History, Technology and Conservation of Ancient Metal, Glasses and Enamels

International Symposium

Program and Abstracts

November 16-19, 2011, Athens, Greece

Cotsen Hall, The American School of Classical Studies at Athens

Organised by
N.C.S.R. “Demokritos”, Athens
School of Chemical Engineering, N.T.U.A., Athens

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History, Technology and Conservation of Ancient Metal, Glasses and Enamels

Scientific Program

	Wednesday 16-11-2011	
17:00-18:30	Registration and Reception meeting at the Cotsen Hall	
18:30-18:40	**Opening of the Symposium**	G. Kordas (Chairman)
18:40-18:50	Welcome address	N. Kanellopoulos President of N.C.S.R. “Demokritos”
18:50-19:20	***Aspects on the role of metals, glasses and enamels in the Greek prehistory and antiquity***	P. Themelis ***(invited)***
19:20-19:50	***Self-healing coating as a way to extend life of metallic materials***	M. Zheludkevich ***(invited)***

	Thursday 17-11-2011	
	History and Technology of Metals	
09:00-09:10	Introduction in the Metals Session	Y. Bassiakos
09:10-09:40	***The rapid development in making iron clamps for the erection of the archaic and classical temples***	G. Varoufakis ***(invited)***
09:40-10:00	Manufacturing experiments with Minoan double axes and chisels	M. Lowe Fri
10:00-10:20	Analytical Investigation of the Lead Finds from the Mycenaean Settlement and Cemetery of Lazarides on the Island of Aegina (Greece)	P. Polychronakou-Sgouritsa, C. Tselios, Y. Bassiakos
10:20-10:40	Object life circles and the study of ancient metals: theories, methods and limitations	A. Brunno, M. Kostoglou
10:40-11:10	**Coffee break**	
	History and Technology of Metals	
11:10-11:40	Votive metal zoomorphic small objects from the pan-Rhodian sanctuary of Zeus Atavyrios	P. Triantafyllidis
11:40-12:00	Archaeometallurgy in the Levant: Past, present and some thoughts about the future	S. Shalev
12:00-12:20	Greek Geometric waxwork –A new research on Bronze tripod cauldrons	M. Kiderlen , H. Born
12:20-12:40	Characteristic metallurgical relations and qualities of the iron clamps of the Epikourios Apollo	G. Dasargiry
12:40-13:00	Early Byzantine metal workshops in a settlement near Saint Catherine’s Monastry (Mount Sinai, Egypt)	D. Mourelatos , A. Hein
13:00-13:20	The Metallurgical Investigation of Copper-Alloys Metalwork of the Benaki Museum Dated in the 4^{th}-7^{th} Centuries A.D.	D. Kotzamani, A. Phoca, G. Karydi, M. Zaxaria,V. Kantarelou G. Karatasios, S. C. Boyatzis, V. Perdikatsis
13:20-14:30	**Lunch break**	
14:30-16:00	**Poster Session**	

	Thursday 17-11-2011	
	<u>Studies on Conservation and Authentication of Metals</u>	
16:00-16:30	***From excavation to exhibition –The conservation project at Aiani Museum***	M. Lykiardopoulou-Petrou **(invited)**
16:30-17:00	***Electrochemistry and surface analysis to prevent deterioration of Heritage artifacts***	M. F. Montemor **(invited)**
17:00-17:20	Iron weapons and armour from Macedonian graves	P. Faklaris
17:20-17:40	Cleaning of sulphidae from silver and gilt silver threads in silk textiles using laser in the visual and UV range	B. Taarnskov, P. Pouli
17:40-18:00	The Derveni board game revisited	E. Kotoula, D. Ignatiadou, G. Earl
18:00-18:20	**Coffee break**	
18:20-18:40	Corrosion of archaeological bronze in non-hostile burial environment	A. Siatou, A. Lekatou, D. Sioulas
18:40-19:00	Lead clamps for repairing clay pots from the acropolis of Vergina	V. Stamatopoulou
20:30	**Gala Dinner**	

	Friday 18-11-2011	
	Hyalos-Vitrum-Glass	
9:00-9:30	***Glass Votive Offerings in the Great Rhodian Sanctuaries***	P. Triantafyllidis ***(invited)***
9:30-9:50	Glass of Amenhotep II from Tomb KV55 in the Valley of the Kings	C. M. Jackson, P. T. Nicholson
9:50-10:10	Lefkandi's vitreous beads at the beginning of a new tradition of vitreous materials in the Aegean	G. Nightingale
10:10-10:30	Investigation of ancient glass beads by means of macroscopical and microscopical observations	K. Beltsios, A. Oikonomou, N. Zacharias, P. Triantafyllidis
10:30-11:00	**Coffee break**	
11:00-11:30	***Glass working in Roman and Early Christian Thessaloniki: Older and more recent finds***	A. C. Antonaras ***(invited)***
11:30-11:50	Early Byzantine Glass from Eleutherna Pyrgi (Sector II)	N. Coutsinas
11:50-12:10	Roman glass as the ritual object and its iconography	J. Dolezalova
12:10-12:30	Raman spectrometry investigation and identification for natural and ancient glasses	Th. Katsaros and Th.Ganetsos
12:30-12:50	Evaluation of archaeological glass samples from the archaeological site of Vergina via a combination of analytical techniques (μ-XRF, ICP-AES, AAS)and subsequent statistical analysis	C. G. Makarona S. A. Drougou, N. C. Tsirliganis, J. A. Stratis
12:50-14:30	**Lunch Break**	

	Friday 18-11-2011	
	Hyalos-Vitrum-Glass	
14:30-14:50	Archaeological glass weathering and resulting implications to analytical glass studies	M. Kaparou, N. Zacharias, J. Murphy
14:50-15:10	Preliminary study of Mycenaean glass finds from S.W. Peloponnese Sites	G. Mastrotheodoros, K. G. Beltsios, N. Zacharias, X. Arapogianni
15:10-15:30	A preliminary study of Roman glass fragments from Thessaloniki agora	N. P. Kalogiouri I. Nazlis, D. Ignatiadou, J. A. Stratis
15:30-15:50	$\delta^{18}O$ and chemical measurements of Greek Roman glass	A. Longinelli, E. Dotsika, A. Silvestri, B. Raco, D. Poutoukis, D. Ignatiadou, E. Iliadis
15:50-16:10	The use of optical absorption spectroscopy for the study of ancient glass	A. Ceglia, W. Meulebroeck, K. Baert, K. Nys, H. Thienpont, H. Terryn
16:10-16:30	**Coffee Break**	
16:30-16:50	Chemistry, Structural and Technological Examination of a Greek Glass Archaeological Collection Spanning from the Mycenaean to Roman Period probed by SEM/EDS, IR and Raman Spectroscopy	D. Möncke, D. Palles, N. Zacharias, M. Kaparou, M.Papageorgiou, E. I. Kamitsos, L. Wondraczek, A. Oikonomou
16:50-17:10	Glass gaming pieces from the Viking-age early urban centre Gnezdovo	N. Eniosova, T. Pushkina, E. Stolyarova
17:10-17:30	A Provenance Study of Cypriot Byzantine Glazed Pottery and Ceramic Tripod Stilts	Charalambous A.C., Charalambous E.N., Kantiranis N.A, Stratis J.A.
17:30-18:40	**Closing of the scientific part of the Symposium**	G. Kordas (Chairman)

	Saturday 19 November 2011	
11:00-13:00	Guided visit at the New Acropolis Museum	
13:00-14:00	**Lunch Break**	
14:00-19:30	Guided excursion to the archaeometallurgical area of Laurion (departure from the New Acropolis Museum)	

	Thursday 17-11-2011	
14:30-16:00	**Poster Session**	
	1. The Aegean type Sword found at Hattusas, Silver as rare metal and the written Sources, Contribute to the dating of Trojan War?	K. Giannakos
	2. Study, Analysis and Conservation of the Roman water lead pipe in “Aeolus” excavation, Plaka, Athens	P.Pitsiri, D. Sourlas, S. C. Boyatzis, S. Golfomitsou, T. Karabotsos
	3. A contribution to the galvanic coupling cleaning of tarnished silver	V. K. Gouda, A.M. Awad
	4. Analytical and Technological Examination of Two Bronze Vessels of the Archaic Period from Boeotia, Greece	D. Oikonomou, V. Aravantinos, E. Zimmi, Y. Bassiakos
	5. What are we really analyzing? The peculiar story of Middle Bronze Age II battle-axes from the Southern Levant	S. Shalev, E. N. Caspi,S. Shilstein, A. M. Paradowska,W. D. Kockelman, Y. Levy
	6. Evaluation of three cleaning methods applied on Cl-rich patinas of two bronzes	O. Papadopoulou, J. Novakovic, P. Vassiliou, E. Filippaki, Y. Bassiakos, C. L. Xaplanteris, A. Giatsidou, M. Mariaki
	7. The zinc content of copper alloys as a criterion in authenticating ancient metallic objects	S. Protopapas, K. Polikreti, R. Proskynitopoulou, G. Kouros
	8. Metallographic evidences of bronze casting working conditions at Moscow-Volga region during Early Iron Age	I. Saprykina
	9. Eco-friendly protection methods for ancient metallic artifacts	S. Grassini, E. Angelini, G. M. Ingo, M. Parvis, P. Vassiliou
	10. Corrosion processes on ancient coins as indicators of authenticity	E. Angelini, T. De Caro, F.Faraldi, S.Grassini, G. M. Ingo , C. Riccucci, P. Vassiliou

