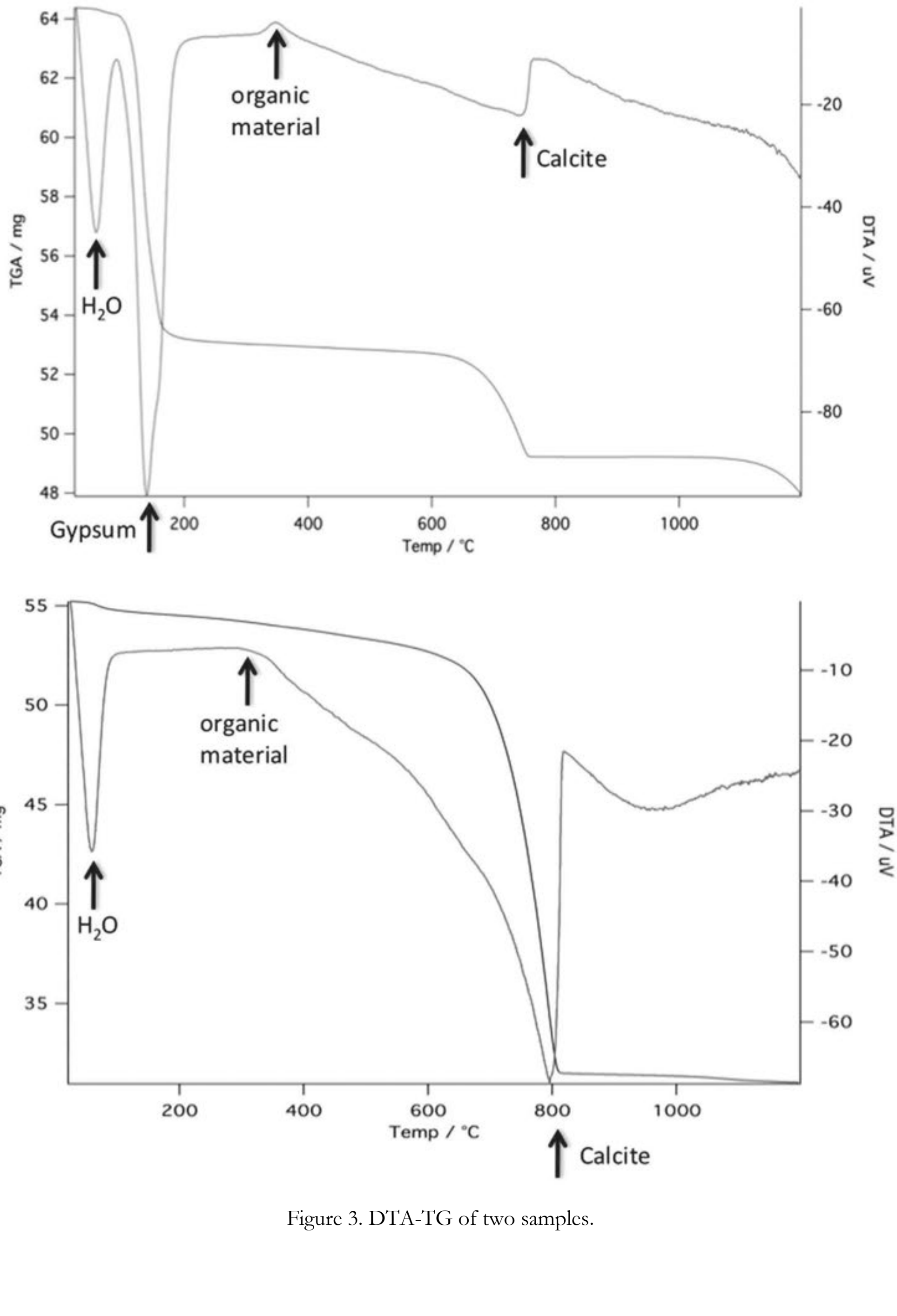

Figure 3. DTA-TG of two samples.

phases (Moropoulou 1995). The main minerals found in the composition of the mortars studied were calcite, quartz, and gypsum while other minerals such as dolomite, plagioclase, gypsum, portlandite, and chlorite were also detected on some samples.

Finally, MIP was used for the characterisation of the mechanical properties of the mortars. The total porosity, as well as its distribution between macro-pores (diameter >50nm), meso-pores (diameter 2-50nm), and micro-pores (diameter <2nm) according to the IUPAC classification (Rouquerol *et al.* 1994) was measured. The pore structure defines the performance and durability of the mortars. Furthermore, the water permeability is a consequence of the pore size distribution (Lawrence 2006).

Glass tesserae

SEM-EDX spectra were first processed with a built-in ZAF standardless algorithm for elemental identification and quantification. A copper stub was used to check if the current remained constant. Glass standards from the Corning museum of glass were used to check the error margin for each element. A range of graphs were plotted in order to process the data and identify the kind of raw glass used and further investigate their origin (**Fig. 4**). The combination of ternary SiO_2-MgO+K_2O-CaO, and binary K_2O-MgO diagrams allows the differentiation of raw glass by the fuse used during production. Other diagrams, such as CaO against Al_2O_3 contribute to a better understanding of the nature of the raw glass and can provide indications regarding the glass provenance. The use of the SEM-EDX was also helpful for the identification and quantification of elements responsible for the colour and opacity of the tesserae.

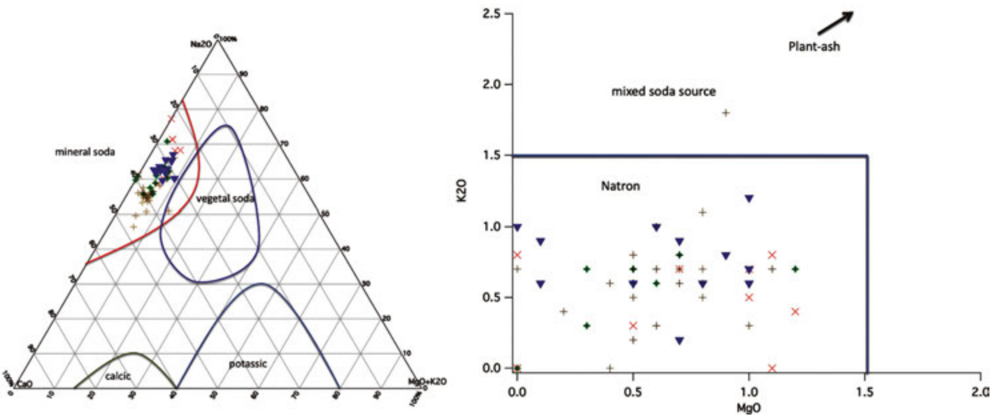

Figure 4. SiO_2-MgO+K_2O-CaO ternary diagram, and K_2O against MgO graph for a selection of samples.

UV-vis spectrometry was used for the identification of some colourants and opacifiers, and for providing an accurate measure of the colour of the tesserae. From the spectra, the CIE L*a*b* coordinates were obtained as described in the CIE ISO reference standard (CIE 2008). In the CIE L*a*b* colour system, L* stands for the lightness, ranging from 0 for black to 100 for white, while a* and b* measure the chrominance. The a* dimension has a range of values on a green to red axis, while b* has values on a blue to yellow axis (**Fig. 5**). UV-vis spectroscopy is a particularly promising technique as it is non-invasive and non-destructive and yet it can provide reliable qualitative and even semi-quantitative information about the colouring species in glass (Meulebroeck *et al.* 2010; Meulebroeck *et al.* 2012).

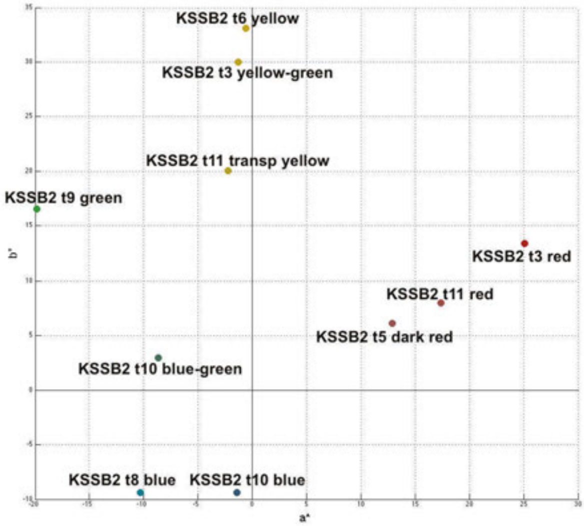

Figure 5. b* against a* in CIELab coordinates for samples from Kourion.

Raman spectroscopy was used to quickly differentiate the different kinds of raw glass used and to identify the main colouring and opacifying minerals and therefore complements the use of SEM-EDX. .

Conclusion

Analysis of the samples with the techniques described above is still in progress. The results will be published in a later publication. Combined results will be analysed by statistical tools such as PCA to detect different groups. The results will also be compared with similar studies found in the literature. Finally, in spite of all the care taken, SEM-EDX remains a "semi-quantitative" technique and results were found to be accurate only up to about 0.5 wt% for most elements, which was not enough to conclude on the nature of the glass used in the tesserae. For more precise results, analysis with EPMA is planned. Nevertheless, a few points can be noted from the first results:

- Concerning the mortar, both lime and gypsum mortars seem to have been used, sometimes both on the same site. Comparing the results with the geology of the areas around the sites will allow us to see whereas this choice was a consequence of the available local materials or not.
- Concerning the glass tesserae, the raw glass used seems to be soda-lime-silica glass. More precisely, it seems mostly related to the Levantine 1 type, although some glass tesserae may have been made using some other kinds of glasses like HIMT. This result is similar to what has been found in 6th century glass fragments from Maroni, Cyprus (Freestone 2002). No major differences were noted among the sites, except a stronger consistency of the glass from Amathous, which may indicate that the glass used to make the tesserae for this site came from the same batch. Opacifiers were found to be exclusively tin-based with no calcium or lead antimonates in the samples.

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THE STATE OF CONSERVATION OF THE ARCHITECTURAL STRUCTURES AND MORTAR CHARACTERISATION AT THE CASTLE OF AZRAQ, JORDAN

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Abstract

This paper presents a research project that aims to assess and quantify the scale of masonry damage at the castle of Azraq, in central Jordan. This is an ongoing interdisciplinary study that involves the digital documentation of the masonries and the compositional characterisation of the mortars used in the castle construction, with the ultimate objective to develop a conservation and management plan for the site.

This research involves two different stages. The first stage included the collection of historical information about the castle from the time of its foundation as a *castellum* in the Roman period and its subsequent transformations. The *in situ* digital documentation of the present state of conservation of the castle was complementary to the literature review, and contributed to our knowledge regarding the historical, cultural, technological and mechanical transformations of the castle throughout its period of use. During the second stage of this research, selected mortar samples will be studied in the laboratory using a combination of mineralogical, micro-structural and chemical techniques of analysis. The compositional and technological study of the mortars will provide information about the technology of mortar production during the periods that the samples represent, but it will also provide useful indications regarding the conservation of the castle as an important component of both Jordanian and Mediterranean cultural heritage.

Introduction

Azraq is a small town located on the highway that connects Amman (Jordan) to Bagdad (Iraq), *c.* 90km eastern from Amman. It is founded in the major oasis of central Jordan, comparable to Damascus and Palmira, whose perennial pool and vegetation attracted human habitation since the Palaeolithic (**Fig. 1**) (Harding 1967; Kennedy and Riley 1990).

The actual fort is a medieval reconstruction of a Roman *castellum*, settled along the 'Voie des Hans', a section of the *Strata Diocletiana* which linked the Euphrates with Damascus (Kennedy and Riley 1990). Fragments of milestones found on the road into Azraq and the building inscriptions from the dependent fort at Uweinid, both related to Septimio Severus (193-211 AD), provide the earliest certain date for the Roman occupation of the oasis (Kennedy 2004). In the past the same dating was suggested for the castle of Azraq

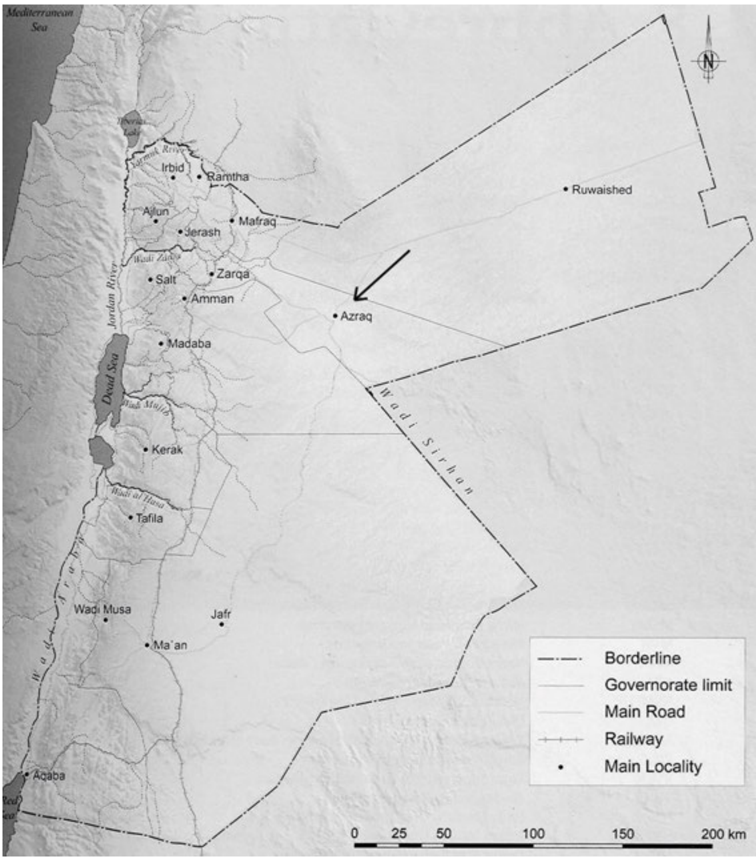

Figure 1. Map of Jordan, with indication of the position of Azraq (Ababsa 2013).