	11. Some considerations regarding the Glass Vessels from the East-Carpathian Dacian settlements (2nd century B.C. – 2nd century A.D.)	C. Chiriac, S.P. Botan
	12. The discovery of cobalt colourant raw materials as inclusions within Anglo-Saxon glass beads	A. S. Meek, S. Marzinzik
	13. Islamic Glass of X – XV cc in Eastern Europe	S. Valiulina
	14. A glass-making technology study used in Amathouda (Cyprus), 5^{th} - 6^{th} century A.D. by Micro X-ray Fluorescence Spectroscopy (μ-XRF), Inductively Coupled Plasma Emission Spectroscopy (ICP-AES), Flame Atomic Emission Spectroscopy (FAES)	J. A. Stratis, G. L. Tzebrailidou, A. C. Charalambous, E. N. Charalambous, N. C. Tsirliganis
	15. Technological change or consistency: strontium isotope analysis of Egyptian faience from the Middle Kingdom to the New Kingdom	E. A. Hammerle, J. Evans
	16. A radioactive shamanic apron: analysis and conservation	A. S. Meek, R. Swift, N. Rode, A. Komlosy
	17. The influence of dewatering and carbonating on the strength of lime and cement mortars	A. El-Turki

SESSION 1
METALS

Corrosion processes on ancient coins as indicators of authenticity

E. Angelini[1], T. De Caro[2], F. Faraldi[1], S. Grassini[1], G. M. Ingo[2], C. Riccucci[2], P. Vassiliou[3]
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The problem of counterfeit of works of art occupies a central place in the management of Cultural Heritage for its implications on art history and for the legal implications that derive from the origin and trade of artefacts. The relevant international trade in art works, through auction houses and antiquarians, requires, in order to protect both buyers and sellers, an objective survey to certify the authenticity of the objects. The problem is very sensitive in the field of metal artifacts, with special attention to jewelry and coins, the latter representing a particularly fruitful investment for forgers. The assessment of the originality of an artefact is made, in most cases, by means of macroscopic analysis based on experts advices, while the collection of micromorphological, microchemical and microstructural data may help in defining a sort of fingerprint of the artefact and may help in distinguish between original objects, ancient or modern counterfeits. Examples of counterfeited coins of ancient Roman and Phoenician-Punic ages, and of Italian Kingdom of late XIX century, characterized by means of different analytical techniques such as optical microscopy (OM), electron microscopy equipped with microprobe (SEM + EDS), X-ray diffraction (XRD), X-ray fluorescence (XRF), are presented. With the use of the simple optical microscopy (OM), only fakes macroscopically different from the original ones can be distinguished. If counterfeiting is more accurate, deeper analyses should be carried out by means of the other analytical techniques mentioned above. The physical and chemical parameters to be determined are mainly the chemical composition and surface structure micro-morphology of the artifacts, result of the production techniques of metals or alloy and of the long-lasting interaction with the environment, air, water, soil. As a matter of fact, the techniques of production of metals used in antiquity, although comparable with modern ones, may originate differences with respect to the chemical composition and the microstructure of the metallic material. Furthermore ancient artifacts, due to aging and long-lasting burial in soil, have developed patinas whose kinetic and nature may differ substantially from the corrosion products obtained by accelerated aging procedures or with the employment of specific chemicals for patination. Therefore, the presence of

Fig. 1 Counterfeited Adrano's coin

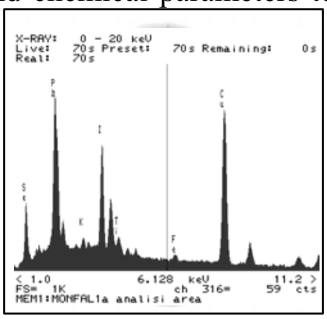

Fig. 2 – SEM+EDS analysis of the surface of the Adrano's coin

silicates, phosphates, carbonates, lower oxidation numbers oxides may indicate the establishment of a slow process of interaction between the artefact and the environment, and may be considered as an index of authenticity.

On the contrary, the presence on the surface of artefacts coming from archaeological excavations, of chemical compounds containing sulphates or, for example, selenium, element unknown to ancient metallurgists, may be considered as an index of counterfeiting actions. As an example, Fig.1 shows the optical image of a modern reproduction of an Adrano's coin of the third century BC, whose patina contains noteworthy amounts of selenium as clearly evidenced by the SEM+EDS analysis of the artefact's surface, shown in Fig. 2.

The identification of reliable microchemical, micromorphological and microstructural parameters that characterize original and counterfeited metallic artefacts, provides the basis for creating a database containing the most typical and relevant chemical and physical information that can help to define the authenticity of metallic artefacts.

Object life circles and the study of ancient metals: theories, methods and limitations

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The goals and results of any comprehensive study of ancient metals are as diverse as the range of their application. Aspects of ancient metal studies range from the history of technology, to the study manufacturing techniques, to the economic and social dynamics of prehistoric metalwork, and to the ritual significance of particular treatments of the surface of objects to name but a few. Nevertheless, these studies often exist in isolation and they rarely employ holistic methodologies. The aim of this paper is to demonstrate that any research project designed to understand the social significance and meanings of historic metal objects should be developed by employing a different range of methodologies and tools and a solid archaeological context. In other words, we aim at answering the question: how a researcher extrapolates cultural meanings from a series of observations and scientific results?

Typological analysis usually fails in recognizing different stages within the use-life of metal objects (i.e. shape and use of objects altered and modified through time), which participate actively to social transformations, bearing signs and marks of their involvement; signs and marks contribute to personalize a given artifact against the class of objects it is supposed to belong to. Accordingly, edge-wear studies can reasonably help archaeologists to understand different stages in the artifact biographies. Systematic studies regarding edge-wear studies revolve predominantly around the treatment of the surface of the objects. One of the first problems the archaeologist may encounter when dealing with edge-wear examinations is the interpretation of the traces as in most of the cases their integrity is affected by heavy corrosion and post-depositional processes. Equally, the chemical composition of the soils is determinant in the process of patina formation which may affect the preservation of the traces. Moreover, there are some other factors related to the treatment of the object after its retrieval from the ground: conservation procedures and modern damage can make the scientific examination blurred. At the same time the variety of uses that objects were employed to could hide the traces of previous uses. Therefore, the method does not provide secure answers about the use or manufacture of specific artefacts, rather the observations of wear attributes.

Nevertheless, typological, edge-wear studies and contextual archaeological approaches should first be employed in order to formulate the research framework and define the questions for the application of scientific techniques in archaeological studies. One such area where the importance of a well thought contextual framework is essential is the study of ancient metallurgy and this of the manufacturing techniques of ancient objects.

In this paper, authors employ a range of tools such as typological studies, chronological information, visual examinations of the surface of metals and edge-wear analyses, metallographic analyses and contextual archaeology to examine the fabrication, use and meaning of ancient metal objects; case studies include Bronze Age spears from Italy, Iron Age swords from the collections of the British Museum and various sites in Greece and Iron Age tools and weapons from an Iberian fort in the hinterland of Valencia in Spain. All case studies are used in order to highlight methodological issues and limitations that are common in the study of ancient metal objects, their fabrication and meanings and how to overcome them.

Thus, on the one hand this paper demonstrates how the application and the constant cross-checking of different methodologies can balance their own limitations; on the other, it demonstrates how the researcher can produce culturally meaningful results and explore the active relationship between individuals and metal objects in ancient complex societies.

Characteristic metallurgical relations and qualities of the iron clamps of the Epikourios Apollo

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The subject of the present research work refers to the metallurgical examination of five iron clamps taken from the Epikourios Apollo by the Conservation Committee. The said temple constitutes one of the most famous ancient temples dedicated to the said god, who according to a legend saved the people living around from a severe disease. It was built the second half of the 5^{th} century B.C. (420-410 B.C.) by Iktinos, the same civil engineer who had previously created Parthenon. That is why, the new temple was characterized as “the twined Parthenon”.

Basically, the aims of this research work were the following:
-Conditions applied for their production.
-Metallurgical knowledge at that time.
-The process followed in shaping iron to the final product, the clamps.
-Did standard specifications were applied at that remote time?
-The way each technician followed in making the final clamps.
-The origin of the iron ores used in primitive furnaces.
-Technological differences between the classical and archaic temples.

Taking into account the results of the present research work in comparison to previous ones, it is interesting to note the following final conclusions regarding the clamps of Epikourios Apollo:

1) Each technician did not follow a certain way or specifications in making the clamps.
2) The clamps in classical times did not show to contain islets of steel, as in the case of archaic clamps. Actually, they consist of iron or steel layers, hot welded at high temperatures (about 1200^{o}C).
3) In fact, steel layers exist between soft iron layers, all welded together as already mentioned; and what is more, the technicians were leaving free both ends, which they opened horizontally to produce the tees without any further proceeding. In this way there was no any welding between two single tees into one double tee, as in the case of the archaic temple of Trapeza and that of the Parthenon. Therefore, the technology applied in the case of the clamps of Epikourios Apollo show clearly an impressive development compared with temples of the archaic Trapeza and that of the Parthenon.
4) Since metallurgists of that time did not know how to produce iron or steel in their primitive furnaces, because they could not smelt iron ores at temperature as high as 1500o to 1600o C under reducing conditions, they were making a sponge iron, which then they shaped it at temperature of about 1250^o C. The latter procedure was actually ascertained by optical and electronic microscopic examinations.
5) Examining the clamp B9 under the electronic microscope, many large grains of slag were found in the main body of the clamp, while no similar grains were detected at its ends. The latter means hard hammering at high temperatures.
6) In the center of the same clamp ferrite was found, while at the ends more and more pearlite was detected, due to local carburization.

7) Finally, the iron ores used to produce the iron clamps of all temples, archaic and classical periods were confirmed to originate from Laconia–Peloponnese.

Weapons and armour from macedonian graves

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The luxurious early Hellenistic burials found in the excavations of Macedonian cemeteries during the last thirty years have yielded a large number of iron findings, mainly weapons and armour. During the reign of Alexander the Great the use of iron is no longer limited to lances (spears and javelins) and swords, but extends to defensive weapons as well (helmets, peritrachelia, body armour and shields), excellent examples of which have been found in tombs of Macedonia, testifying the technological developments in iron working during the Asian Campaign of Alexander III. A distinctive feature of these pieces of weaponry is the high craftsmanship that ensured their reliability and efficiency and their opulent decoration with precious materials (gold, silver, ivory, glass, purple dye) and elaborate motifs that lend luxury and magnificence.

The archaeological iron, a material difficult for conservation, in the case of these weapons is found in two different types of condition.

The first includes weapons deposited in the graves after they were placed on funeral pyres. Thus, the material is affected by the high temperatures which it suffered during the burning of the deceased warrior. They are found stripped of organic materials that perished in fire, bearing the evident effects of burning, often stuck together and covered in parts with other materials of the funeral pyre.

The second category includes iron weapons that were placed in the tombs as they were. Their iron surfaces are found bearing remnants of organic materials, ivory, wood and fabric, originating either from their own structure or from their straps and cases or sheaths. Impregnated with the products of iron corrosion the organic materials preserved much of their original form, providing important evidence for the construction of the weapons, presenting however serious difficulties for conservation. Moreover, the iron sheet surfaces are usually found covered by layers of corrosion that conceal their decoration.

This paper presents iron weapons and armour found in the most important Macedonian funerary contexts, those of Vergina, Derveni and Pydna, focusing on the construction details they preserve and the condition of their surfaces which raises serious issues and challenges for conservators.

The Aegean type sword found at Hattusas, silver as rare metal and the written sources, contribute to the dating of Trojan War?

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On August 1991, during repair work on the road running south from the west side of Hattusa, the capital of the Hittite Empire which flourished between 1650 B.C. and 1177 B.C., a bronze sword was unearthed, recognized possibly as of Aegean type and origin. Silver as rare and precious metal is –possibly- connected with Hattusa and Hatti by Homer in the phrase "*αργύρου έστι γενέθλη*". In the present paper the Archaeological Evidence as well as the Ancient Greek Literature, are combined in an effort to register the exchange of Technology among the countries around the Aegean Sea at the Late Bronze Age. Since technology and its products are irrefutable agents about the attested and implied interpretations of the findings, they are a significant factor to the determination of the relations among the civilizations of that era. The archaeological findings are in a good compatibility to the Ancient Greek Literature, according to the present paper. Passages from both the Greek mythology and extracts of ancient authors are cited and compared to the written tablets unearthed at Hattushas and in Greece as well as with texts from ancient Egypt. Conclusions are derived for the exchange of technology and the relations among Mycenaeans, Cretans, Hittites and Egyptians, with the Aegean Sea being a connecting area. Finally a hypothesis for a probable dating of Trojan War is attempted.

A contribution to the galvanic coupling cleaning of tarnished silver

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Tarnishing of silver is caused by the attack of hydrogen sulphide and carbonyl sulphide to the silver surface, creating aesthetic degradation of the artefacts exposed in Museums or in storage conditions that permit the ingress of the urban-industrial pollutants.

The aim of this work is to investigate the optimum and appropriate conditions for tarnish removal from silver artefacts surfaces by an electrochemical galvanic cell of silver/aluminium in an electrolyte of sodium bicarbonate. The conditions tested were temperature, anode to cathode ratio and strength of the electrolyte. Visual inspections as well as gloss measurements were applied to follow tarnish removal.
From the results it can be concluded that the optimum temperature of tarnish removal is 20˚C -30˚C, where a highly bright surface is obtained at 30˚C, while a semi bright surface is obtained at 20˚C. A wide range of CO_3 / HCO_3 ratio 7:1 to 1:1 can be used for detarnishing. Different salt ratios CO_3/HCO_3 (7:1- 1:7) were examined at 25˚C and Al/Ag area ratio (10:1). The results indicated that ratios 7:1 up to 1:1 did not show considerable effect on the time of tarnish removal.

Eco-friendly protection methods for ancient metallic artefacts

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The archaeological metallic artefacts are subjected to the action of the environment around them and often, at the moment of finding in the excavation site, they appear deeply modified with respect to the original surface chemical composition and microstructure. These modifications may be attributed to the chemical and physical conditions of instability experienced by the metallic materials during the long-lasting contact with the environment, air, water and soil. Therefore the microchemical and microstructural characterization of the artefacts as well as the study of eco-friendly, reliable and effective methods of conservation, are fundamental steps for the preservation of the metallic cultural heritage.

Two innovative methods for the protection of metallic artifacts are presented: a low pressure plasma treatment and a chemical treatment that have been tested on copper and silver-based reference alloys specifically produced with microchemical and microstructural composition similar to that of ancient materials.

The plasma treatment has been carried out on copper and silver based alloys, by PECVD, plasma enhanced chemical vapor deposition, of SiO_x thin films in plasma fed with TEOS (tetraethoxysilane), Ar and O_2, with different values of applied power. Before the PECVD deposition, a glow discharge in a low pressure hydrogen plasma eventually removes tarnishing, reducing the corrosion products layer back to metal.

Fig. 1 Silver medaillon coated with Paraloid B72 added with 2% Al_2O_3 nano-pigments after 1 year exposure to the atmosphere

The chemical treatment has been carried out on Ag-based alloys in alkaline dithionate solution in order to clean the surface and eventually remove the patina on aged samples, then the surface has been protected by means of a Paraloid B72 coating containing different percentages of Al_2O_3 nanopigments.

The anti-corrosive layers have been evaluated by electrochemical impedance measurements (EIS) at various times of immersion in solutions containing chlorides and by accelerated ageing tests.

Both the layers typologies reveal a good protective effectiveness against environmental aggressive agents if deposited in optimized conditions, respectively coating Paraloid B72 added with 2% Al_2O_3 nano-pigments and PECVD SiO_x coating with 51% TEOS.

In particular for the plasma treatments, the tests show good protective efficacy of the SiO_x films, which increases by increasing the oxygen-monomer ratio in the gas and the applied power and the adhesion increases when the deposition process is carried out after pre-treatment in hydrogen. Moreover the PECVD deposition technique, very versatile and with a low environmental impact (air emissions and waste generation is negligible), results in coatings with modulated properties and may be used, because of the low pressure and low temperature of the process, for the treatment of different materials such as paper, fabrics and polymers.

On a series of real artefacts, as the one shown in Fig.1, the coatings have been deposited in the optimized conditions and a monitoring is running on the protective effectiveness of the layers.

Greek geometric waxwork-A new research on bronze tripod cauldrons

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According to a recent reinterpretation of stratified clay-moulds found in the 1960s at Lefkandi (Euboea) many of the large bronze tripod-cauldrons of the so-called geometric type must date as early as the 10th century BC. In some Greek sanctuaries like Olympia, dedications of these large and valuable objects seem to have started just at the beginning of the protogeometric period. This sheds new light on the political and social situation, indicating that at this time these sanctuaries already had become places of social interaction of an elite or, in other words, that they already functioned as knots of regional and interregional communication networks.

In 2011 a research program started to map in detail all the known findspots of bronze tripod-cauldrons with heavy cast copper/bronze handles and copper/bronze legs dating between ca. 1100 and 700 BC according to subtypes and chronological phases for the discussion of the historical implications. This research is housed at the *Humboldt-Universität* in Berlin, in collaboration with the *Deutsches Archäologisches Institut (DAI)*, the *Greek Antiquity Service*, and the *Museum für Vor- und Frühgeschichte, Staatliche Museen zu Berlin*. It is funded by the *Deutsche Forschungsgemeinschaft (DFG)*.

Mapping subgroups of the tripod-cauldron only makes sense if the applied typology expresses the interrelation of the involved workshops and regional groups and their relative chronology. In this regard the aim is to combine and check the typology of stylistic features with the evidence of the technical processes in the antique bronze-workshops and with the evidence of scientific analysis of the involved material. An extensive program of describing and documenting traces of manufacturing processes as well as the analysis of the samples will include both: the bronzes and the adhering remains of their clay moulds.

One of the most exciting features of this material is the wax modelling of the solid cast cauldron handles and legs in copper alloys. The wide variation of the artistic wax modelling for the lost wax casting techniques gives the possibility to group the differences not only typologically but also to make workshop qualities, workshop characteristics and working processes and tools visible.

This paper deals with the different ways to manufacture the wax models of the large ring-handles of the cauldrons, with the extent of cold overworking of the metal after the cast and with the traces of long-term use. All these criteria prove to be very effective for grouping the material according to workshop and handling practices and for controlling and revising the existing typology. As reference group serves the material excavated at Olympia since 1875 and now in the New Museum of Olympia/Elis, studied in March and from May to July 2011.

The Derveni board game revisited

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The paper presents the results of our recent study on the board game from Derveni, Tomb B, both from archaeological and conservation perspective and proposes a novel methodological approach for finds analysis and conservation, focusing on theoretical aspects of conservation treatment methodology along with sophisticated computational tools.