(Kennedy 2004). However, there is no evidence that directly relates the fort to the Severan period and the inscriptions found at the site are all later; specifically two building inscriptions (326-333 AD) and one inscription found on an altar of Diocletian and Maximilian (287-305 AD) (Gregory and Kennedy 1985; Kennedy 1982; Kennedy and McAdam 1985; Parker 1986).

There is no evidence of occupation at Azraq during the 5^{th} and 6^{th} centuries AD (Kennedy 2004; Kennedy and Riley 1990; Parker 1986), while a later use during the Islamic period is attested by the Medieval Arab historian Tabari (744 AD), which recorded that the Umayyad caliph Walid II had a residence at Azraq (Kennedy 2004; Lash 2009). An Arabic inscription over the gate of the fort dates the reconstruction of the castle to 1237 AD (Kennedy 2004; Lash 2009). Among the many transformations of the castle, it should be noted that a mosque was built inside its courtyard, during the Islamic period. Under the Ottoman period, the use of the castle, probably as a station on the pilgrim road into the Arabian Peninsula, is attested by the presence of scattered surface sherds. The last occupation of Azraq goes back to the beginning of the 20^{th} century, when it served as the headquarters of the Arab Army during the years 1917 and 1918 (Kennedy 2004; Lash 2009). Finally, the castle was used by Druze refugees coming from Syria, between 1920 and 1930 (Kennedy 2004; Lash 2009).

Considering the long history of the Azraq castle, this project was established with the aim to assess and quantify the scale of damage of its masonries and to understand the causes of deterioration at the site. The ultimate aim of the project is the development of a conservation and management plan based on the integration of *in situ* observations, historical data and archaeometric investigation. Furthermore, the technological and compositional characterisation of building materials, particularly mortar fragments, from the castle will enhance our knowledge about the building techniques and technology at different phases of the castle's lifespan.

Geological background

Azraq lies in the geomorphologic region of the Central Plateau province, in the Azraq Basin. This is a shallow depression covering approximately 12000km^2, expanding from the Druze area in southern Syria to the Saudi Arabian frontier, and west to 20km from Amman. The elevation at the centre of the Azraq Basin is roughly 500m, while along its northern boundary it reaches 1800m, and 900m along the western, southern and eastern boundaries. The northern region is covered by basalts and tuffs emitted from volcanoes and fissures from between the Miocene and Pleistocene (**Fig. 2**). The southern part of the basin is made of Cretaceous and Tertiary limestones, chalk and marls and the surface is coated with a flint hamada. At the east, towards the modern Saudi Arabia border, there are valleys 30-50m deep that pass through the Cretaceous and Tertiary limestone and marl formations, and form more recent deposits of a 55m thick marly sequence of brackish to saline lacustrine deposits that contain gypsum and halite evaporites (Bender 1963; Garrad *et al.* 1985).

Castle building materials: state of deterioration and preliminary conservative works

Archaeological surveys have indicated that the actual building is a later reconstruction of the Roman *castellum* that has undergone continuous rebuilding and numerous modifications. However, it still reflects the original structure (Kennedy 2004; Kennedy and Riley 1990). The castle has a square plan with large projecting square towers at the four corners, and one tower in the centre of the northern wall (**Fig. 3**). There is a gate in the southern side and a large structure, a *praetorium*, in the westerner wall. Internally, the rooms are located on the external walls leaving an open courtyard at the centre. The technique of linear stone corbelling is used for the construction of the ceiling of the building; this technique is still used in traditional Jordanian and Syrian architecture (Jäger *et al.* 2012). The *praetorium* projection at Azraq has many architectural similarities with the forts at Khan Aneybeh (Syria), Qasr Bashir (Jordan), Avdat I (Israel) and at Bourada (Numidia), while the

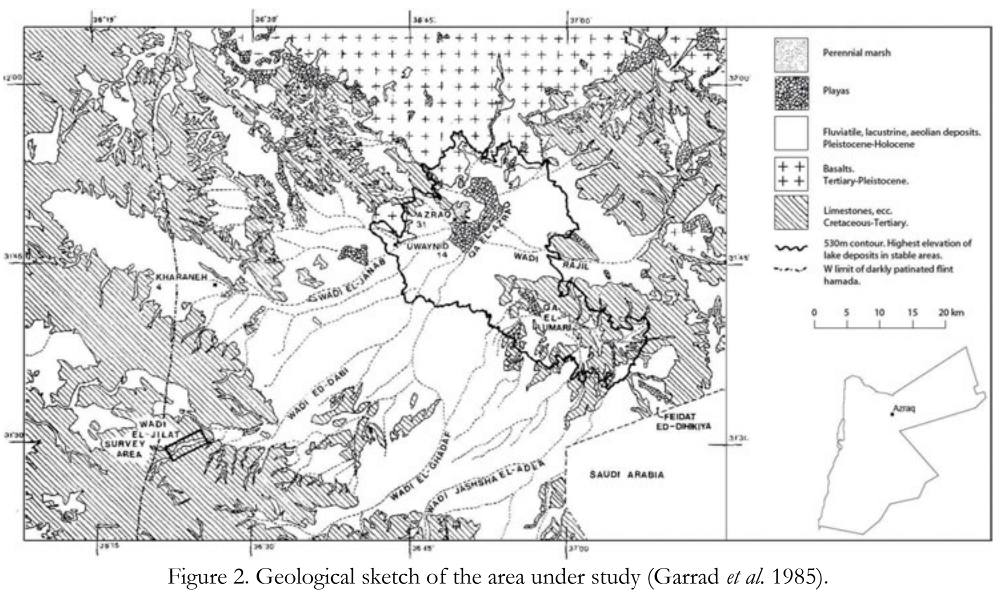

Figure 2. Geological sketch of the area under study (Garrad *et al.* 1985).

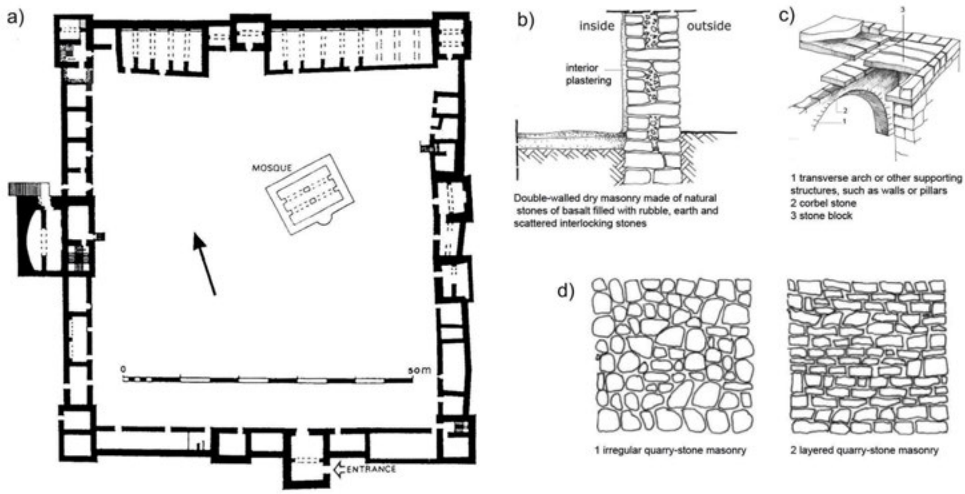

Figure 3. (a) Map of the Azraq castle (Kennedy 2004); (b-d). Details of the building techniques at Azraq (Jäger *et al.* 2012).

entire fort has similar stylistic parallels at Deir el-Kahf (Jordan) (Kennedy 2004; Kennedy and Riley 1990).

Dry masonry is used for the construction of the castle that is entirely made with basalt blocks laid in layers (layered quarry-stone masonry), and only in some parts in an irregular structure. The lowest layer of large basalt blocks, present in many areas, seems to be the one originally constructed by the Romans (Kennedy 2004). The interior walls of the rooms were filled with a thin layer of earthen mortars, rubble and scattered interlocking stones and then superficially plastered. The external walls of the fort were probably completely plastered, even if now the plaster is preserved in only few areas.

Nowadays, at first glance, the castle appears in an outstanding state of preservation. Basalt is a rock with low porosity, high hardness, and high resistance. Therefore, there are no deterioration patterns on the masonries visible to the naked eye (Verges-Belmin 2008). However, the site has undergone mechanical damages, such as the destruction of plasters in some points of the walls surfaces and the partial collapse of wall structures. Moreover, the proximity to a very busy highway and the natural enrichment of the ground with salts are among factors contributing to the castle's deterioration. For these reasons, the castle has undergone several restorative interventions during the last 40 years (**Table 1**), which were supervised by the Department of Antiquities of Jordan (Lash 2009; Lash pers. comm).

AZRAQ	
Ancient name	*Dasianis*
Site typology	Castrum
Country	Jordan
Governatorate	Zarqa Governatorate
Latitude (X)	36°49' E
Longitude (Y)	31°53' N
UTM zone	37
Elevation (in meters above sea level)	525 m
Site size	Approx. 79x72m
Proximity to any ancient roads or passages	Strata Diocletiana
Proximity to modern roads and modern connection	Highways connecting Jordan to Saudi Arabia and Iraq
Excavations	Trenches
Research/analysis	Surveys, restorative campaigns and archaeological trenches excavation (campaigns: 1975-77; 1999, 2002; 2005; 2006; 2008; 2009)
Findings on the site	Pottery; mile stone
Presence of inscriptions	Latin, Greek, Arabic inscriptions
Site dating	Roman, Byzantine, Umayyad, Ayyubid, Ottoman periods, last occupation during the first half of the XX cent.
JADIS ref. code	3214.001
MEGAJORDAN ref. codes	35928: castrum - 58140: palace - 58074: mosque - 35939, 35940: Greek inscription - 35925, 35944, Latin inscription - 35931, Arabic inscription - 35942: milestone - 58076: latrine - 58075: water structure - 35927, 35932, 35933, 35934, 35936, 35937, 35941, 35943, 35945,35946: sherd/flint surface scattered (unexcavated)
Useful website	APAAME Jordan: http://www.apaame.org/ MEGAJORDAN: http://megajordan.org/

Table 1. Summary of information about the castle of Azraq.

Figure 4. Rectified images of the western internal façade of the Azraq castle.

Analytical methods

The present complex and multi-stratified structure at Azraq is a result of a long history of occupation, transformations and reconstructions. This is an important heritage site, not only for Jordan but also for the Mediterranean region. During the first stage of this research project, it was thought wise to verify information deriving from earlier studies on the castle (Letellier *et al.* 2007), to collect new data about the deterioration mechanisms at the site, and to evaluate all information integrated together for the development of an efficient strategy for the conservation and management of the site. Some basic information about the castle is summarised in **Table 1**.

Digital documentation

Since the existing graphic documentation was insufficient (absence of accurate site maps and façade drawings), photogrammetric methods have been employed to document the elevations of the façades (**Fig. 4**). This is a work currently in progress.

Photogrammetry was used for the precise measurement of two-dimensional and three-dimensional objects and allowed the processing of precise photographs that were taken from different positions and angles using Agisoft PhotoScan software. This technique gives reasonably true-to-scale images of objects that can be converted in drawings and be measured (Eppich and Chabbi 2007). Photographs have been taken with a calibrated Canon EOS 400D digital camera, with a resolution of 12 megapixels and a Nikon D3100 digital camera with a resolution of 14.2 megapixels. Control points have been measured with a total station. The graphic documentation has been of great importance in subsequent work, as its outcomes were used for the definition of the sampling strategy. Furthermore, the data deriving from the graphic documentation of the castle will be used in the near future for the identification of the building techniques, and the *in situ* observations of the site stratigraphic sequence.

Sampling and plasters characterisation

The selection of samples was planned and executed after the analysis of the existing documentation and several visits to the site. Since the castle is entirely built with blocks of basalt and does not feature surfaces with evident deterioration, it was decided to focus on the mortars. A general heterogeneity in mortar typology has been observed, hence, a mortar sample for each different type macroscopically recognisable has been selected for each structure (external and internal walls and towers). The 43 mortar fragments collected form part of a representative sample from the site (**Fig. 5**).

Before the beginning of analytical work, all samples were macroscopically examined and information about the matrix colour (using the Munsell 2000 soil colour chart) and the concentration, distribution and maximum and average size of inclusion grains were recorded (Pecchioni *et al.* 2008). The macroscopic examination of the samples was followed by their compositional characterisation. The mineralogical study of the mortars will be conducted using polarised light microscopy. The finer fraction (of both the binder and the aggregate), will be mineralogically characterised through XRD. Microtextural and microchemical characterisation will be performed with the employment of SEM.

Finally semi-quantitative concentrations of major elements will be determined on selected areas of the binder using a SEM equipped with a EDS spectrometer and the quantitative concentrations of major, minor and trace element through XRF (Al-Saad and Abdel-Halim 2001; Artioli *et al.* 2010; Borrelli and Urland 1999; Doehne and Price 2010; Pecchioni *et al.* 2008; Torraca 2009).

Environmental monitoring and salt analysis

Soluble salts represent one of the most important causes of stone decay and can cause damage in several ways: the most important is the growth of salt crystals within the pores of stones and the subsequent generation of stresses (Doehne and Price 2010). In those samples where the salt contamination will be detected with the use of XRD, a subsequent step would be to further study the salt types and the quantity of cations and anions present in the solution with the employment of IC and ICP (Borrelli and Urland 1999; Doehne and Price 2010; Pecchioni *et al.* 2008; Torraca 2009). Salt crystals are stable only within well-defined conditions of temperature and humidity; hence they strictly depend on the surrounding environment (Borrelli and Urland 1999; Doehne and Price 2010; Torraca 1981). Therefore, an environmental monitoring program has been established aiming at a detailed microclimate investigation. For relative humidity and temperature measure-

Figure 5. Mortar samples from Azraq.

ments, a Gemini Tinytag Plus TGP-4500 data logger has been placed in the castle. The data, which include minimum, maximum and average values of temperature and relative humidity, are recorded every 30 minutes, for a period of six months (Camuffo *et al.* 1999).