The survived remains of the artefact under examination are mainly glass and metal components, in particular glass *pessoi* or draughts (B126, B145), iron board fragments (B118) and bronze hinges (B123), interpreted as pieces of an ancient *kyvia* board game, the precursor of contemporary backgammon.

The artefact's conservation, interpretation and display raise interesting questions considering the material evidence, non-material issues of the object and the available non-object-specific data.

Apart from the integrity of the discovered fragments and the appropriate identification of their position and use, the conservation proposal and concise analysis take under consideration the diachronic presence of this type of games, its discovery in a burial full of luxurious grave offerings and other similar objects excavated in the region or elsewhere. Hence, the balance between intervention, investigation, prevention and communication of the treatment in order to meet the objectives of conservation, accessibility, durability, integrity and practicality, is not self-evident, in case of such complex conservation projects.

Problematic issues are the bad state of conservation of the extant remain, especially the large number of board fragments. Some are simple, intended to support the outer or external sides of the wooden board, while others are complex couples of its iron assembly, which currently form a non-separable mass due to wood collapse and metal corrosion. Among the most interesting fragments are those from the corners of the board, which was fully supported from both sides. Moreover, the properties of glass *pessoi*, such as colour and shape, in addition to the three bronze hinges are considered an intriguing matter of discussion.

Timeline and values analysis outline the artefacts biography, underlining moments of extreme significance during its lifetime, such as its creation, use, burial, excavation, conservation, examination, interpretation and exhibition. The alterations in values during the artefacts biography determine the ideal state and guide the treatment proposal. Moreover, making use of advances in computer graphics and the almost limitless possibility for representation by means of high-fidelity ultra-realistic modelling, this paper examines other methods of interpretation outside the object. In that way, it offers an improved understanding of the object which can lead to a better interpretation of it into the treatment in accordance with conservation ethics and even with the strictest material fetishism conservation ideas, following contemporary concepts of 'minimal loss of potential meanings' or 'post-minimal intervention'. Virtual reconstructions of the board game, whose parts are heavily disfigured and fragmented, not only fulfils documentation requirements, but also improves decision making and can help test hypothesis and justify treatment proposal. Its further implications into replication and restoration, by means of rapid prototyping, provide improved alternatives to traditional conservation operations. Worth mentioning is the application of other techniques, such as polynomial texture mapping for documentation, examination, and analysis in addition to spectral rendering as a comparison to RGB Mental Ray/ iRay.

The metallurgical investigation of copper-alloys metalwork of the Benaki museum in the 4^{th}-7^{th} centuries A.D.

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Since 2006, the metals, glass and bony materials conservation lab of the Benaki Museum (henceforth called BM) of Athens, undertook after the proposition of the curator of the Byzantine collection A. Drandaki, the examination of the technology and composition of 128 ‘copper’ artifacts dated between the 4^{th} and 7^{th} Century A.D. In the context of this research their systematic conservation was considered essential, during which important technological data were brought to light. In addition, the lab had the opportunity to examine in detail the preservation state of the artifacts which due to space limitations will not be presented in this occasion. However, it has to be pointed out that their condition was always kept in mind during the research, since many had suffered from severely post excavation treatments before they entered the Egyptian markets from which they were acquired by A. Benakis himself in the early 20^{th} Century.

The artifacts of the BM collection were thoroughly investigated using several analytical techniques. Stereoscopy, Optical and Scanning Electron Microscopy coupled with Energy Dispersive X-ray analysis (SEM-EDX) were used for the surface and structural examination. Milli and Micro X-ray Fluorescence were performed for the composition analysis of the metals and joins while FTIR and Reversed phase High performance Liquid Chromatography (HPLC) were used for the identification of the black material left in the interior of the cosmetic vases and the organic resin found inside the oil lamps of the collection respectively. X-Ray diffraction (XRD) was applied in order to analyze specific corrosion products detected during conservation treatments.

Most of the artifacts -although some with very thin walls- were cast. The few wrought pieces of the collection were made of relative pure copper or brass, an ideal metal for hammering. The lathe was merely applied to all the objects either for decoration, or polishing or even to prepare borders for inscriptions, scrolls or other motifs. Engraving was the main decorative technique but chasing also appears on the surface of several objects. Conventional wipe or dip tinning with slight post –tinning heat treatment was applied as a coating for decoration and protection purposes.

Particular interest was given to the method of casting used. Lost wax or piece mould? And in the second case clay or sand moulds? Conclusions were based on characteristic features such as pores, chaplets, omphalos marks on the base, large dendrites, segregation phenomena, etc. The way of attachment brazing versus as-casting seemed also an interesting field.

Regarding their composition, the objects were mainly made of either a leaded quaternary copper alloy or leaded brass. The compositional patterns show a clear chronological sequence in the use of the alloying elements zinc and tin and their combination with lead which enabled us to understand the reasons of their selection. Were they used for debasement purposes depending of course on the availability of the material (primary –secondary) and/or because they were judged as more suitable alloys for casting with respect to impurity elements and their effects on metallurgical behavior?

All the aforementioned subjects are discussed contributing to the cultural preferences of the inhabitants of a period (between Classical and post Medieval) in which little attention has been given up to this date. It was really important that the sample of analysis was big enough for such an ambitious diachronic study, in order to result in a complete picture by concentrating not so on higher quality ‘art’ pieces, but on common everyday artefact types.

Manufacturing experiments with Minoan double axes and chisels

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There are a lot of tools in the archaeological records from Minoan Crete but these are seldom studied in order to understand the manufacturing process and are merely classified and placed in a typology. The manufacturing chain involves several steps, i.e. casting and finishing treatments and by "only" classifying and placing the tools in a typology the manufacturing process is not fully understood. By using experiments as a method, I believe that we can come beyond the classification and typologization and come closer to a real understanding of the manufacturing processes of tools.

I have (so far), in order to understand the manufacturing processes of Minoan double axes and chisels studied casting defects on 21 double axes and 4 chisels. The visual examination showed that they were cast in different kinds of moulds, had various casting defects and had been finished off in different ways. In order to comprehend these results several experiments were conducted (and are being conducted, this is work in progress). Several double axes and chisels were cast using the flask technique which is not believed to be a Bronze Age way of casting; however the results on the tool's bodies show otherwise and I believe that we have to consider this casting technique as in use during the Bronze Age. Casting defects have also been studied on the replicas. Certain features as the so called "wedging grooves" on the long side of the axe's bodies and "ears" in the shaft holes are believed to have been deliberately made on the Minoan double axes. These can be explained in technical terms as caused by shrinkage during solidification, which could be concluded from the replicas. A secondary use of these are imaginable, though, at least concerning the "ears" which are situated in the shaft hole, these were not worked on after cast. The finishing treatments involve many steps: cleaning the axe or chisel from flash, removing the running system, giving the tool the final shape by hammering and also grinding the cutting edges. By conducting these steps it was obvious to question existing typologies. It is not a matter of what shape the double axe was cast into, it is a matter of how the finishing treatments were conducted and finally how the tool was used to arrive at the double axe or chisel that we find during excavation and which we typologize.

By combining theoretical work and experiments the archaeological material reveal aspects of manufacturing and use that otherwise would have been shrouded in obscurity. My hopes are that this contribution can open for a fruitful discussion of how we best should combine different methods in order to come to new conclusions of the manufacturing processes of ancient and historical objects.

Archaeological finds. From excavation to exhibition. The conservation project at Aiani museum

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The conservation project of Aiani Museum started nineteen years ago, before the establishment of the Museum, at the cultural center of the village, where the plethora of finds, coming from the excavations of the area, were stored. This fact gave us the opportunity to design and establish up to date conservation laboratories in the Museum, from the first moment of its construction.

The Museum boasts two spacious laboratories for the conservation of ceramic, metal, stone, glass and organic origin objects. The laboratories are very well equipped and cover the needs for the scientific nature of conservation. Apart the equipment for conservation treatments they are also equipped with some analytical instruments for the examination of objects and in the near future some others are going to be bought.

The systematic archaeological excavations at Aiani have revealed monuments of a brilliant civilisation which lasted from prehistoric times to the Roman era. Aiani was the capital of the ancient kingdom of Elimeia and flourished in the archaic and classical period. It was also a metal production center like the other Macedonian cities, Vergina, Pella, Lete (Derveni), Sindos, etc. It is located 20km south of Kozani.

The numerous finds and the rich variety of cases, materials, manufacturing techniques and different problems, that every find presents, offers to the conservator and other scientists a great opportunity for permanent interest, research and study.

The paper aims to present the organization of the laboratories and some interesting cases following the whole process of conservation from the first moment of the objects exposure, the measures taken for their safe carriage to the laboratory, until their exhibition and the control of the museum's environment to prevent future deterioration.

Electrochemistry and surface analysis to prevent deterioration of heritage artefacts

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From a cultural point of view, the preservation of heritage is a fundamental action. This heritage is indeed the witness of a historical reality transmitted to the future generations. The best way to keep and transmit this heritage is to perform preventive conservation. The best way to protect our heritage is, of course, to act preventively. However, not all cultural artifacts need to be protected. The option to protect it or not must be taken by the conservator, balancing the risks of damage to the costs of the preventive conservation. Many times protection involves control of environmental parameters around the parts to be protected or application of protective layers (e.g. coatings). There are several strategies and all of them demand careful knowledge of the material and surface to be protected. Therefore, surface analysis techniques play a major role in characterising the material to be protected. Also, electrochemical tools are essential to assess the durability of exposed parts or the performance of protective coatings.

This talk highlights the potential of surface analysis and electrochemistry as essential tools to assess and to prevent deterioration of heritage parts.

Early Byzantine metal workshops in a settlement near Saint Catherine's Monastry (Mount Sinai, Egypt)

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Since 2001 archaeological research was undertaken by the Greek archaeological mission in South Sinai at a site, east/southeast of St. Catherine's monastery's walls under the direction of Professors Maria Panayotidi and Sophia Kalopissi-Verti (University of Athens).

The main written source (originally in Arabic) concerning this site is the text of Eutychius (Patriarch of Alexandria in 10th century and former Prior of St. Catherine's brotherhood). According to Eutychius this site is identified as the settlement of the soldiers, brought with their families in the area, during the reign of Eemperor Justinian and it was destroyed during the reign of Calif Abd el Malik ibn Marwan (685-705 AD).

The historical data indicate furthermore that the settlement has been inhabited during 6th-7th centuries and it was abandoned before the beginning of 8th century (the expansion of Arabs in this area), since very few sherds of Islamic pottery have been found.

The archaeological research, until 2004, has revealed three main room complexes. Complex I, which seems to be the most important in this site, must have been extended in dimensions aprox. 55x44 m. The two secondary complexes (Complex II and Complex III) are located south of Complex I. Complex II has been fully unearthed it's extended in three different levels. Its dimensions are aprox. 17x15,5m. Complex II consisted of 14 rooms built around an internal yard.

Another complex (Complex III), partly yet unearthed, is located between the two main building complexes of the site. It is much smaller and is consisted of –at least- 4 rooms and 3 secondary places.

In both these secondary complexes several constructions –basins and multiform fire places of probably differentiated usages- have been discovered which must be related with the existence of workshops in this site. Furthermore, masses of metal slags (iron and copper) have been discovered in both these complexes in the same archaeological context with the fire places. Most likely, if we combine these finds, we can assume that perhaps at least in some rooms of this site metallurgical workshops existed. Analyses of samples, taken from ceramics, which were used for the construction of the fire-places, seem to reconfirm their usage or at least their applicability for metallurgical processes.

Main objective of this presentation is to clarify the usage of the differentiated fire-places. It is noteworthy that there have been found three different types, from which at least the two of them could be related to the metallurgical activities. Additionally, the study of the metal finds, the slags and the written sources may give us more details about the character and the nature of the metallurgical workshops in this area.

Analytical and technological examination of two bronze vessels of the Archaic Period from Boeotia, Greece.

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Two bronze phialai (pots used for pouring libations or drinking) from the same site excavated in Boeotia will be examined.

The two bronze phialai were found in a stone public treasury in the city of Thebes, which was excavated in 2003 by Dr. Vasilios Aravantinos, director of the archaeological museum of Thebes and of the IX Ephorate of Prehistoric and Classical Antiquities, Ministry of Culture and Tourism. The treasury also contained bronze inscriptions of the end of the archaic period, related to economic and political issues of the city. The decoration is typical of that period: it belongs to the *mesomphalos* fluted type. Unfortunately they are not preserved very well. Their preservation status is not complete since pieces are missing. After their transportation to the Museum of Thebes the items were cleaned.

The current study of the two *mesomphalos* fluted type bronze phialai, which demonstrate comparable typological characteristics, aims to determine the copper alloys used for their manufacture, and examine their consistency in order to identify possible regional characteristics of the alloys used in these location of Archaic Boeotia. It should be emphasized that this is the first attempt to analyze Archaic bronze artifacts from Boeotia and is expected to provide useful data for future reference.

In situ non-destructive analysis by portable X-ray fluorescence (XRF) unit has been employed, aiming at determining the nature of the used bronze phialai and, probably, their chemical composition. Furthermore, data collected from the application of Scanning Electron Microscopy and Metallographic Microscopy is likely to provide answers on issues related to the technology employed for the manufacture of the three archaic bronze phialai from Boeotia and to the degree of their corrosion (oxidation/chlorination), which could contribute to more effective conservation treatments.

Evaluation of three cleaning methods applied on Cl- rich artificial patinas of two bronzes

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Employing plasma reduction methods to clean metal artefacts is a novel technique with positive results on metals [1-6]. This work attempts to compare the results of the application of low pressure and temperature (80°C) hydrogen glow discharge plasma with two conventional methods currently used in conservation practice [7-9]. These trials are made on the grounds of improving the effectiveness and minimizing the aesthetic limitations of hydrogen plasma treatment at 200°C discussed in previous works [6]. A re-evaluation of the advantages and disadvantages of chemical cleaning with alkaline solutions (1% alkaline dithionite and 1% aqueous Na(OH) solution) and the study of the individual behaviour of each alloy during those stabilization procedures is another interesting issue. The third aim was to endeavour a possible combination of immersion in 1% Na(OH) solution and further reduction by hydrogen plasma at mild conditions. Two different copper alloys a Zn- and a Pb-bronze, produced by casting [10], are employed as substrates for the formation of artificial patinas rich in chloride species. The samples were corroded, in two stages, under accelerated corrosion conditions (immersion in a $CuCl_2$ aqueous solution 1M for 24h and subsequent exposure at 100%RH for 24h) in order to achieve the most representative corrosion products, with particular interest in the formation of chloride corrosion products associated with the process of 'bronze disease'[11-12]. The corrosion behaviour of the alloys and the surface transformations induced by the three cleaning methods and the combination of chemical treatment/plasma reduction were investigated by means of XRD and SEM with EDS microanalysis. The reduction by plasma treatment eliminated the chlorides incorporated in the thick patinas. The immersion with alkaline dithionite lead to the reduction of the basic copper chloride compounds on the surface, which were replaced by CuO, Cu_2O, metallic copper and zinc. The treatment with Na(OH) solution, transformed the copper tri-hydroxy-chlorides to a stable layer of $Cu(OH)_2$ while removing a significant amount of the chloride content. All three methods gave some positive results regarding the chemical aspects of this research field, although neither of them resulted individually in the complete removal of chloride compounds or fulfilled the aesthetic requirements.

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Study, analysis and conservation of the Roman water lead pipe in “Aeolus” excavation, Plaka, Athens

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INTRODUCTION

“Aeolus” was the first hotel built in Athens, Plaka, in 1837. During the excavations conducted in the two – chambered basement of the building, almost the entire south-east corner of the Library of Hadrian was found. In the eastern chamber, a lead pipe was found in short distance from the outer surface of the south enclosure wall of the Library to the axis south-west. It is the only single specimen of this type of piping found in the area of Hadrian’s Library and the Roman Agora.

Scientific investigations were carried out to assist the identification of the corrosion products and the extent of corrosion before any conservation work takes place.

HISTORICAL ELEMENTS AND CONSTRUCTION TECHNIQUES

According to all indications, the pipe was constructed around the middle of the 2nd century A.D. or a little later; however there are no inscriptions discernible on its exterior surface.

Such pipes were made by lead sheets rolled around a template with the edges bent round and soldered with lead. The junctions along the length were reinforced by a short collar into which the two ends of the sections fitted and the joint was pressed tight.

The lead pipeline was in fact a pressure water line, sometimes used for fountains, and wherever it was necessary, to make water run uphill.

CONDITION ASSESSMENT

The lead pipe was profoundly corroded particularly where it was adjacent to the dividing wall of the basement and was found broken into many small pieces. In some areas towards the wall it has even been deteriorated to the extent of being found in tiny pieces and dust. Corrosion products covered the surface in the entire length of the pipe and earth residues could also be observed forming soft crusts particularly in the interior of the pipe whereas the inner surface of the pipe presented a different texture, possibly because of salt encrustations from its original use.

MATERIALS CHARACTERIZATION

Some of the removed pieces were visually examined under a stereomicroscope whereas samples were analyzed with Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-Ray Analysis (EDAX).

CONSERVATION

The main intention was to restore the largest possible part of the pipe; therefore the cleaning of the surface of both the main body of the pipe and the fragments was our primary aim. Considering the conditions in the excavation and the conservation of the lead pipe in situ, Paraloid B-67 dispersed in white spirit was used as adhesive whereas ethanol and white spirit as solvents to clean the surface.

In conclusion it should be emphasized that the analytical study will allow us to make decisions on the need for the inhibition of corrosion and on the appropriate methods for stabilizing and thus securing the preservation condition of the lead pipe.

Fig. 1 Aeolus excavation, A΄EPKA. Lead pipe and the outer side of the south wall of the Library of Hadrian, view from west

Fig. 2 Conservation work in progress

Analytical investigation of the lead finds from the Mycenaean settlement and cemetery of Lazarides on the island of Aegina (Greece)

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A Mycenaean settlement, with finds dating from the end of the 17th until the beginning of the 12th century BC (MH/LH I - LH IIIC early period), developed in the neighborhood of the modern semi-mountainous village Lazarides on the island of Aegina. It is situated on a high (361m.) plateau on the eastern part of Aegina, ten kilometers from the harbor and Kolonna, about an hour's walk from the eastern coast and unseen from the sea. To the S and in a short distance from the settlement a cemetery with spacious built chamber tombs, was discovered. The finds from the settlement and the cemetery include a great amount of locally made and imported, mainly from Argolid, pottery, figurines of various types, seals, nine from the cemetery and one from the settlement, jewels made of glasspaste, fayence, amber, semi-precious (such as rock-crystal, carnelian, steatite) and common stones, as well as bronze and silver, items made of stone, bone and ivory, and also a small but very interesting group of metal artifacts.

Apart from a number of bronze artifacts, the vast majority of the metal finds consists of lead objects of everyday use. Lead clamps, pieces of wire, but also a unique lead ingot, a shapeless drop and a very interesting weight in the form of a duck, were discovered both in the settlement and the cemetery.