Mosque dating

Even after the excavation of the mosque between 1975 and 1977, it was still impossible to assign a date to its foundation, and there is still an uncertainty whether the mosque was built in the Early or Middle Islamic period. To address this important issue of dating, 3 macroscopically different mortar samples have been selected inside the mosque and will be radiocarbon dated (Nonni *et al.* 2013). It is important to note that the samples will be first comparatively studied with other mortar fragments from the site, in order to record any similarities, and whether these samples can be macroscopically/technologically related to a specific period of the castle's long history. On the basis of these preliminary results it will be decided whether to proceed with the analysis.

Conclusions

This paper introduces a comprehensive conservation study on the Azraq castle, one of the main historical and cultural sites in Jordan. The main research objectives include the assessment of masonry damage at the castle, the comprehension of the factors affecting material deterioration, and the enhancement of our knowledge regarding building techniques and materials used throughout the life of the castle. The first steps of the work have been the collection and evaluation of earlier documentation and the production of a graphic record of the masonry facades. From the data so far obtained, a complex situation has resulted given that the fort has undergone several modifications and changes of use during its history. Different mortar typologies have been macroscopically recognised. The second phase of work will be the characterisation of the mortars and the study of possible contaminations, to be achieved through the application of a multi-analytical approach and the establishment of an environmental monitoring program: a detailed microclimate investigation has already been undertaken. Finally a conservation and management plan for the site will be developed taking into account and integrating all the aspects presented so far: i.e. *in situ* observations, historical data and scientific investigation.

Acknowledgments

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APPLICATION AND DEVELOPMENT OF COMPUTATIONAL INTELLIGENCE METHODS IN THE ANALYSIS OF ARCHAEOLOGICAL DATA

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Abstract

In this work the problem of clustering in archaeological data is discussed. Archaeological data are notoriously complicated and often come in multiple forms and types. In this study the application of computational intelligence methods is evaluated through the exploration of archaeological data. The emphasis is on the clustering of compositional ceramic data that might have been derived over a time span of many centuries. An exploratory study is designed to investigate the effectiveness of techniques, well known to the machine learning community, but not commonly employed by experts within the archaeological domain. In particular the k-means and fuzzy c-means algorithms are evaluated along with the visual assessing tendency approach.

Introduction

Archaeological questions vary from straightforward analytical questions to much broader behavioural analytical questions. Common analytical questions include those relating to the existence of chemically distinct groups within the data and their association with different manufacturing technologies and their origins. Over the last few decades, the development of advanced statistical methods has been proposed to help answer various archaeological questions. One of the main concerns in the areas of pattern recognition and data mining is how to organise observed data into meaningful structures. Within the context of archaeology and ceramic analysis, this can be used to address issues concerning pottery provenance and distribution.

As such, archaeological data cluster analysis can be achieved using clustering algorithms while also taking into account material characteristics of the artefacts being studied. Cluster analysis aims at grouping objects of a similar kind into their respective categories according to measured or perceived intrinsic characteristics of similarity (Jain 2010: 651).

Generally, the aim is to form groupings/clusters in which the similarity of artefacts in a group is greater than the similarity between artefacts of different groups. However, similarity is a broad term and often difficult to measure, and therefore we opt at measuring the complementary term known as the dissimilarity/distance, and this is measured with an appropriate distance metric. The terms similarity and dissimilarity/distance are related, when the similarity among objects is large and the distance is small.

Chemical compositional data are defined as strictly positive vectors of components of proportions with a constant sum. Chemical analysis is involved in enumerating the number of each type of atoms in a sample; concentrations are usually given in relative numbers (as percentages (%) or as parts per million (ppm)) (Aitchison 1986). The chemical constituents of an archaeological specimen can be categorised into main and trace elements. Main elements comprise large proportions of the artefact while the trace elements are present in concentrations less than 0.01%. As the majority of the major elements in the composition of ceramics is present in most artefacts, the discrimination of specimens into groups makes the utilisation of trace elements also necessary.

The objective of the project is to develop and apply techniques commonly deployed within the computational intelligence community on archaeological data, while taking into consideration the idiosyncrasies of the different types of data. The purpose of this study is to traverse the limits of typical archaeological datasets knowing that they only form a mere snapshot and are incapable of telling the whole story alone; archaeological data needs to be interpreted. An expert's knowledge is always required in making inferences and removing bias.

Ceramic Analysis in Archaeology

Archaeological data are notoriously complicated data; much attention is given not only upon the gathering of the archaeological artefacts but also their contextual, cultural, historical and chronological characteristics. Despite this, their statistical analysis often takes the form of simple projection, a feature against another, and in the best cases the use of very simple clustering or other dimensionality reduction methods. Many parameters influence the reliability of the produced data. Different people execute the same procedures in different ways; thereby increasing the variance within the class. This problem becomes even more pronounced when taking into account that apart from variations generated due to human factors, acquired variability is also caused due to environmental and aging decay of the source material.

Archaeometric analysis

The analysis of archaeological data is not a straightforward task. The objective of the archaeologist is to make inferences by taking into consideration as many parameters as possible. Subsequently, sampling usually takes into account chronological, contextual and typological characteristics of the material under study, where possible. Ceramic classification remains the principal approach to the study of pottery in identifying patterns in pottery assemblages and consequently the accumulated ceramic data. The most common way to categorise pottery is primarily based on technological attributes and morphological types; extra attention is given to the shape, size and surface treatment (Dikomitou 2012: 80). A relatively recently integrated complimentary part of this method is the characterisation based on their composition by isolating ceramic groups of similar chemical profiles and by statistically testing the validity of those groups (Garca-Heras *et al.* 2001: 325). The use of techniques that increase the separation of present groups also results in increasing their interpretability. The validity of the emerging groupings can be further evaluated through typological and potentially mineralogical comparisons with data bearing known fingerprints so as to address different aspects of ancient ceramic production and distribution.

The number of studies whose primary objective is to characterise artefacts is countless (e.g. Deutchman H. L. 1980; Crown 1983; Bishop *et al.* 1988; Dolata *et al.* 2007; Grove 2011; Gialanella *et al.* 2011; Erb-Satullo *et al.* 2011) and they all share the need to identify some structure or pattern in the ceramic assemblage, mainly through chemical analysis. This is all based on the assumption that ceramics made from the same raw material will be to a certain degree chemically similar.

The Archaeological Data Clustering Problem Formulation

An operational definition of the clustering of archaeological compositional data can be stated as follows: *given a presentation of n archaeological artefacts, find c groups based on a measure of similarity* such that the *similarities* between objects in the same group are *high* while the similarities between artefacts in different groups are *low*. Considering a set of *n* archaeological findings $O = \{o_i, \ldots, o_n\}$. We assume that there are groups (the clusters) of similar artefacts in O which however do not bear any class identifier. The analysis of the actual-tangible artefact o_i with the use of ED-XRF or any other method of chemical analysis will produce the compositional representation o_i which has the form $X = \{ x_i, \ldots, x_n\} \subset \Re^p$, where p is the number of analysed chemical elements and vector consists the chemical compositions of the artefact.

The process of discriminating unlabelled data aims to provide a solution to two problems. The first is concerned primarily with the clustering approach and involves: assessing cluster tendency, partitioning and cluster validity (Wang *et al.* 2009). Assessing cluster validity is of great importance and the performance of clustering methods greatly depends on specifying the parameters correctly. While the second problem is concerned purely with the way similarity between the different *compositions in X is measured*. An ideal cluster can be defined as a set of points that is compact and isolated (Jain 2010: 652).

Possible solutions to the clustering problem require an integer number c representing *the number of clusters* which can be either *crisp* or *fuzzy* partitions. Crisp clustering can be formulated, in general, as a problem of partitioning the finite set X into a given number c of disjoint clusters (see equation 1).

$$M_{hc} = \begin{Bmatrix} U \in \Re^{cn} | \, u_{ij} \in \{0,1\} \forall i, j; \\ \sum_{i=1}^{c} u_{ij} = 1 \; \forall j; \; \sum_{j=1}^{n} u_{ij} > 0 \; \forall i \end{Bmatrix} \quad (1)$$

where u_{ik} is the *membership* of artefact o_k in cluster i, the partition element $U_{ik} = 1$ if o_k is labelled i and is 0 otherwise.

On the other hand, fuzzy clustering introduces the principle of partial membership. That is, because of uncertainties about the integrity of an artefact, errors caused due to the deterioration of materials or other analytical reasons, an artefact may simultaneously belong to more than one cluster. Given the set X of chemical compositions, assign each artefact x to one or more clusters while also specifying the degree of membership for each assignment; this represents the likelihood of the artefact x to belong to that specific cluster (see equation 2). The idea of fuzzy clustering fits perfectly to archaeology since many ceramic attributes and the heterogeneous nature of pottery *per se* do not allow separable clusters. One of these is the frequently non-discrete transition of archaeological technological practices related to ceramic production.

$$\boldsymbol{M_{fc}} = \left\{ \begin{matrix} \boldsymbol{U} \in \mathfrak{R}^{cn} \mid \boldsymbol{u_{ij}} \in [\boldsymbol{0}, \boldsymbol{1}] \forall \boldsymbol{i}, \boldsymbol{j}; \\ \boldsymbol{0} < \sum_{i=1}^{n} \boldsymbol{u_{ij}} < \boldsymbol{n}, \forall \boldsymbol{j};\ \sum_{j=1}^{c} \boldsymbol{u_{ij}} = \boldsymbol{1}\ \forall \boldsymbol{i} \end{matrix} \right\} \tag{2}$$

Clustering Algorithms

The complexity and dimensionality of the ceramic data makes the use of clustering methods necessary to allow the characterisation of pottery samples based solely on their composition, while acknowledging that the presence of noise in the data makes the detection of the clusters even more difficult.

One of the clustering algorithms widely used within the data analysis community (Jain 2010) as well as in several archaeological studies (Principe *et al.* 2000: 247) is the k-means algorithm. K-means has a rich and diverse history as it was independently discovered in different scientific fields by Steinhaus (1956), Lloyd (proposed in 1957, published in 1982), Ball and Hall (1965), and MacQueen (1967). Even though it was first proposed over 50 years ago (Jain 2010: 653), it is still one of the most widely used algorithms for clustering, mainly due to ease of implementation, simplicity and efficiency. Numerous variants of the original approach have been developed with the aim to improve specific aspects of the algorithm and subsequently its effectiveness on specific problems.

Visual clustering is an innovative and alternative approach for clustering multivariate data. VAT (Bezdek 2002) is one of these methods and relies on the very simple principle that similar objects should be placed near each other. The output of the algorithm allows the visualisation of similarities between artefacts through a grey scale image.

K-means

Given the set of objects x with n dimensions, the goal is to partition the data in the n-dimensional space into c clusters; such that the objective function J (see equation 3) has an optimal (usually minimal) value. The idea behind the operation of this approach is that elements should belong to their closest cluster. The clustering operation terminates when the changes from iteration to iteration fall below the pre-specified positive threshold.

$$J = \sum_{i=1}^{c} \sum_{j=1}^{n} u_{ij} d^2(x_j, v_j) \rightarrow min \tag{3}$$

$$d^2 = \left\| x_j - v_j \right\|^2 = (x_j - v_j)^T (x_j - v_j) \tag{4}$$

where u_{ij} signifies the membership of object o_i in cluster *j*, *d* is the distance metric (defined as in equation 4) and v_j is the centre of cluster j. Inputs to the algorithm are the set of n-dimensional vectors $\{x_1, x_2, \dots, x_n\}$ as well as the parameter *c* which signifies the desired number of clusters. The algorithm's output is a mapping of the vectors into c clusters (disjoint subsets).

Fuzzy c-means

Fuzzy c-means is an evolution of k-means and incorporates the principle of partial membership allowing data samples to belong partially to more than one cluster. Set *X* is grouped into *c* clusters with every data-point in the dataset belonging to every cluster by a certain degree. A data-point lying close to the centre of a cluster will have a high degree of belonging to that cluster and a lower membership when lying further away. This principle allows the algorithm to model in some means the uncertainty in unsupervised learning. In equation 5, *m* is the fuzzifier determining the level of cluster fuzziness and *v* the set of cluster centres or prototypes ($v_i \in$).

$$J_m = \sum_{i=1}^{c} \sum_{k=1}^{n} u_{ik}^{m} \|x_k - v_i\|^2 \tag{5}$$

The cost function of the algorithm is almost identical to the one already presented in k-means since the objective is to minimise the Euclidean distance among the clusters. The only difference is that since we do not have crisp clustering, the membership matrix *U* takes floating point values where each column sums up to 1 (the total probability of a sample is 1). The algorithm takes the same inputs as the k-means but produces a mapping of the input vectors into *c* fuzzy clusters.

Most clustering algorithms currently deployed in the archaeological domain are parametric, in the sense that at least one or more parameters need to be specified by the user (Jain 2010: 656). The parameter that is usually required as a prerequisite is the number of clusters (Jain 2010: 656). Luckily, a range of methods have been developed over the years allowing the determination of this parameter, avoiding the problem of running the clustering algorithm multiple times, and then selecting the best performing run.

Visual Clustering

The VAT technique (Havens *et al.* 2009) uses a visual approach to find the number of clusters in data. For object data, visual clustering was initially performed by inspecting scatter-plots in p = 1, 2, and 3 dimensions (Havens *et al.* 2009: 506). The VAT algorithm reorders the rows and columns of any $n \times n$ scaled dissimilarity matrix *D*, denoted as D^*. In **Figure 1**, on the left is the unordered distance matrix and produces the ordered matrix D* and on the right the ordered version of the same matrix. If the image I (D^*) has *c* dark blocks along its main diagonal, this suggests that *D* contains *c* clusters. The size of each block may even indicate the approximate size of the suggested cluster. Hence, VAT images suggest both the number of and approximate members of object clusters (Havens *et al.* 2009: 508).

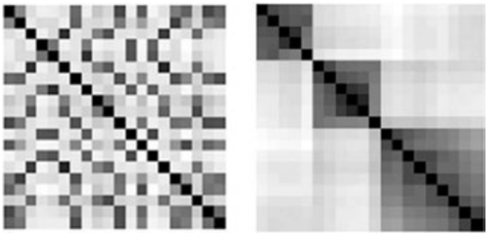

Figure 1. The unordered and ordered D matrix: the input and output of VAT. Each block in the image represents the dissimilarity between the samples in the two axes. The darker the block the higher the similarity between the samples (Yingkang and Hathaway 2008: 442).