Since the ingot along with waste and finished products, were discovered in the same archaeological context, the lead finds of Lazarides provide an excellent opportunity for a holistic study of the production and use of lead, in the settlements of the Mycenaean period. Thus, a combined archaeological and analytical investigation of the lead find was undertaken with the collaboration of the Group for Paleoenvironmental and Ancient Metal Studies of the Laboratory of Archaeometry of the N.C.S.R. "Demokritos".

The lead objects were initially examined with portable ED-XRF equipment at the storerooms of the Archaeological Museum of Aegina. The data that was obtained from the non catastrophic XRF superficial analyses was combined with the analytical information provided by the observation of minute samples under both an optical microscope and a Scanning Electron Microscope equipped with an EDS microanalytical system. Moreover, provenance studies are expected to supply useful information concerning the nature of the metal that was used in Lazarides during the period and the involvement of the settlement in the Late Bronze Age trade networks of the Aegean and the Eastern Mediterranean.

The zinc content of copper alloys as a criterion in authenticating ancient metallic objects

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Brass was a quite rare alloy in antiquity. According to research results [1] the deliberate production of brass (up to 10% zinc) began at the ancient Phrygia between the 8th and the 7th century B.C. Later on, by the middle of the 1st century B.C., the large scale production of brass started by the Romans. The zinc content of Roman copper alloys varies: statues usually show less than 1% of Zn, decorative work 12-15% and coins show a decrease in zinc content with time [2]. The cementation process is supposed to give brass with maximum of 28% zinc [2].

According to a general authentication criterion, pre-Roman objects are expected to have less than 13% of Zn while Roman material may show larger percentages. However, only Roman "gunmetal" has been reported to have Zn content higher than 25% [3]. The exceptional content of 35% has been found only in Bohemian brooches [4]. In addition, to the zinc content, Sn, Mn, Fe, As and Co concentrations may give important information on the possible ore source and consequently the object authenticity [2, 3].

The case of a female head (No. 15187) donated to the National Archaeological Museum of Athens in 1931, will be presented in the paper as an example. The head is very similar to another, excavated at Herculaneum in 1756 and dated to 4th - 3rd c. B.C. (Naples Museum) [5]. Some scholars have suggested that both heads are Roman replicas of one original but lately, additional technical observations gave very strong indications that the Athens head is a modern copy of the Naples one [6]. Careful examination of the Athens head with X-ray radiography and chemical analysis using Atomic Absorption spectroscopy shows that the head was cast in one piece and its zinc concentration is 31%. The results prove beyond any doubt that it is a modern copy of the Naples head.

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Metallographic evidences of bronze casting working conditions at Moscow-Volga region during Early Iron Age[1]

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The Volga – Oka watershed is situated in the central part of the Eastern European plain. The Dyakovo tribe populated the Volga - Oka watershed in the Early Iron Age. The studies of the Dyakovo tribe have lasted for more than one hundred years. The investigations of non-ferrous articles have focused only on typological interpretation. For the first time these objects have been researched using the combined method which includes the study of technological characteristics of production and the compound chemical analysis of it.

The greater part of the studied collection consists of jewelry which was obtained during the Nastasyino, Troyizkoy, Cherbinka, Dyakovo hill forts excavations in 1960-2000. This article is an attempt to summarize the results of chemical analysis that can be divided into some periods: the Scythian, the Roman, and the Great Migration. Archaeological data of the Dyakovo tribe's culture have varied during various chronological periods.

The most intensive changes of the character of archaeological data were connected with the advent of non-ferrous metalworking in this territory in the Scythian period. Studies show that the basics of non-ferrous Dyakovo metalworking originated in the Southern region of Eastern Europe, but the Roman period introduced a variety of chemical compounds and some progress in jewelry making methods in the Volga – Oka watershed. These changes are probably more characteristic for the cultures with highly developed non-ferrous metalworking. The Dyakovo tribe metalworking within the Great Migration period differed from the Roman traditions – more soiling alloys and predominance of one technological method. In our opinion these data indicate changes that were caused by the events of the Great Migration period.

Our paper is devoted to metallographic evidences of bronze casting working conditions in this area.

[1] Research under grant of President of Russia (MK-678.2008.6)

Archaeometallurgy in the Levant: Past, present and some thoughts about the future

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At 2pm, 21 March 1961, fifty years ago the Israeli archaeologist Pesah Bar-Adon uncovered in a remote cave in the Judean desert – a magnificent metal hoard. This treasure contained 429 objects wrapped in a straw mat. Almost all (416) are made of metal and dated to the Chalcolithic period, 4000-3500 B.C.E. This extraordinary find mark the beginning of modern archaeological study of metals in the Southern Levant. Soon after the discovery, two major metallurgical pioneering studies were conducted and published: a chemical surface analysis of 33 objects, performed by C.A. Key using spark-emittion analyzer, and an optical metallography of 2 objects conducted by Potaszkin & Bar Avi. These studies mark the beginning of archaeometallurgy in the southern Levant.

If we follow the history of this hoard, we could see that intensive research with varied 'modern' analytical tools was performed on the material from the mid Nineties and on (1984: Notis *et al,* 1987: Shalev & Northover, 1991 and on: Shalev; Levi; Goren; Tadmor *et al;* Segal). These studies are currently followed by a new generation of scholars (i.e. Namdar, Goldin, Shugar). Just recently in 2011, Aron N. Shugar published a detailed survey of the subject.

So what do we know better after 50 years of such intensive study?

1. The Chalcolithic cultural context of the hoard was solidified with more parallel examples from well-dated sites in the region, and the sequence of dates was clarified.
2. Metal composition was corrected with better and more suitable analytical systems such as ICP, AAS, WDS, EDS.
3. The metallographic first results were verified.
4. The copper 'tools' production was put in a wider context of its all chain of production and source material origin.
5. The Prestige/cult products show more local affinities, but no more knowledge was acquired on the origin of the material and place of production.

If we summarize the above in a critical view: not really so much was achieved for the archaeological understanding of the metal production and utilization in this period although an intensive research has been performed using 'state of the art' modern analytical techniques.

In the meantime, intensive excavations and archaeomineralogical and metallurgical studies were conducted in the major source areas for copper in the region in Feinan (Levy and Hauptmann), Timna (Rothenberg and Bachmann) clarifying dates and intensiveness of ancient copper production and contributing mainly to the overall picture of ancient production, clearing the archaeological picture from some unproven and uncorrected pre-conceptions.

If we try to look at the state of research through the publication issue we could see that the publications are in major 2 separate contextual areas:

1. Chapters or appendixes in archaeological publications reports: accessible mainly to archaeologists in specific area and period.

2. Papers in specific periodicals of archaeometry and archaeological sciences: accessible mainly to the relatively small community of archaeometallurgists.

So, what does all this mean for the future of our field? In this presentation, I will try to clarify the state of research with its strength and week aspects and assess the possible meanings of it to future aims.

What are we really analyzing? The peculiar story of Middle Bronze Age II battle-axes from the Southern Levant

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Hundreds of copper- base objects dated to the Middle Bronze age II (henceforth MB, end of 3rd – middle of 2nd millennium BCE) have been unearthed, in burials, all over the Levant in the last 150 years of archaeology. In this period the development of more complex weapons (longer daggers, swords, complex battle axes, etc.) was made possible by alloying the copper either with arsenic (As) or with tin (Sn) to produce arsenical copper and tin bronze. The MB also saw lead (Pb) begin to play a greater role in alloying, in particular for thick and relatively large copper based castings such as battle axes.

The already known appearance of both arsenical copper, tin bronze and lead, in similar objects is visible in all major weapons' types during several hundreds of years with relatively high quantity variations of the alloys between similar objects analyzed by different scholars and in various methods (i.e. Shalev 2009).

In this presentation we wish to proceed in this direction and try to better understand the possible causes for such high variability in quantities of the major elements detected in different objects of the same type and identical shape. For that we choose 13 battle-axes, from all three major known types, found in a single MBII cemetery in Rishon Le-Zion, south of Tel Aviv, on the coast of the eastern Mediterranean, Israel.

In order to better differ between a 'real analytical effect' (i.e. actual difference in the quantities of major elements used for the production of these objects) and what could be the result of an analytical 'artifact' (i.e. the actual metal state of preservation, compositional alterations caused by selective corrosion and/or conservation treatment, or – the use of different analytical methods or protocols), we analyze systematically different parts of the same object surface in a single method (ED-XRF) using exactly the same conditions for all analyzed areas. The results of these measurements show that we could eliminate the possibility that the high variability is caused solely by different analytical methods mainly because a similar variability was found when using a single method and a uniform measuring protocol. Moreover, such similar high variability in alloy's content could be measured in different points of a single axe surface. So, in order to better understand the origin of such heterogenic compositional picture, we decided to check the level of homogeneity in the whole preserved volume of metal in these ancient objects.

For that we exposed 6 of the 13 axes to neutron beam (ND) for studying their diffraction in different areas of the cast. For our study we used the instrument ENGIN-X in ISIS, U.K., which is optimized for measurements of internal stresses in different limited parts inside an object and is highly suitable to such archaeological artifacts (Kockelmann *et al* 2006).

The results of these analyses have a great effect on our knowledge concerning the production process of these objects and the thermal and mechanical manipulations they were undergoing after their casting. These aspects will be discussed in more details in the presentation. The ND results also show that the MBII battle-axes from Rishon Le-Zion have much greater homogeneity in their bulk metal than in their measured composition of the surface. These results have, in our opinion, an important impact on the use and limitations of surface metal analyses. In our particular case here, we could show that ‘cleaned’ and conserved surface of ancient metal objects show an inhomogenity in metal composition that reflect more the metal corroded state, even after ‘cleaning’ and conserving and much less – the original bulk metal of the ancient artifact.

Corrosion of archaeological bronze in non-hostile burial environment

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Significant research has been carried out on the corrosion formation on archaeological bronze artifacts in soil [1, 2]. Few works have attempted to simulate corrosion and understand the electrochemical processes [3, 4]. Most researchers focus on the corrosion of bronze in soil containing chloride species; moreover, in their electrochemical experiments they employ as electrolytes standard solutions simulating chloride containing soils and ground water [3.4]. However, archaeological bronze artifacts have suffered from notable corrosion even when they have been buried in non-hostile burial environments, namely, soils with non chloride contents. In these cases, the mechanisms, the forms and the products of corrosion are expected to be different owing to different types of electrolyte/soil.

This paper presents the corrosion formation in such burial environments. Five bronze artifacts, dated in the late Hellenistic - early Roman times, from the excavation site of Episkopi-Serbiana in Ioannina Prefecture, were studied in terms of alloy content and corrosion product formation-stromatography. SEM-EDX and metallographic observation of cross-sections revealed a single phase copper-tin alloy (Cu-10Sn). Corrosion of ***type I*** [1] with high tin content in the outer layer was identified. In parallel, soil analysis was performed and revealed a sandy-clay soil with a pH of 5.4. Subsequently, possible corrosion mechanisms were identified.

An attempt was then made to electrochemically simulate this type of corrosion using the excavation soil. The set-up involved a three electrode corrosion cell, more analytically consisting of:

- A reference electrode: WE 100 by Silvion Ltd, Ag/AgCl electrode, specially manufactured for measuring potential in concrete and soil
- A counter electrode: made from solid-state platinum manufactured by XENON
- A working electrode: Cu-10Sn bronze alloy, forged and annealed to resemble the archaeological artifacts
- An electrolyte: All electrodes were immersed in soil collected from the excavation site.

Cyclic potentiodynamic polarization was carried out (scan rate:10 mV/min, at least 5 scans for each measurement) by means of the Gill AC potensiostat-galvanostat. The corroded surfaces were investigated by means of SEM/EDX and Raman spectroscopy. Corrosion rates were extrapolated on the basis of the Tafel technique [5] and correlations were made with the original artifact surface state and corrosion stromatography.

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Lead clamps for repairing clay pots from the acropolis of Vergina

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The large numbers of lead clamps that constitute a regular excavation find, indicate that repairing broken clay vases in antiquity with lead clamps was a widespread practice. These clamps form the most common lead find in settlement excavations and are found either free or still on the repaired vase. Since they repair vessels of all sizes, their form has standard features, but their dimensions can vary dramatically. It is clear that they were the easiest and cheapest way of repairing clay pots. However, scholarly work on the technique of joining the pieces of a broken clay pot with lead and clarification of the process is still lacking.

The large numbers of lead clamps and (amounting to hundreds) and residue from the casting of lead found in the excavation of the Aristotle University of Thessaloniki on the acropolis of Vergina was assessed as suitable to form the basis of a study that could contribute to the approximation of the technical process of repairing clay vases in antiquity. Observations on the finds were tested by experimental reconstruction of lead clamps on modern clay pots. The conclusions of this study form the main subject of this paper. The effectiveness of these joints are also examined, the sources of the lead as well as the possibility of recasting used clamps.

Cleaning of sulphidae from silver and gilt silver threads in silk textiles using laser in the visual and UV range

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Cleaning of silver and gilt silver threads that decorate brocade, embroidery and passementerie in museum collections represents a great challenge for conservators, as it involves a variety of delicate materials with diverse properties. The cleaning intervention aims to restore the tarnished silver and gilt silver textiles to their previous brilliance and luxury, while preserving the fragile silk fibres that form the base of the textile construction. A variety of methods involving mechanical and chemical cleaning techniques have been used to remove silver- sulphide, oxide and chloride from the metal threads. All of these techniques have the disadvantage that residues of polishing particles or chemical compounds are left in the textile after the treatment. A two-stage electrolytic technique has been used with good results. However because it involves immersing the pieces to be cleaned into water, its utility is limited. On this background, the feasibility of lasers was studied.

Towards this aim, a series of tests was performed both on model and historic samples using lasers in the visible and UV regime in order to define the cleaning threshold and the optimal laser parameters at 532 nm and 248 nm for the removal of silver sulphide from silver. Good results were obtained with the use of ultra-short laser pulses in the pico- and femtosecond regimes compared to pulses in the nanosecond regime. Hereby the heat diffusion and other photochemical phenomena are minimized.

Evaluation of the tests involved microscopic observation (OM, SEM), while tensile strength tests were performed on irradiated silk threads.

The results of the laser studies will be presented. In addition the cleaning methodology used to restore such complicated and fragile materials will be discussed. Furthermore, we will deal with the important issue of whether to clean the metal threads, which is not a preserving treatment, but gives the textiles an aesthetically acceptable appearance in order to show them in an exhibition. Alternatively, they can be kept in a more dull-looking condition, which provides them with a longer life.

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Votive metal zoomorphic small objects from the pan-rhodian sanctuary of Zeus Atavyrios

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A significant number of metal votive zoomorphic small objects dated from the late ninth century BC to the early Hellenistic period (early 3rd c. B.C.), was found in the pan-rhodian sanctuary of Zeus Atavyrios at the top of the homonymous higher mountain of Rhodes; a small part of this group is currently exhibited in the archaeological exhibition for the "2400 Years of Rhodes' in the Grand Master's Palace at the medieval town of Rhodes.

The zoomorphic metal objects were found in the *sacred apothetes* or *bothroi* of the sanctuary, part of which was excavated for a short period in 1927 by the then Italian Archaeological Service. Although the excavation of the sanctuary has not yet been completed, the area has been extensively looted, until recently, due to the remoteness and to the impeded accessibility of its region.

These votives are mainly bronze zoomorphic figurines, mostly animals in a variety of shapes (bulls, buffaloes, oxen, bison, etc.), or models of insects (grasshoppers, etc) with particular morphological features related to the nature of the cult of Zeus Atavyrios in Rhodes, which also, suggest the existence of a local metal-workshop where they were manufactured. Among those of particular interest are the bronze plates in the shape of an ox, which were worthless offerings, substitutes for most precious solid or hollow zoomorphic figurines, some of which have dedicatory inscriptions of their owners.

The current paper refers to matters of chronology and typological classification of these offerings, as well as to interpretation issues associated to the cult and the cult practice in the Zeus Atavyrios sanctuary from the early historical times until the Roman imperial period.

The rapid development in making iron clamps for the erection of the archaic and classical temples

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The present research work deals not only with the making of iron clamps of the archaic and classical temples, but also, and this is very important, with the speedy development of technology in a relatively short time. For instance, the technology in making the clamps of Parthenon and those of Epikourios Apollo differs completely, although the latter was erected by the same engineers, Iktinos and Kallikratis. The research work proves that the technology applied in the case of Epikourios Apollo could be considered as a revolutionary one compared with that applied in the erection of Parthenon.

1) Following chronologically the erection of the temples, the author starts by describing the making of the iron clamps of the archaic temple of Trapeza (end of the sixth century B.C.), a few kilometers south of Aigion Peloponnese. The research work of the author leads to the interesting conclusion, that ancient technicians of that period used iron as produced in their primitive oven, i.e. a mixture of iron and steel. Specimens taken from double T clamps show under the metallographic microscope, and after grinding, polishing and etching with an appropriate chemical reagent, the existence of dark islets in an environment of almost white metal. The dark islets are steel with a carbon content of about 0.30% - 0.35% carbon, while the rest is soft iron, whose carbon content is not more than 0.04%. Finally, metalworkers welded at high temperatures (almost at 1250^{o}C) two simple T's into one double T. Another important point of the said research is that the double T clamps of the archaic temple of Trapeza are almost free of non desirable foreign impurities, and mainly of S and P, which above a certain limit provoke serious problems during hot or cold shaping of the said metals.
2) The metallurgical examination of the iron clamps of Parthenon and Erechthion (5th century B.C.) shows a tremendous evolution of the applied technology in making double T's iron clamps for joining together the huge marble pieces of the temples. Metallurgists of this period knew, in contrast of their archaic colleagues, how to produce separately soft iron and steel, and then to join them together by hot forging at about 1250^{o}C. Therefore, in the case of iron clamps of Parthenon and Erechthion there are no islets of steel in an environment of soft iron, but separate layers of both of these. In classical period, technicians were welding together, as in the case of the archaic period, two simple T's into one double T. Chemical investigation showed again, that undesirable foreign impurities were very low.
3) The making of the Epikourios Apollo iron clamps, as already mentioned, can be considered a revolutionary technology: A) Their dimensions were quite smaller than that of the Acropolis temples. This means the use of much less iron, whose production was actually not an easy process at that remote time. B) There was no any welding of two separate T's into one double T clamp. They were using layers of soft iron or steel, welded together at high temperature (1250^{o}C) into one piece, leaving the two side ends free. The latter then were shaped (always at high temperatures) into T shape, one at each end. In other words they used less iron in making the double T clamps, and there was no welding at all between two simple T's into one double; this means

therefore great saving of time. Finally, as in the case of the previous clamps, those of the Epikourios Apollo were almost free of foreign undesirable impurities. The latter is the only in common characteristic.