The ordered D^* matrix may serve as the input to the CLODD algorithm which will determine the number of clusters in the data. CLODD is a completely autonomous method for determining cluster tendency, extracting clusters from the ordered dissimilarity data, and providing a cluster validity metric (Havens *et al.* 2009: 508). This leads to a distinct advantage of CLODD since it is not tied directly to any distance metric or reordering scheme (Havens *et al.* 2009: 508).

Experimental Results

For demonstration purposes the above algorithms are deployed for the analysis of real compositional data. The dataset was obtained from the ED-XRF analysis of Early and Middle Bronze Age utilitarian pottery from Marki *Alonia* in Cyprus (Frankel and Webb 1996, 2006; Dikomitou 2012). The analysed sample includes a variety of pottery shapes such as tableware, cooking pots and other coarse pottery from the successive occupational phases of the settlement at Marki. The analysed sample had already been studied using a range of analytical techniques, including ED-XRF and ceramic petrography. According to the mineralogical study of the sample, it can be divided into ten fabric groups, which are also confirmed by chemical analysis (Dikomitou 2012).

The aim of the experiment was to obtain quantitative comparable measures on each method's performance. Pre-processing transformations were applied allowing the original variables to become comparable with each other; this was necessary since they were measured for both main and trace elements. A series of external validity indices, the Rand Index (Rand 1971), the Adjusted Rand Index (Hubert and Arabie 1985), the Mirkin Index

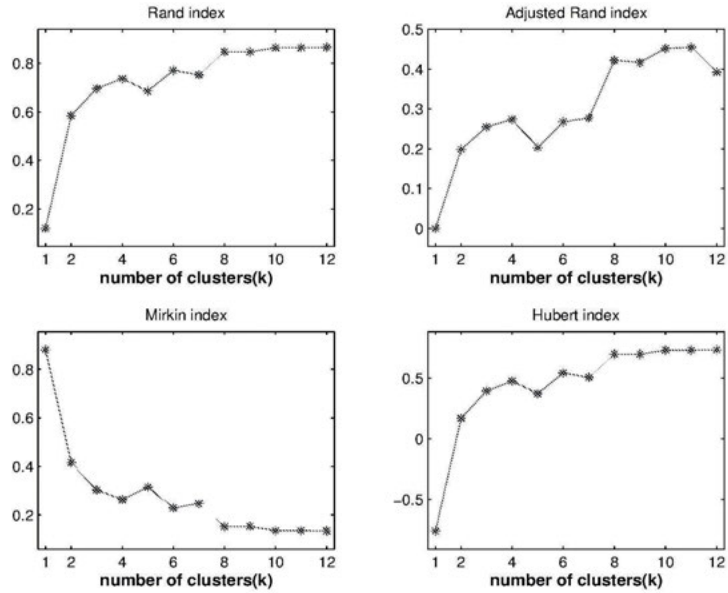

Figure 2. K-means evaluation: The score of each index for a given number of clusters. As expected, clustering with the true number of clusters, which is 10, returns the best – in terms of scoring - results.

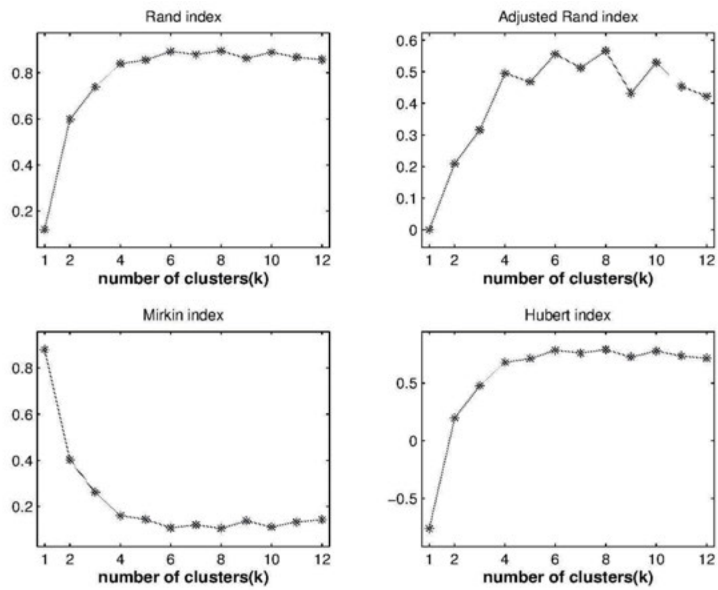

Figure 3. FCM evaluation: The score of each index for a given number of clusters. As expected, clustering with the true number of clusters, which is 10, returns the best – in terms of scoring - results.

(Mirkin 1996) and the Hubert Index (Hubert and Schultz 1976), were calculated after the application of each clustering method.

Figures 2 and 3 show the results of calculating the above indices for each clustering, with respect to the different values of c. For FCM the fuzzifier parameter was chosen to be $m=2$; a reasonable selection based on literature (Bezdek *et al.* 1984). A matching factor was also calculated determined by the successful assignment of elements to the correct target class; a yield percentage of matching elements of each cluster was calculated. For the fuzzy solutions, a crisp membership matrix was produced by assigning each artefact to the cluster with maximum membership.

The figures illustrate that the fuzzy solution (**Fig. 3**) produces more stable results than the crisp k-means (**Fig. 2**). This result was expected; the archaeological data form non-separable (i.e. overlapping) clusters due to inherent compositional similarities among the different specimens, but also due to the fact that artefacts chronologically span many centuries. The performance problems of the algorithms become apparent with the calculation of the adjusted Rand index; this is consistently below 0.6 with FCM being the method which produces the highest values. The performance of the algorithms against the adjusted Rand index is of great importance due to its sensitivity and ability to not be affected by the granularity of each particular clustering.

The matching percentage of the k-means algorithm was consistently around 33.5-35.2% while FCM tended to produce higher percentages of the order of 47.5-48.75%. Overall, less than 50% of the artefacts were assigned to the correct clusters.

VAT Clustering

The VAT and CLODD algorithms are non-parametric and only accept as input the symmetric distance matrix of the objects in set X. The output of the VAT algorithm was then used as the input to CLODD which produced the estimate of the number of clusters.

The evaluation of the algorithm against the external validity indices was performed (**Fig. 4**). The VAT algorithm, according to the values of the adjusted Rand index, managed to produce the best results out of the algorithms we have evaluated, by reaching values sometimes higher than 0.7 and a mean number of clusters: *9*; a quite impressing result considering the complexity of the data.

It is important to note that archaeological studies involve analysis on a large number of artefacts, however sometimes only a smaller number of these is selected to undergo compositional analysis; this is also the case in Dikomitou (2012) from where the data

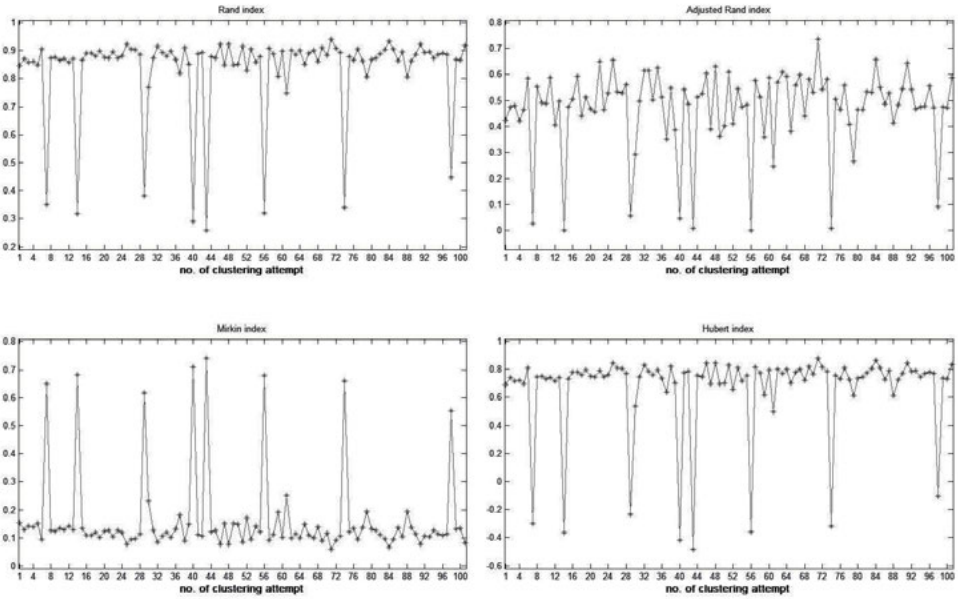

Figure 4. VAT evaluation: Each point indicates the score of each of the 100 runs in the experiment.

derive. While the classification of the selected artefacts was performed based on the entire population, unfortunately many times an inadequate number of samples is selected from each class, thereby not enabling the establishment of clusters to be convincingly identified.

Conclusions

Clustering of archaeological material is not a straightforward task. Fuzzy clustering solutions seemed capable of capturing amounts of data uncertainties which can be of great use to the archaeologist since it may reveal similarities between compositional groups (or types of pottery in archaeological contexts). The application of visual clustering techniques on data may provide a good indication to the important decision of selecting the number of clusters prior to any other analysis, while it may also provide information about the clusters' size and in-between distance. In particular, the application of visual clustering techniques on archaeological data may provide an insight of the groupings (number, size, similarity) within the data without the need for parameterisation.

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WORK PACKAGE 6

Dating Techniques and the Palaeoenvironment

WORK PACKAGE 6

Dating techniques and the palaeo-environment

The uniqueness of the Mediterranean region, with a particular emphasis on its eastern part, consists of a number of physical and cultural features that do not coexist in any adjacent regions. Among them are: a) the intensive sea-land interaction during Upper-Pleistocene/Holocene, imprinted on the very long Mediterranean coastline, with lacey up-growth and vertical disruption, b) the drastic, alpine-type, geotectonic, volcanic and seismic regime, acting on geologically polysynthetic pieces of crust, that hosts important mineral resources, c) the nodal location, bridging three continents -and merging civilisations-, at a region lying on a middle latitude, thus retaining mild climatic conditions known as the "Mediterranean clime", d) a wealthy material culture that is suggestive of constant interaction among local populations that have been navigating across the Sea transmitting goods, ideas and customs, e) the fact that the region was inhabited since the Paleolithic times, fulfilling a diachronic role, as a cultural-producer, embodying the coastwise sector of the so-called "fertile crescent".

For many of the Mediterranean locations that partially or entirely share the abovementioned characteristics, the absolute dating / palaeo-environmental studies seem to comprise highly indicated approaches, in order to resolve problems deriving from archaeological or other relevant studies referring to past landscapes and their evolution; unfortunately rather few studies of these categories had been undertaken until recently.

Within the framework of the NARNIA project, two research projects were established aiming at the basic research required for the upgrading of already employed dating techniques, while at the same time addressing important methodological and archaeological issues. Specifically, the first project conducted by Ioannis Christodoulakis aims at the establishment of the chronological framework of the recorded palaeo-environmental changes in the South-West Peloponnese. In order to achieve this goal we applied luminescence dating (OSL dating), combined with the SAR protocol. In addition, an attempt was made to reconstruct patterns of atmospheric circulation during the Late Quaternary in order to evaluate the contribution of airborne dust transferred from distant areas to the local sedimentary record. The preliminary results are presented and discussed in the first of the two papers in this section.

The second project within this work package focused on the island of Cyprus. Acknowledging the fact that the study of sedimentary formations, which bear traces of human presence, provides an excellent opportunity to understand the palaeo-environmental context, this second project was established to investigate sedimentary formations, in which prehistoric activity in southern Cyprus took place. The purpose of this project, conducted by Evangelos Tsakalos, was to examine the chronology of coastal deposits of South-East Cyprus and provide preliminary comments on the Late Quaternary environmental change by using up-to-date luminescence dating methods. Another objective of the project was the analysis of microtextures present on quartz grains of coastal dunes from South-East Cyprus in order to determine their depositional history.

One of our ultimate objectives is to underline the importance of interdisciplinary studies, i.e. palaeo-environmental, geoarchaeological absolute dating and so forth, for holistic approaches in composite and fast evolving landscapes. Moreover, it will be worthwhile to accentuate the absence of some important background information on Mediterranean palaeo-environment issues, such as the complete Upper-Quaternary palaeo-temperature record, which obviously obscure more integrated studies in the region. It is anticipated that the research conducted in the framework of work package 6 will provide a starting point for filling gaps in research and in our knowledge about the palaeo-environmental regimes of the region.

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LUMINESCENCE DATING AND THE PALAEO-ENVIRONMENT IN SW PELOPONNESUS

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Abstract

Palaeo-environmental studies are considered important to examine past environmental conditions, to interpret the current status of the environment and also where possible to predict future changes. The South-West Peloponnesus, specifically the peninsula of Mani located in south-western Greece, is an area which provides much palaeo-environmental and palaeo-anthropological interest. Former investigations suggest that environmental changes which took place during the Upper Quaternary period have been recorded in the terrestrial and marine sedimentary record, thereby providing a natural "archive" suitable for further research. The most important, and maybe unique, factors which led to the development of this "archive" are believed to be Mani's geographic position between three continents, its long coastal zone, in addition to local tectonic regimes. It is worth noting that excavations conducted on Mani revealed important palaeo-anthropological remains. Recent publications conclude that Neanderthals inhabited this region and were active there for a long period of time. We have focused our study on the Diros area which comprises the whole Mani peninsula.

This project aims to establish the chronological framework of the recorded paleoenvironmental changes. In order to achieve this goal we applied luminescence dating (OSL dating), combined with the SAR protocol, which is a widely used technique for providing information about the age of sediments. In addition, an attempt is made to reconstruct patterns of atmospheric circulation during the Late Quaternary in order to evaluate the contribution of airborne dust transferred from distant areas to the local sedimentary record. The preliminary results are hereby presented and discussed.

Introduction

This present paper is a review of the preliminary results of the project undertaken by the author as part of the NARNIA (New Archaeological Research Network for Integrating Approaches to ancient materials studies) project. The main objective of this research is the investigation of the regional palaeo-environmental changes that occurred during the Upper Quaternary by applying OSL analysis with the intention of establishing a chronological framework of these changes. Dating results will be compared with former geochronological investigations in the area conducted using the ESR technique. One of the aims of this research is to reconstruct the patterns of atmospheric circulation over the Late Quaternary, taking into consideration the contribution of airborne dust transferred from distant areas to the local sedimentary deposits. Finally, all the results will be correlated with data from archaeological excavations which have been carried out in the studied area.

It is well known that the development of the radiocarbon dating technique by J. R. Arnold and W. F. Libby in 1949 (Arnold and Libby 1949; Libby *et al.* 1949) has greatly influenced the field of archaeology, at the same time prompting the development of new dating methods. Currently, a considerable number of methods are used by archaeologists, and other scientists, in their studies: luminescence dating techniques are included among them. The TL technique was developed in 1957 for dating heated materials. In 1979, it was recognised that TL could also be used for the dating of sediments (Wintle and Huntley 1979). By 1985, it was clear that TL was only suitable for old sediments because the TL signal produced by modern quartz and feldspar grains was small (Wintle 2008). During the same year, a new technique, called OSL, was developed (Huntley *et al.* 1985). The palaeo-environmental reconstruction of South-West Peloponnesus presented here is based on the application of this technique.

TL and OSL are based on the estimation of the impact of radiation on the crystalline structure of minerals while shielded from light. The main minerals studied are quartz and K-rich feldspar, which can be found in almost all sedimentary environments. The radiation (a, β, γ) comes from radionuclides which are present in the mineral and its natural environment, mainly uranium, thorium (and their decay products), rubidium and potassium, and for a small proportion from cosmic particles. They lead to the emission of electrons which are subsequently trapped in crystalline lattice defects. Some of the traps are considered 'unstable' ("shallow traps"), which means that an electron inside will not remain trapped for the whole duration of burial.

On the contrary, defects situated deeper inside the lattice have a higher thermal lifetime. These "deep traps" (stable traps associated with high energy levels) can adequately be used for dating. The total amount of trapped electrons within a crystal is proportional to the total energy absorbed and retained by the crystal (or dose), hence the time it was exposed to radiation. As soon as the mineral is exposed to sunlight, for example during its transport, trapped electrons absorb photon energy (from the Sun), and are released from the traps. So, the "clock" is set to 0 and starts to count as soon as it gets buried. This process, the transportation or what other event zeroed the "clock", is dated through luminescence dating (Huntley *et al.* 1985; Aitken 1998). SAR protocol is a methodology proposed by Murray and Wintle (2000) for measuring the total amount of trapped electrons and estimating the amount of radiation energy the quartz (or feldspar) has been exposed to during its burial period. This amount is called Equivalent dose (D_e) or Paleodose and is expressed in grays (Gy) (Murray and Wintle 2003; Duller 2003).

In order to determine the age of the sample another parameter, the Dose rate (D_R), is also needed. The Dose rate reveals the rate of radiation budget per time interval that affected the sample during its burial period and is expressed in grays per time unit, more commonly as Gy/ka. Dose rate calculation is based on the concentration of radionuclides in the sample and the cosmic radiation parameter. Dividing Equivalent dose by Dose rate the age of the sample is calculated. Preliminary results and conclusions are presented and discussed in the remaining part of the paper.

The study area and its importance

This study focuses on Mani, specifically the west coast of the Mani peninsula, an area which is also known as Mesa Mani. The tectonic regime of the wider area is notably active due to movements along the boundaries of the Aegean microplate (Mariolakos *et al.* 1985; Bassiakos 1993). The area, marked within the ellipse in **Figure 1(a)**, was chosen because according to the literature it has great palaeo-environmental and palaeo-anthropological importance: for example, rich sequences of terrestrial and marine sediments classified stratigraphically are known here. They also includeresidues of Palaeolithic remains, extending over a period of several tens of thousands of years before the present era. These sedimentary deposits, fluvial or coastal, are an excellent repository of environmental changes that have occurred during the past 120,000 years at least, thus offering the possibility of extensive and in-depth study of these changes.

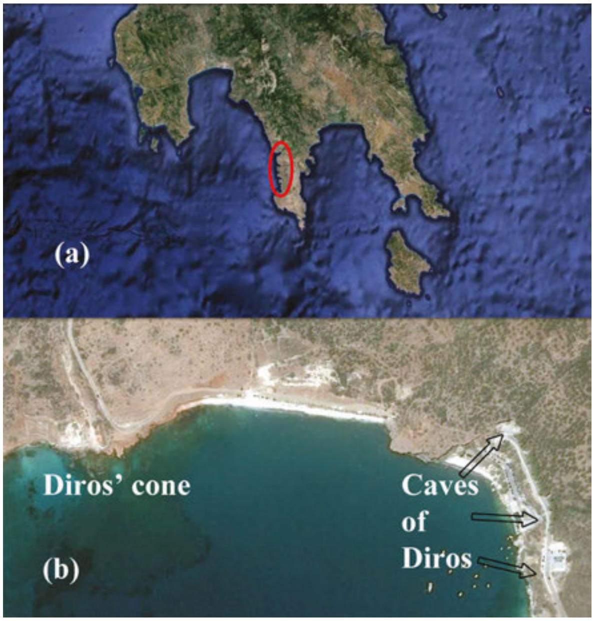

Figure 1. (a) Map of Peloponnesus. The area of interest is marked within the ellipse; (b) General view of the area of interest.

Apart from its palaeo-environmental importance, Mani also has great palaeo-anthropological significance. Both older and more recent archaeological studies conducted in the area have also recognised this significance: for example, Mani is one of the few areas in Greece where human fossils dating as early as the Middle Pleistocene have been discovered (Harvati *et al.* 2009). Among others, two of the most important sites in the area are the caves of Apidima and Kalamakia. Skeletal remains and lithics have been retrieved from these caves and have been associated with Homo Neanderthalensis (Pitsios and Liebhaber 1995; Harvati *et al.* 2011; 2013). It is worthy to note that these caves are situated close to the studied area, and this has helped to correlate our results with the archaeological discoveries.

The central area of this research, at Diros' Cone, presented in **Figure 1(b)**, is situated almost 600m north of the Caves of Diros. A closer view of the cone is presented in **Figure 2**. It is a fluvial deposit formed at about the last 50m of a stream which is known as Rema Koukou.

This fluvial deposit consists of 4 horizontal red clay Palaeosol layers 1, 2, 3 and 4 in **Figure 2**. Among these layers there are 3 horizontal conglomerate layers, lower, middle and upper which are shown in the same figure. The thickness of the clay layers ranges from 5cm to 60 cm and that of the conglomerates from 10 to about 60cm. A calcrete layer is also present between palaeosol layer 2 and the middle conglomerate and its thickness is about 15cm. The total height of this deposit is almost 4 meters.

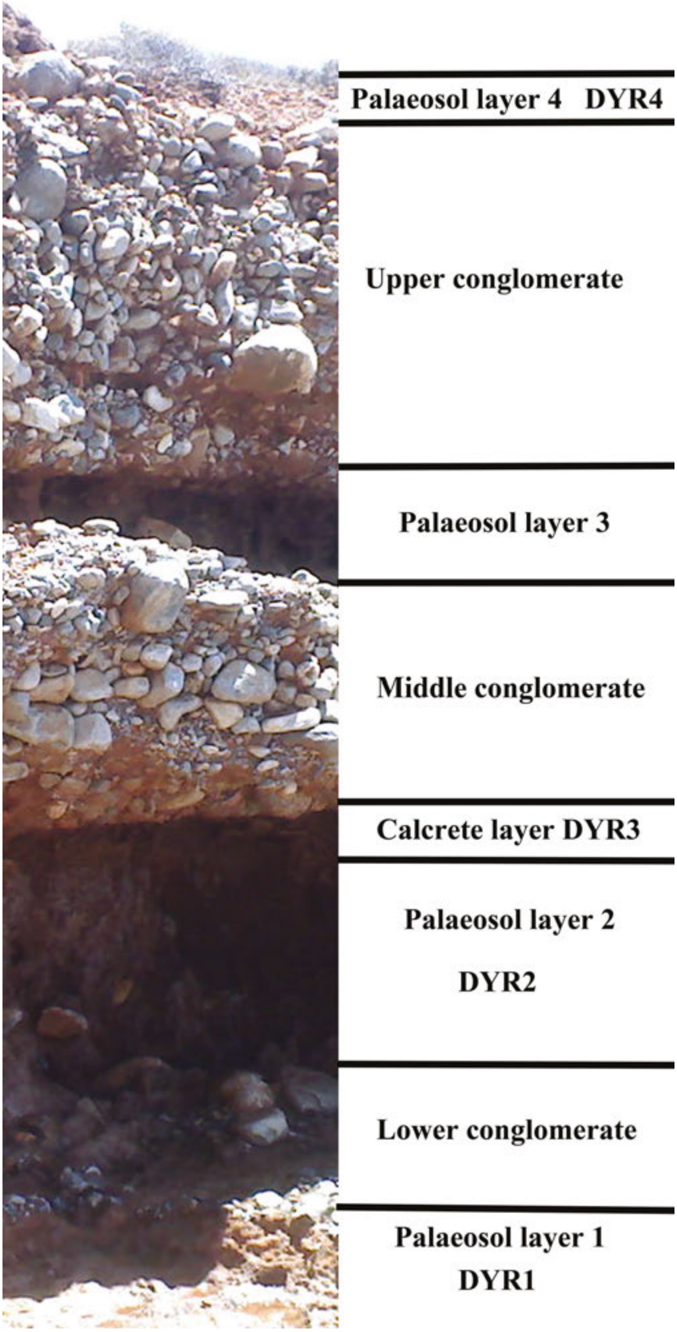

Figure 2. Stratigraphic profile of Diros' Cone. DYR 1, 2, 3 and 4 are the names of the samples collected for further research.

This deposit lies over a corroded solid layer of marine origin which today is almost 50cm above sea level. This implies that this solid layer was formed after the Tyrrhenian stage. This layer is also present in neighboring areas further to the south on the coastal zone in front of the Caves of Diros, and also to the north. DYR 1, 2, 3 and 4 are the code names of the samples collected for further research. More samples have been already collected from other sites around the Diros' Cone and also by the stream's bank.

Results and discussion

Following the standard procedure, the collected samples were chemically treated in an attempt to isolate quartz grains (Preusser *et al.* 2008). After this stage, we made test measurements on quartz grains of different size in order to determine the most suitable fraction. The results obtained revealed that the most suitable fraction is the fine one (4-11μm). Then, pre-heat and dose recovery tests were also carried out on this fraction of the quartz grains. The pre-heat test is used in order to determine the appropriate temperature under which OSL measurements should be made (Murray and Olley 1999) while the dose recovery test is used in order to verify the suitability of the quartz for OSL measurements. A typical natural decay curve and its corresponding growth curve for the sample DYR2 is presented in **Figure 3**. Natural signals of all samples are characterized by a dominant fast component while the growth curves are characterized by sub-linearity for the majority of the aliquots. These results imply that the samples are suitable for dating. ICP-MS analysis was used to determine the concentration of Uranium, Thorium, Potassium and Rubidium in the samples. These data, along with other parameters like the water concentration of each sample and information about the location where the samples were collected, have been used to calculate the Dose rate.

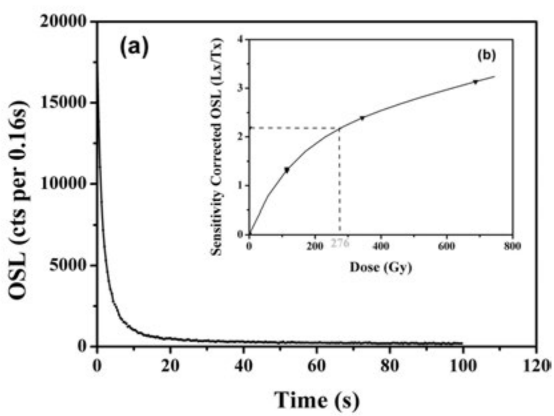

Figure 3. Typical natural decay curve (a) and its corresponding growth curve (b).

Initial dating results indicate that the stratigraphy of the cone is probably reversed. Possible mechanisms for the interpretation of this reversion, such as the transfer of large parts of layers due to tectonic reasons or due to high energy flow of the river, are proposed in the literature;

however we are still working on this issue in order to clarify what has happened. More samples have been collected from the wider area but these dating results are not yet available.

In a palaeo-environmental context, the Mani Peninsula simultaneously constitutes a terrestrial barrier and a natural impasse, preventing any further movement to the south, of faunal or human populations, seeking better living conditions and new lands, perhaps due to the deterioration of the environmental conditions which prevailed in central Europe during the last era of the glaciers. The progress of the glaciers to the south in central Europe resulted in even worse climatological conditions in the north together with a decrease in valuable land. At the same time, in the south the land-mass was increasing because of the lowering of the sea level, while the climatic conditions were more favorable for both animal and human settlement. Accordingly, it is not unexpected to find numerous deposits containing a plethora of fossilized animal bones (with several of them burnt). Further proof for human occupation (developing in two, at least, successive strata), is provided by the presence of hard rocks, such as the 'stone of Krokee' (a green porphyritic andesite), which was brought to the area from some distance for the manufacture of stone tools.

Trying to investigate the past action of another major environmental parameter, the wind, it was decided to search for exotic minerals or elements in isolated sedimentary deposits that do not match the geology of the area and which could be attributed to transport by the wind over long distances, such as from the Sahara desert. We looked for and finally located suitable formations (dolines) over a broad area. Samples from these formations were collected and are under chemical analysis in order to examine whether we can detect airborne materials. Furthermore, additional samples were collected in order to examine if dating is achievable.

It is worthy to note that in the literature there are no reports regarding the detection of airborne materials in sedimentary deposits. This kind of research is common in glaciers where the detection of the transported material is easier because it usually forms a distinct layer (Wagenbach and Geis 1989; and references therein): The preliminary results are expected soon.

Recently, samples for palaeo-magnetism measurements were also collected. These have enabled us to investigate the possibility of detecting information about the temperature changes at this particular site through the examined period. These samples are currently been subject to initial processing before measurement and initial results are expected in the near future.

Conclusions

The significance (palaeo-environmental, palaeo-anthropological and geotectonic) of Mani is confirmed by *in-situ* observations. This fully justifies the selection of this particular site for the needs of this research project. In addition, the initial results confirm that the OSL dating technique can provide accurate and reliable results in order to reveal the chronological framework of local paleoenvironmental changes. These results seem to agree well with results obtained by former studies using different dating techniques, namely ESR. Concerning the attempt to reconstruct patterns of atmospheric circulation over the Late Quaternary, the area under study provides unique opportunities to investigate the contribution of airborne dust transferred from distant areas to the local sedimentary record as isolated sedimentary deposits have been located. Of course, much further research has to be done before we can attempt to reconstruct atmospheric movements during the Late Quaternary.

In addition, new sites, both underground and in the open air, have been located for further investigation (including excavations, bio-stratigraphic, archaeological and anthropological research), due to the presence of relevant features and other indicators. The possibility of revealing temperature changes in the area through measuring palaeomagnetism is being attempted at this particular site for the first time: initial results should be able to clarify if this approach is successful and can be used further. Finally, several points of interest have been highlighted to show how the basic OSL research might develop in relation to the results of the current study and analysis.

Acknowledgements

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LUMINESCENCE DATING AND THE PALAEO-ENVIRONMENT IN SE CYPRUS

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Abstract

The coastal zone of southern Cyprus is of great palaeo-environmental interest and archaeological significance. Specifically, repeated fluctuations of the global sea level during the Quaternary (the last 2.5 million years) have created distinctive formations which now appear as geomorphological features along the coastal areas of Cyprus. In addition to the palaeo-environmental interest, the coastal areas of southern Cyprus have a rich cultural history. Recent archaeological fieldwork has identified the earliest evidence of human presence on the island in several coastal sites, the most important of which are Akrotiri *Aetokremmos*, Nissi Beach, and Akamas *Aspros*. They date to the Late Epipalaeolithic (ca 11,000-10,000 cal BC) (Ammerman 2010; Knapp 2010; Simmons 2013). Permanent settlement of the island by farmers occurs in subsequent periods, namely the Pre-Pottery Neolithic A (Manning *et al.* 2010; Knapp 2013). Traces of prehistoric human activity in coastal areas of Cyprus are also evident in those geological formations which reflect the aforementioned palaeo-environmental changes (Galili *et al.* 2004; Kuijt 2004; Ammerman 2010; Ammerman *et al.* 2006; Knapp 2010).

The investigation of the sedimentological/lithological characteristics of the sedimentary formations which bear traces of human presence provides an excellent opportunity to understand the palaeo-environmental context in which prehistoric activity in southern Cyprus took place. However, the study of palaeo-conditions can be better understood when a time-frame of these events can be provided.

The purpose of this research is to examine the chronology of coastal deposits of southeast Cyprus and provide preliminary comments on the late Quaternary environmental change by using up-to-date luminescence dating methods. Another important aim of this

study is to analyse the microtextures that are present on quartz grains of coastal dunes from South-East Cyprus in order to determine their depositional history.

Introduction

Coastal deposits and their development and evolution are significantly affected by past changes in climate and the substantial fluctuations in sea level. Coastal formations are the main exposed sedimentary features found along the South East coast of Cyprus. They are arranged in a more or less monotonous stratigraphy: shallow marine to beach sediments covered by calcite-cemented aeolian sediments, with the latter dominating in both thickness and spatial extent (Poole 1992). These sedimentary coastal deposits provide both a key for coastal development and an excellent climate archive in the southeastern Mediterranean for the Upper Pleistocene.

The dating of coastal formations, and the establishment of a chronological framework, is key to the analysis and interpretation of environmental changes in the past. Luminescence dating as an absolute dating technique has been proven to be suitable for dating various Quaternary deposits (aeolian, fluvial, glacial, etc) and there have been a number of recent reviews on the subject (*cf.* Singhvi and Porat 2008). However until recently, luminescence dating had mainly made use of quartz alone. Lately, advancements in luminescence dating have included IRSL using an IR signal (*cf.* Buylaert *et al.* 2011, 2012). This is less affected by anomalous fading (a signal decrease with time leading to an age underestimation) (Wintle 1973), an issue that had previously prevented the use of feldspar.

Furthermore, the presence of Pre-Pottery (Aceramic) lithic artefacts on Cyprus, an island which is located between Africa and Europe/Asia, make this area of particular interest for archaeological research. Although many studies have been carried out on a number of areas of the Mediterranean regarding their coastal evolution and the associated paleo-environmental changes, little has been done on the coasts of Cyprus. From an archaeological point of view, until recently, there was no interest in searching for archaeological evidence on the coastal formations that occur along the coasts of Cyprus. Because of the barren nature of these formations, this kind of landscape was considered inhospitable for human habitation.

However, a recent study (Ammerman *et al.* 2006) revealed the existence of pre-Neolithic artefacts on the aeolianite formation at Nissi Beach (in the modern coastal village of Agia Napa). This prehistoric site is now considered as providing the oldest evidence for seagoing in the eastern Mediterranean. Further, the excavations at Aetokremnos, and

Akamas *Aspros* provide evidence that for at least two millennia prior to the advent of farming, foraging seafarers persisted with a coastal way of life, continually adapting to the sea and exploiting the marine and other resources available along Cyprus' shores (Simmons 1999; Ammerman *et al.* 2008; Ammerman 2010). The establishment of a reliable geochronological framework is therefore fundamental not only for a better geological and climatelogical understanding of the coastal paleo-environment but also because it provides an improved framework for understanding human expansion in the eastern Mediterranean.

The application of SEM in examining irregularities on quartz sand grains has been developed into a common method in determining different sedimentary environments and deciphering their palaeo-environmental/depositional history (*cf.* Moral-Cardona *et al.* 1997; Newsome and Ladd 1999). These quartz features and the frequency, in which they appear, in turn, can be used to determine the sedimentary histories of quartz grains, allowing the clear distinctions between aeolian, marine, glacial and diagenetic depositional environments to be made. If grains have been through different environments, their surface imprints may incorporate a combination of different textures produced during sediment transport, deposition and diagenesis. Principally, mechanical processes leaving signatures as different impact and abrasion marks on the grain surfaces during transportation in different dynamic environments are the key diagnostic features which record those mechanical processes. Marks as a result of chemical processes, consisting of a range of different overgrowth and etching types, can further facilitate the identification of the diverse post-depositional course of action that the grains have experienced.

Geological setting

The studied area is located in the coastal zone of south east Cyprus, (**Fig. 1**), more specifically the area of Agia Napa and Cape Greco, where Late Pleistocene deposits are well developed. These coastal deposits form a stratigraphic sequence of shallow marine to beach sediments covered by calcite-cemented aeolian sediments, with the latter dominating in both thickness and spatial extent, sitting on a marly limestone base dating to the Miocene age. The shallow marine deposits found at the base of the late Pleistocene deposits are rich in biogenic material and marine shells. This marine depositis superimposed by a beach layer containing some fragments of broken shells. This layer is overlaid by carbonate rich coastal dunes (aeolianites) of lithified wind-blown, fine-to medium-grained, well-sorted sand. This is composed mainly of quartz and feldspar grains and a high percentage of shell fragments most probably a result of onshore transportation

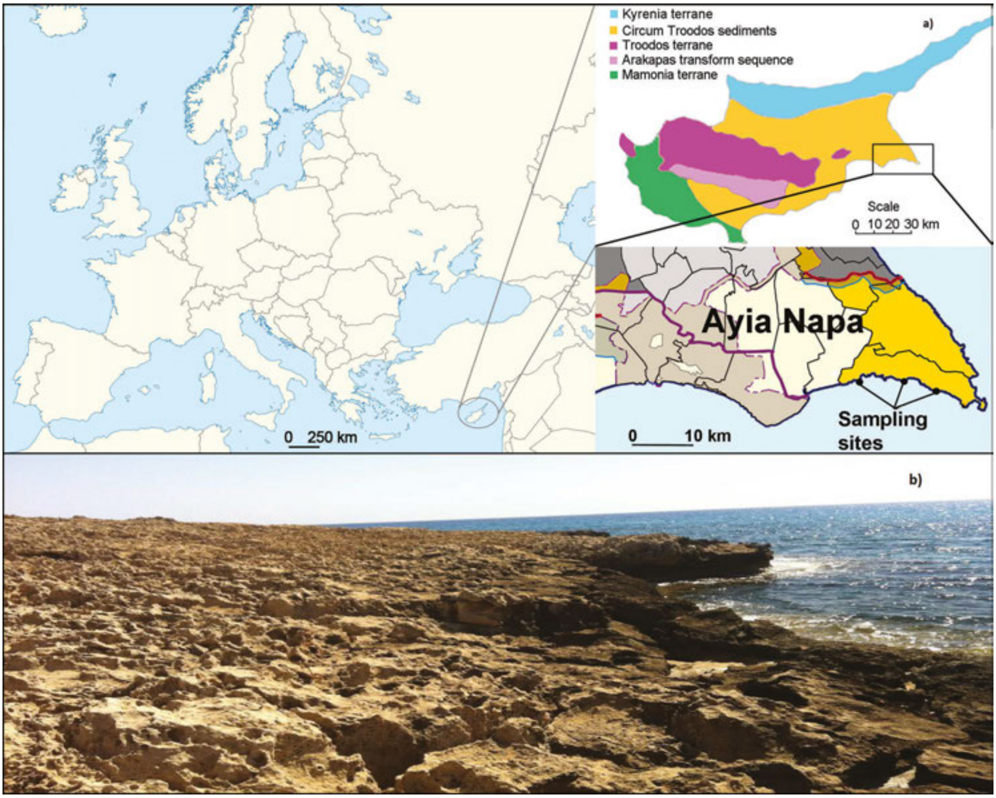

Figure 1. a) Sampling site of Agia Napa coastal deposits in south east Cyprus; b) Typical appearance of the aeolianites of the study area.

of marine-exposed fauna by prevailing south, south-west winds (McCallum 1989). Samples of the aeolianites and the underlying marine sediments that are preserved at Cape Greco and the greater area of Agia Napa were collected for luminescence dating and micromorphological analysis of their constituent quartz grains.

Methods

Sample preparation for luminescence dating

Due to the cemented nature of the deposits, sampling involved extraction of eleven rectangular blocks from specific areas of interest. Quartz and feldspar coarse-grains were prepared using the procedure of chemical treatment with 10% HCl to remove carbonate cements and 10% hydrogen peroxide to remove organic content, drying and sieving. Fractions were treated with hydrofluoric acid (40% and 10% for quartz and feldspar respectively) to avoid contribution of the alpha-irradiated outer part of the mineral, followed by a rinse with 10% HCl (to remove fluorosilicate by-products) and a final sieving to separate traces of any remnant byproducts. Purified quartz (treated with 40% hydrofluoric acid for 90 minutes to remove all other minerals) and feldspar (heavy liquid separation) fractions mainly fell in the range of 80-125μm and 200-250μm.

Luminescence measurements were performed using an automated Risø TL/OSL DA-15 luminescence reader. All samples were first prepared for luminescence dating using quartz: however, it was revealed that derived OSL ages of quartz were unexpectedly low, greatly deviating from the expected palaeo-environmental framework, and highly scattered, even though the standard validation tests were in most cases successful. We therefore decided to use feldspar grains to obtain "equivalent dose" (D_e) values that could be used to estimate accurate ages.

Quartz preparation for microtexture analysis

Aeolian samples collected for luminescence dating were also used for quartz surface textural analysis. In order for the quartz grains to be prepared for SEM analysis, steps to isolate feldspar grains which were used for luminescence dating were also undertaken for quartz, except the treatment with hydrofluoric acid as this would affect the minerals' surface. Quartz grains falling in the range of 80-125μm were taken for analysis. Grains were then placed on aluminum stubs and coated with carbon in a rotating vacuum evaporator. Quartz grains were examined and photographed with a SEM having first been verified by an EDS. Observations were based on both mechanical and chemical features displayed in quartz grains which enabled a description of their geological history. Images of surface textures of quartz grains were also acquired.

IRSL measurements

Since quartz could not be used for age calculations, the pIRIR protocol of feldspar (Thiel *et al.* 2011), shown schematically in **Table 1**, was applied. The dose response curve and the decay curve of one aliquot for $pIRIR_{290}$ are shown in **Figure 2**. These curves are representative for all the other samples measured. Prior to standard dating using the SAR procedure, validation of the protocol parameters was verified by a pre-heat plateau test (Murray and Wintle 2000) using different temperatures and a dose recovery test (Murray and Wintle 2003). A test to investigate the bleachability (Klasen *et al.* 2006) of the $pIRIR_{290}$ signal by natural light was further performed in one sample. A retained signal was observed

Step	Treatment
1	Give dose
2	Preheat, 60 s @ 320 ˚C
3	IR stimulation, 100 s @ 50 ˚C
4	IR stimulation, 100 s @ 290 ˚C
5	Give test dose
6	Cutheat, 60 s @ 320 ˚C
7	IR stimulation, 100 s @ 50 ˚C
8	IR stimulation, 100 s @ 290 ˚C
9	IR stimulation, 40 s @ 325 ˚C
10	Return to step 1

Table 1. pIRIR SAR protocol for coarse-grain feldspar measurements (after Thiel et al., 2011).

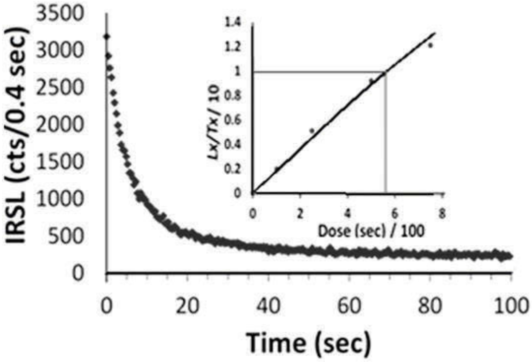

Figure 2. Decay and dose-response curve for an aliquot showing the $pIRIR_{290}$ signal from coarse grain (80-125μm) feldspars.

and this was subtracted from the derived D_e values of all other samples before age calculations. A fading test was also performed (Huntley and Lamothe 2001). A negligible g-value was obtained indicating that using this protocol, feldspar experiences no loss of signal. It is therefore secure to assume that D_e values derived by the $pIRIR_{290}$-SAR protocol are accurately calculated. Equivalent dose values were chosen for further analysis if they had (i) recycling ratios within 10% of unity, and (ii) thermal transfer <3% of the natural signal.

Dose rate relevant elements (external and internal) of the all samples were determined by ICP-MS and using the conversion factors of Adamiec and Aitken (1998). An internal alpha dose rate of 0.1 Gy/ka was also included in our calculations as suggested by Mejdahl (1987). Sediment moisture content was determined using present sediment moisture with an error of ±5%. The contribution from cosmic rays to the total dose rate was calculated using present day depth.

Results and Discussion

Luminescence ages

pIRIR ages were obtained from the ratio of the equivalent dose (D_e) accumulated in feldspars during the burial time of sediment material to environmental dose rate. pIRIR ages showed the existence of coastal sediment development during the Marine Isotope Stage 4 and 5 which are characterised by a prolonged sea level low transition from a high sea level. At one of our sampling points an exposed stratigraphic column shows that an aeolianite formation conformably superimposes the beach calcarenite which in turn overlies the shallow marine

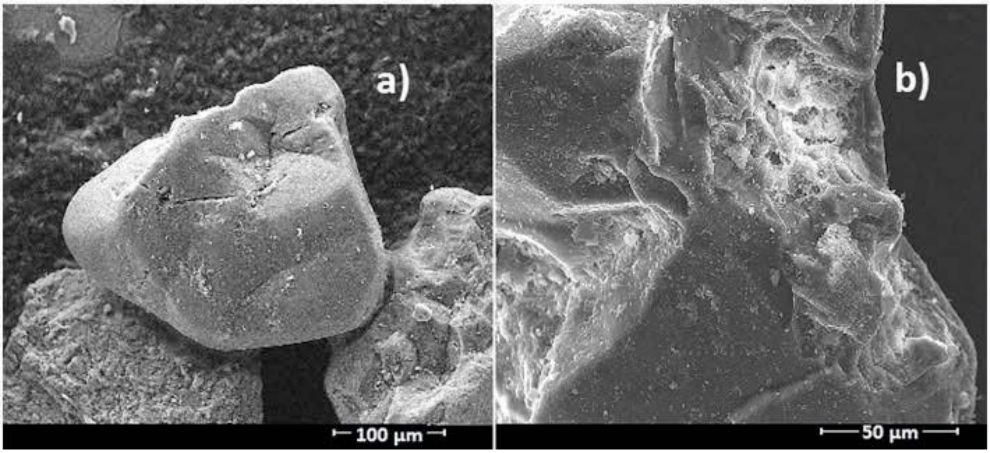

Figure 3. Quartz grains surface analysis of an aeolianite sample from Agia Napa, SE Cyprus. (a) a rounded quartz grain with some mechanical impact features; (b) Precipitation of silica in a depression.

deposits with pIRIR ages being in stratigraphic order, thus confirming their marine-aeolian association. Studies have shown that aeolianites may be formed during both sea-level highstands (e.g., Murray-Wallace *et al.* 1998, 2010) and lowstands (Porat and Wintle 1995; Engelmann *et al.* 2001; Frechen *et al.* 2001). Geochronological studies in the eastern Mediterranean have assigned aeolianites and underlying littoral deposits within the late Pleistocene, mainly during several episodes in the time interval of the MIS 2, 3, 4 and 5 (e.g. Porat and Wintle 1995; Engelmann *et al.* 2001; Frechen et al. 2001; 2002; Athanassas and Zacharias 2010; Elmejdoub *et al.* 2011). Our dating results are in good agreement with these studies, in a common late Pleistocene geochronological framework.

Quartz surface microtextures

The rounded and sub-rounded shape of quartz grains of the late Quaternary aeolianites suggest that they have been transported over long distances (**Fig. 3a**). Deeply marked fractures indicate friction caused in a high energy environment. Furthermore, silica accumulation can be seen inside some abrasion marks (**Fig. 3b**), implying that quartz grains have been passed through a moderate energy environment (Chakroun *et al.* 2009) of wet/dry saline and carbonate conditions.

Conclusions

Little has been done so far to study the Quaternary history of the Cypriot coastal deposits based on numerical ages and surface textures of quartz grains. Our luminescence dating estimations indicate that the formation of the dated coastal dune in SE Cyprus took place during the MIS 4 and 5 when the sea-level was lower than its present position and most probably under a dominant southwesterly wind regime. The coastal deposits in this area are the first to be dated using luminescence signals from feldspar.

Despite this, our chronological results do not include any periods when prehistoric people were present on the island: the strategic position of Cyprus between Africa and Europe/Asia nevertheless makes the establishment of a reliable geochronological framework an important tool to be used by geoarchaeologists and geomorphologists for a better understanding of the Palaeolithic landscape and human evolution of the greater area of eastern Mediterranean.

The examination of the quartz surfaces revealed the presence of mechanical impacts of events which can be used to decipher the coastal palaeo-environmental history of the area. Quartz surface analysis of the dated aeolianites showed that a number of distinctive set of quartz surface features exist. The shape of the quartz grains, as well as the surface marks indicate that the late Pleistocene aeolian deposits of the area are the result of cycles of transportation and deposition through different sedimentary environments, most probably a combination of marine deposition and subaerial exposure. A more systematic application of luminescence dating as well as quartz grains microtextural analysis is required in order to provide further insight into the late Quaternary geomorphological history of the study area.

Acknowledgements

The research was conducted as part of the project entitled "Luminescence dating and the Palaeo-environment in SE Cyprus" undertaken by the author under the supervision of Dr. Yannis Bassiakos within the framework of the NARNIA (New Archaeological Research Network for Integrating Approaches to ancient material studies) Project. NARNIA is a Marie Curie Initial Training Network which is funded by the FP7 and the European Union (Grant agreement no.: 265010). For more information please visit the NARNIA website: http://narnia-itn.eu/.

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WORK PACKAGE 7

HHpXRF application in archaeology

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HHpXRF application in archaeology

Work Package 7 was led by Dr Roger Doonan of the University of Sheffield. WP7 focuses on evaluating the potential of a new generation of analytical equipment, HHpXRF, for archaeological science. The work package had undertaken a number of novel studies and overseen the publication of review and method papers on how HHpXRF may be best employed within archaeological science. As part of the WP studies have been undertaken across the network and have established best practice for obsidian, metals and soils with explorations of other materials including glass, and architectural materials.

WP7 worked closely with SME NITON UK in establishing methods, applications and calibrations and also co-organised a very successful training event. In total two training events (the UK one comprised 2 parts) were organized both in the UK and Cyprus. The UK training event looked at background and instrumentation and then advanced application and use while the Cyprus field school looked at the developed of in-situ method and application for site survey. The UK training school engaged a number of academics from across the NARNIA network. There remain a number of publications outstanding from the work package that will be published in the coming months.

WP7 was the smallest work package with one ER3 Dr Ellery Frahm. Despite the small size the package has achieved a good record of training and publication with a number of fellows making use of their training across the network.

Dr Roger Doonan
Work Package 7 leader
University of Sheffield

KEEPING UP WITH THE EXCAVATIONS: RAPID OBSIDIAN SOURCING IN THE FIELD WITH PORTABLE XRF

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Abstract

Work Package 7 of NARNIA, *Portable XRF Applications in Archaeology*, had an objective of contrasting applications in the field with those in laboratory/museum settings and establishing effective means of field-based analyses. Portable XRF (pXRF) is a means to bring traditionally lab-based studies into the field, and it allows archaeologists to collaborate on-site with colleagues who might otherwise conduct their research off-site. This technology permits us to analyse many more artefacts or samples faster and non-destructively, and those chosen for study can be affected less by export limitations and more by the intellectual framework within which the research was conceived. Ultimately, pXRF enables new (or previously cost- and/or time-prohibitive) research designs. Tasked with teaching and research involving a broad range of archaeological materials, the broad remit of Work Package 7 can be summarised as "work where we couldn't work before, answer what we couldn't answer before." In other words, a core objective was to shift chemical analyses from the realm of "white lab coats" in controlled settings to "muddy boots" in the field. A particular goal was to source obsidian artefacts as they are unearthed at archaeological sites, enabling new research frameworks and informing excavation strategies and interpretations in the field. The setting for this research was Armenia, one of the most obsidian-rich natural and cultural landscapes in the world. I developed two methods to source artefacts on-site in only 10 seconds, including automatic source identification calculated in real-time.

Introduction

Armenia has more than a dozen obsidian-bearing volcanic centres, resulting in one of the most obsidian-rich landscapes in the world. At numerous sites, obsidian composes the majority, if not entirety, of lithic assemblages. During excavations of Lusakert Cave 1 (Adler *et al.* 2012), the Hrazdan Gorge Palaeolithic Project recovered, on average, 470 obsidian artefacts each day. During the 2012 season, I analysed more than 1400 Lusakert artefacts using portable X-ray fluorescence (pXRF). This paper focuses on method development that arose out of that work, specifically a desire to have obsidian sourcing insights immediately available on-site during excavations or surveys. The resulting methods will become routine components of our excavation toolkit and site survey techniques (Frahm *et al.* 2014a).

Moving pXRF from the field house into the field had not previously occurred in obsidian sourcing research. Thus far, pXRF-based studies have been restricted to laboratories, museums, storehouses, and other similar settings (e.g., the Smithsonian's Museum Conservation Institute, Phillips and Speakman 2009; Field Museum of Natural History's Elemental Analysis Facility in Golitko *et al.* 2010). For Craig *et al.* (2007), "*in situ* analysis" refers to "where the artefacts are stored." When sourced, these artefacts are distantly detached from their archaeological contexts. For example, Forster and Grave (2012) used pXRF at an Australian museum to source 26 Near Eastern artefacts excavated decades earlier. Researchers are using ruggedized, battery-powered analysers capable of handheld operation and designed for field use (e.g., geological exploration), but obsidian sourcing has remained firmly entrenched in post-excavation activities and has been rarely, if ever, conducted at archaeological sites. My aim was to shift sourcing from the realm of "white lab coats" in controlled settings to "muddy boots" in the field.

The time for each measurement is, I maintain, a critical factor in the uptake of field-based sourcing. Most recent studies use measurements of 2–6 minutes. The most common duration is 5 minutes, corresponding to 10–12 artefacts per hour. Excavations at Lusakert Cave 1, however, recovered 70–80 artefacts per hour on average. This implies a need for 45-second measurements, but the goal of 10 seconds meant analyses could become incorporated into excavation activities. My aim was that, after 10 seconds, the instrument's screen would display an artefact's source so excavators and surveyors could have immediate feedback. Tests using geological specimens and artefacts established the efficacy of the two methods that I discuss here.

Sourcing at excavations and on surveys

Obsidian sourcing at an archaeological site might result in information that can inform the excavation strategy. Recognising a change in source-use as artefacts are unearthed could effect , for example, how one approaches the lithic scatter, samples the stratum for dating or small finds, or interprets associated features. This information at a later date is useful but disconnected from the excavation process and field interpretations. For example, on-site sourcing would lend itself to investigations involving the integrity of "living floors." At Gatecliff Rockshelter in the North American Great Basin, for instance, excavation strategies changed in light of suspected living floors (Kelly and Thomas 2012: 86–88). When an artefact horizon was encountered, the vertical excavation strategy changed to a horizontal one, opening large areas and paying additional attention to small finds and their surrounding sediments. Geological source is one tangible aspect of obsidian artefacts often not apparent in the field, so on-site sourcing may yield insights when such information would be relevant during excavations.

Obsidian sourcing during a site survey may provide insights into settlement type, resource management, and other patterns that could affect documentation and interpretation. The spatial distributions of obsidians at a site could also influence test pit locations or reveal the existence of activity areas. Comparing artefacts from the surface and strata of a test pit would add a temporal dimension, and correlating sources with artefact typology may reveal shifts in mobility over time. At numerous open-air Palaeolithic sites in Armenia, little more is preserved than, in some cases, millions of obsidian artefacts. A team with several pXRF instruments could study such sites with the methods discussed here and yield behaviourally meaningful interpretations.

Instrument, artefacts, and specimens

This study used a Niton XL3t GOLDD+ instrument with a silicon drift detector, which can attain the same precision 2–10 times faster than the older detectors used in previous studies. More than 500 Armenian obsidian specimens, most of which I collected, and 154 artefacts from Lower Palaeolithic Nor Geghi 1 and Middle Palaeolithic Lusakert Cave 1 were analysed for these tests. All had been previously characterised with pXRF using more conventional procedures, including fundamental parameters (FP) correction and linear-regression calibrations based on 24 obsidians analysed using multiple techniques (i.e., Neutron Activation Analysis (NAA) and XRF at the University of Missouri Research Reactor and electron microprobe analysis at the University of Minnesota).

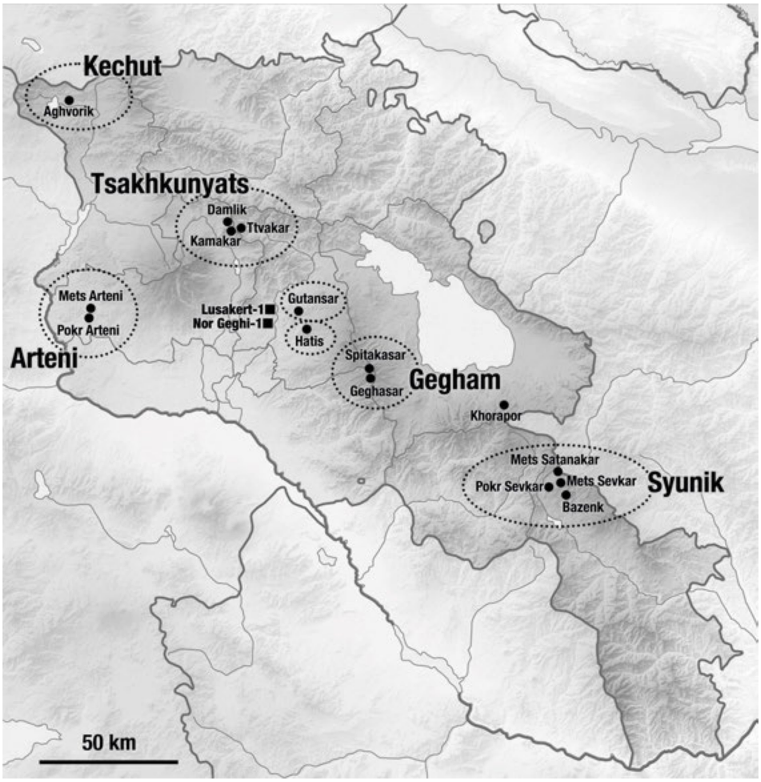

Figure 1. Armenian sites (squares), obsidian sources (dots), and source complexes (dashed ovals) in this study. Digital elevation data: Shuttle Radar Topography Mission.

Method 1: Spectrum matching

One frequent use of pXRF is automatic identification of metal alloys in 3–5 seconds. The analyser's software compares a measured spectrum to a library of hundreds of alloys and metal grades, and the built-in LCD screen shows the closest statistical matches. The same algorithms can be used with other materials and custom libraries. This is known as *Spectral Fingerprint* mode in the Niton software. First, one records spectra from a series of reference materials and creates a custom library. Then, when analysing a specimen, the software uses Pearson's χ^2 test to calculate goodness of fit between a measured spectrum and those in the library. Specifically, the X-ray intensities of 24 elements are used to calculate the mean squared distance between the values from the specimen and each reference. As soon as one begins analysing a specimen, the screen displays the best matches and corresponding χ^2 values (**Fig. 2**).

The principal drawback of this method is that, to simplify the real-time χ^2 calculations, raw X-ray intensities are not converted into elemental concentrations. Nevertheless, this method is quantitative, not qualitative, because all X-ray intensities are recorded, statistically matched, and downloadable as a spreadsheet for documentation and additional statistical analysis. If possible, of course, pXRF measurements should be compatible with elemental data acquired by stationary analytical instruments in archaeometric labs (*cf.* Frahm 2014). For this specialised application, however, it is worth considering a method based on X-ray intensities because rapidly identifying the correct sources was considered paramount.

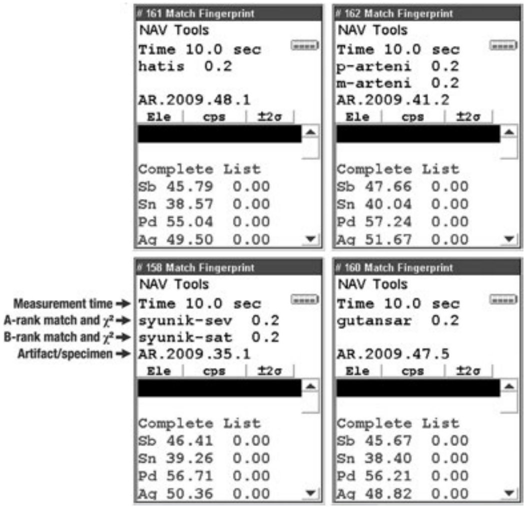

Figure 2. The pXRF instrument's screen displays the best matching sources (and their χ^2 values) after 10 seconds using the *Spectral Fingerprints* method.

For this study, the software was "taught" the spectra from twelve obsidian sources (**Fig. 1**; Pokr and Mets Sevkar were grouped as Syunik-1, Mets Satanakar and Bazenk as Syunik-2). Each source was represented by a polished specimen analysed with NAA, XRF, and EMPA. To assess the method, first, 459 obsidian specimens from these twelve sources were analysed for 10 seconds. All were measured on unprepared surfaces, varying from smooth flake scars to highly weathered exteriors. Second, 154 Palaeolithic artefacts from Nor Geghi 1 and Lusakert Cave 1 were measured for 10 seconds, and the waterproof instrument was used entirely as it would be in the field: handheld operation without a laptop or test stand. Analyses were conducted outside in weather conditions that varied from direct sunlight to light rain showers.

Of the 459 Armenian specimens, just seven were misidentified. Five specimens from Mets Arteni were matched to Pokr Arteni, just 3 km away (with Mets Arteni as close B-rank matches). Just one Syunik-1 specimen was matched to the Syunik-2 source, and vice versa. Generally the artefacts had higher χ^2 values than the geological specimens. This is likely due to a combination of the artefacts' weathered surfaces as well as handheld operation adding small geometric errors. Nevertheless, all 154 artefacts were matched to the correct volcanic sources.

Method 2: Discriminant functions

pXRF is often used to test consumer products for compliance with regulatory limits. For example, the software can be used with pass/fail criteria for the European Union's Restriction of Hazardous Substances Directive. Lead above 1000 ppm, for example, is prohibited. A reading over 1300 ppm, results in the measurement highlighted in red to mark a "fail." Below 700 ppm, a green "pass" results. A yellow "inconclusive" indication results if a measurement falls in the intermediate range. Custom pass/fail thresholds can be similarly set for any element.

The Niton software also allows calculation of pseudo-elements. For example, a geologist may be more interested in the CuO-to-NiO ratio in an outcrop than the actual Cu and Ni content. The software can calculate a pseudo-element that is defined as (Cu × 1.252) / (Ni × 1.273) and display the result onscreen. If the geologist is interested in recognising outcrops above a certain ratio, pass/fail thresholds can be defined (based on quantitative elemental data). Fortunately, the arithmetical operations permitted to calculate pseudo-elements are compatible with discriminant functions, which define axes that best discern groups in high dimensions.

Thus, I derived discriminant functions to best discern Armenian obsidians, entered them as pseudo-elements, and calculated thresholds for six obsidian source complexes (**Fig. 1**). Five elements defined the functions: Zr, Sr, Rb, Nb, and Fe. These five elements' concentrations can differ by three orders of magnitude among sources, and elements in the "mid-Z" portion of the periodic table are particularly well measured with XRF. In addition, the elements are measured with a single X-ray filter and, therefore, can be simultaneously quantified. In many prior studies, the measurement time includes the use of multiple X-ray filters inside the instrument to measure different parts of the spectrum. For example, 90-second measurements in Frahm *et al.* (2014b) were two sequential 45-second measurements. Thus, one way to markedly reduce measurement times is to focus exclusively on elements measured well with one filter.

The relationship between measurement time and its uncertainty is not linear. Uncertainty is inversely proportional to the square root of the X-ray counts and, therefore, measurement time. **Figure 3** shows the results of empirical tests regarding this relationship for the elements at hand. For all five, uncertainties are below 10% (at the 2σ-level) after only 10 seconds. In fact, for Sr and Rb, the uncertainty is 6%, and for Zr and Fe, it is 4%. Accordingly, after a mere 10 seconds, the five elements of interest have uncertainties comparable to NAA data.

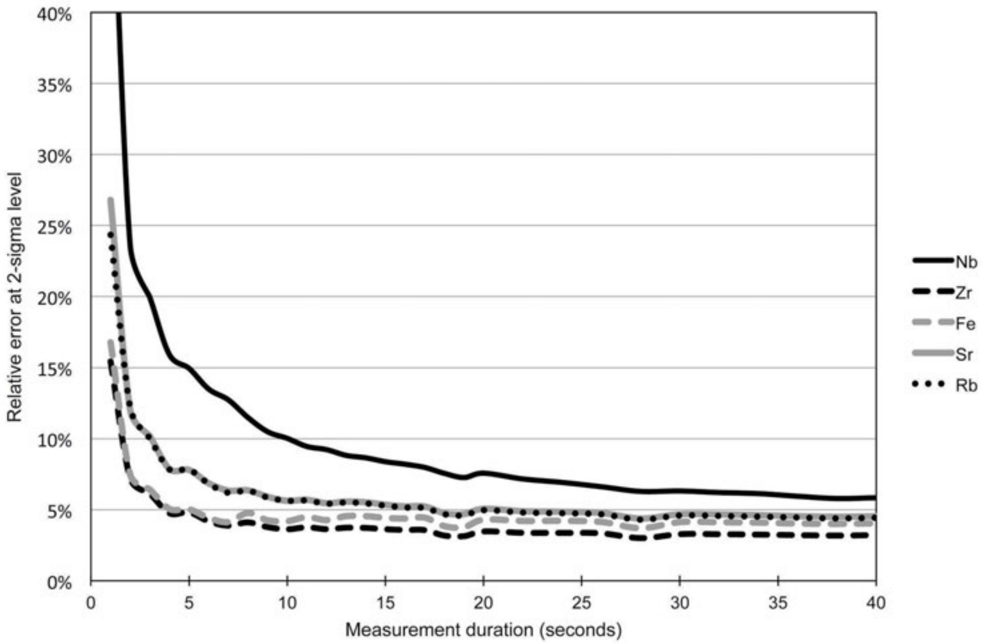

Figure 3. The inverse square relationship between measurement uncertainty and time for Zr, Sr, Rb, Nb, and Fe. Gutansar obsidian was measured for durations from 1–40 seconds.

Three discriminant functions were derived from 1800 analyses of obsidian specimens from six source complexes (**Fig. 1**). The software is currently limited to a maximum of 15 pseudo-elements, so defining sources using two to three discriminant functions restricted this test to just five to seven sources. Therefore, as a concession for elemental data, the distinction between, for example, Pokr and Mets Arteni obsidians would not be evident using this precise configuration. Later data analyses, however, could discern them, as could new functions.

Each obsidian source complex was defined by the first two or all three functions as pseudo-elements, and pass/fail thresholds were based on earlier analyses of geological specimens. Each set of thresholds defined the "intermediate" range for a particular complex. When the value for a discriminant function (as a pseudo-element) falls in that range for some complex, it turns yellow onscreen. Too low a value is green, while too high is red. When the two or three functions that define a complex display yellow values onscreen, there is a match (**Fig. 4**).

To assess this method, first, 467 geological specimens from the six source complexes were analysed three times each for 10 seconds. All measurements were conducted using the

FP-based "mining" mode. Conditions were otherwise the same as the first method. Of the 1391 analyses, only one analysis of a Gutansar specimen yielded no match; however, the elemental data were readily matched to the correct volcano. All other analyses matched the correct source complex. Second, the 154 artefacts were measured once each for 10 seconds. Again the instrument was operated in handheld mode outdoors. All but two artefacts had matches, and all 152 matches were correct. Two Gutansar artefacts had no match; however, like the geological specimen, the elemental data were still readily matched to the correct volcanic source.

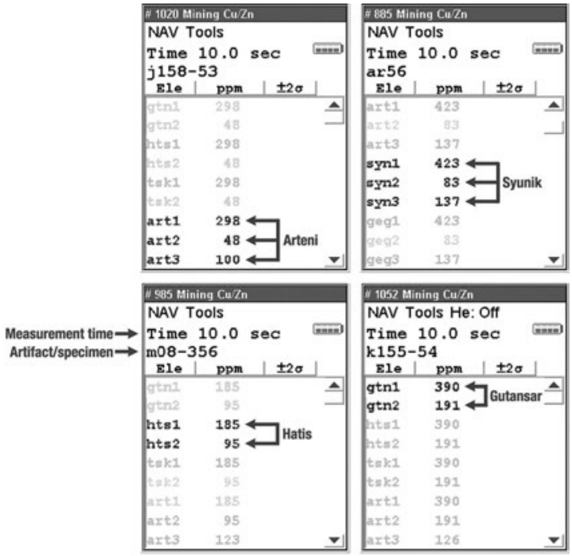

Figure 4. The pXRF instrument's screen displays the matching source complex after 10 seconds with the discriminant analysis method. Gutansar and Hatis are each defined by two discriminant functions, whereas Arteni and Syunik are defined by all three.

Concluding remarks

Here I discuss two methods of sourcing obsidian artefacts in 10 seconds while in the field. Tests of geological specimens and artefacts reveal the validity and reliability of both methods. In fact, the methods are so effective that neither is evidently superior. A preference for either fully quantitative elemental data or more exact source identification could, in a particular instance, be a deciding factor. The two methods are sufficiently rapid that they could be used together. At a site where one obsidian source dominates, for example, any exotics could be recognised with the *Spectral Fingerprint* method and then retested with the discriminant method.

These two methods were not developed with the aim of supplanting conventional sourcing procedures in the field house (using pXRF) or laboratory (using stationary instruments). Instead, these methods are meant to provide archaeologists with observations hitherto unavailable in the field and to optimise scarce resources (e.g., time, money).

Development involved considerable foundational work, including source surveys, sampling, and characterisation, as well as analyses of more than 500 geological specimens and 1700 artefacts. Therefore, these methods depend on, rather than replace, traditional approaches to sourcing obsidian artefacts.

Regarding chert artefact sourcing, Luedtke (1992:117) argued that a "good source analysis is usually complex and expensive, and should not be initiated merely as a fishing expedition in the vague hope that you might find something interesting." Some might view on-site sourcing as a fishing expedition. There are two responses to such criticism. First, the work discussed here is based on *a priori* knowledge of Armenian obsidian sources and their use during the Palaeolithic. During this work, which included sourcing artefacts excavated or collected on surveys mere days earlier, the desirability of this information in the field became evident. For example, by the time recently excavated artefacts were sourced, a chance for specialised sampling of their contexts, if so desired, had passed. Second, pXRF can source artefacts rapidly and inexpensively. Thus, few resources need be committed to targeted, speculative modes of inquiry. With lower financial and time constraints, we can pursue, for example, the use of obsidian sourcing to explore the spatial organisation of sites with high spatial resolution.

Portable XRF permits obsidian sourcing and other chemical analyses to be displaced from the setting of "white lab coats" to that of "muddy boots." Thus, it is a facilitating technology and eliminates physical and temporal barriers that have previously segregated archaeological practice between the field and the distant laboratory, that is, the traditional context of obsidian sourcing and other analytical studies. Portable instruments can bring field and lab practices together in a shared context. Observations regarding the origins of obsidian artefacts, hitherto available only after the artefacts have been distantly separated from their archaeological contexts, can be made on-site, offering archaeologists nearly immediate results.

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