Self-healing coating as a way to extend life of metallic materials

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One major concern of archaeologists and conservators is to limit the alteration and the corrosion of metallic objects which present an important part of human heritage. It is well known that most of the metals are thermodynamically prone to oxidation processes in presence of different corrosive species. There is no possibility to change the thermodynamics and completely stop the degradation of metallic objects. However these processes can be decelerated by reducing rates of corrosion. Organic coatings are one of the most important ways of protecting metal against corrosive agents, thanks to their diffusion barrier properties. However defects normally appear in protective coatings during exploitation because of mechanical impact, abrasion, UV-radiation and thermal stresses. After the defects appear the barrier properties of polymer coatings are locally destroyed. Therefore additional active protection mechanisms are needed in order to prolong life of the coated materials.

The present work reviews main approaches used for creation of self-healing protective coatings for metallic materials. Most of these technologies can also be applied for preservation of metallic heritage as well. The main accent of the paper is focused on transparent self-healing polymer coatings. Different mechanisms of self-healing are addressed including suppression of the corrosion processes by coatings with nanocontainers of corrosion inhibitors as well as strategies based on self-healing polymers.

SESSION 2
HYALOS-VITRUM-GLASS

Glass working in Roman and Early Christian Thessaloniki: older and more recent finds

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Glass working activity in Thessaloniki, in terms of production remains, is attested only in Late Roman period. A recent salvage excavation at the center of Thessaloniki revealed parts of two intersecting streets and parts of two building insulae, that can be dated in the Tetrarchic period (late 3rd c. A.D.). The corner shop, at the south end of the eastern insula was formed in a later, 5th-6th c., construction phase, and was used as glass workshop between late 5th and 7th c. That is the first archaeologically attested antique glass workshop in Thessaloniki.

There are also presumptive evidences that make quite certain the operation of at least three other glass workshops in the city, dated in the period between the 4th and 6th cc. These movable finds have been unearthed in different parts of the city: Just like in many other late roman sites, workshops in general, and glass workshops in particular have been located on the sites of abandoned, roman, public buildings and on the site of the roman forum, where a whole cluster of different workshops flourished, when the site lost its official character in 4th-5th cc. Finally, workshops are also found next to the city walls, both *intra* and *extra muros*, and especially glass workshops appear to be active on the site of the eastern necropolis, very close to the city walls and probably on the road leading from the main eastern city gate towards the hinterland. Next to immovable finds, several forms of glass vessels have been ascribed to the local, Thessalonian production and they will also be presented in this communication.

Investigation of ancient glass beads by means of macroscopical and microscopical observations

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In ancient Rhodes a large number of glass beads dated in the early centuries of the 1st millennium BC (8th and 7th c. BC) were found in the tombs of Ialysos and Kameiros, and also in the deposits of great sancutaries of *Athena Kameras* in Kameiros and of *Athena Poleas* in Filerimos in Ialysos. The majority of the beads are plain, translucent and colorless or slightly colored, cylindrical or semi-circular; some others are triangular eye-beads or bird beads.

Various analytical techniques are employed in structural studies of ancient materials, with the aim of answering questions as regards ancient glass technology involved and distribution patterns.

In the present study a set of 6 carefully selected, similarly sized and colored glass beads originating from a 640-600 BC depository in Rhodes Island is probed by Scanning Electron Microscopy (SEM-EDAX), X-ray Fluorescence (XRF), Optical Microscopy and detailed dimensional measurements. Bead geometry provides support for a shaping technique involving a spherical mould, a stem and the insertion, before full solidification, of an auxiliary pointed object. Also the study of gas bubbles that are impounded inside the glass matrix gives useful information concerning bead shaping and technology used. Specifically the determination of dimensions, long axis orientation and locus of each bubble provide valuable hints as regards forces exerted during sample shaping; hypotheses regarding the technology involved should be compatible with the latter findings.

The use of optical absorption spectroscopy for the study of ancient glass

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The objective of this work is to show some sensing parameters of UV-VIS-NIR absorption spectroscopy for the characterization of ancient glass. The application of visible and near-infrared spectroscopy allow to shed light on many points, such as used materials, applied fabrication techniques, dating and originality of the glass pieces.

First of all, this technique is strongly efficient in the identification of colouring agents as transition metal ions normally employed in glass have specific absorption peaks (Figure 1).Its application is successful also when colour is generated by metal nanoparticles, such as silver and copper colloids. Recognizing colouring agents can also be used in dating because some colourants were only used in certain periods. For example among the green glass of a 15th century stained window, some pieces are coloured with chromium, suggesting that those glasses are not original, as this transition metal was introduced in glass-making only after the second half of the 19th century[1].

By studying the spectral position of cobalt absorption bands, it is possible to identify the main flux, sodium or potassium. This can be explained by considering the lig and field theory. When a transition metal ion experiences an external electrical field, its degenerated *d* orbitals are split in energy. The energy gap depends on the lig and field strength, which in glass depends on the chemistry of the matrix. There is a noticeable 10 nm shift of the lowest absorption wavelength of cobalt between Na-rich and Ca/K-rich glass [2].

Furthermore, cobalt can be detected in very low concentration. In the case of the 15th century stained window, this element was present as impurity in wood ash used to make glass and therefore its identification helps unravel the original areas of the window.

Normally glass is opaque to short wavelength in the UV region. The UV-absorption edge is defined as the wavelength for which only the 50% of incident light is transmitted (Figure 1). In simple silicate glass, this is related to the bonding state of oxygen atoms [3]. When they are bonded weakly, such the case of non-bridging oxygens (NBO), a stronger UV absorption occurs. NBOs are originated by the presence of network modifiers, which disrupt the silica network. In particular, it is seen that the UV-absorption edge can be correlated to the iron content of glass [4].

From the transmission spectra of glass is possible to calculate the colour coordinates [5]. Besides the chemistry, i.e. the presence of transition metal ions, the colour of glass depends on the furnace condition applied during the melting process [6].In particular iron is almost always present in ancient glass as it is added into the batch as impurity of sand. It exists in two oxidation states, which impart two different colours to the glass: Fe^{2+} gives a blue hue and Fe^{3+} produces a yellow hint. It is clear that the colour produced is function of the Fe^{2+}/Fe^{3+} ratio and therefore of the applied redox furnace conditions [7].

When the colour coordinate values are plotted in the CIE1931 horseshoe chart, the dominant wavelength is determined by the intersection between the CIE1931 curve and the line connecting the white point and the sample colour coordinates (Figure 1). This parameter gives an insight into the technological production of a glass fragment.

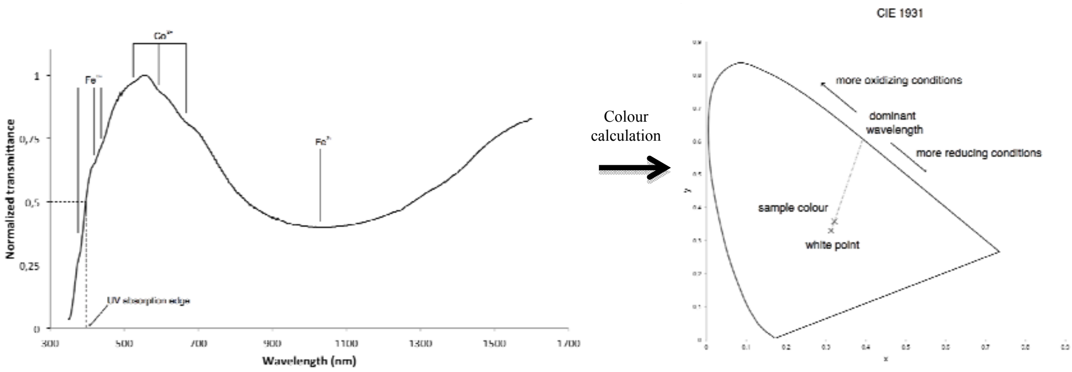

Figure 1 – The left graph shows the optical absorption spectrum of a glass fragment. The main colouring agent is iron, but the presence of cobalt impurities is detected. The UV absorption edge is also pointed. The right graph shows how to determine the dominant wavelength in CIE1931 horseshoe system.

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A provenance study of cypriot byzantine glazed pottery and ceramic tripod stilts

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Glazed ceramics represent the main type of pottery in Cyprus during the late-Byzantine period (13-15th century A.C), displaying the same manufacture technology and decorative techniques as the rest of Byzantine pottery. The most important workshops were at the area of Lemba and Kato Paphos (Paphos District), on the south west side of the island, and in the area of Lapithos, on the north side of the island, in the district of Kyrenia [1]. Concerning Nicosia local pottery production, the discovery of ceramic tripod stilts in several spots of the city, give clues for the existence of a local workshop, but the fact that no kilns were found yet cannot verify this possibility. The discovery of a large number of Lapithos glazed ceramic in Nicosia area can be easily explained by the geographical proximity of Lapithos to Nicosia [2]. The use of tripod stilts in the manufacture technology of Byzantine pottery appeared at the beginning of the 13th century, and its rapid acceptance assisted in the mass production of glazed ware and the development and creating of new trends in the glazed pottery of the late-Byzantine period [3]. Ceramic tripod stilts, because of their simple use only for the separation of the glazed ceramics during the firing process, were made usually of local area clay, and their chemical and mineralogical compositions represent a reliable indicator of the workshops area clay composition, helping out the provenance study of glazed ceramic samples. Although significant research is carried out concerning Cypriot glazed pottery [4, 5, 6], further investigation of glazed pottery from various areas of the island combined with the study of ceramic tripod stilts, will provide additional and important information concerning the identification and manufacture technology of the local glazed pottery.

In this study, 16 samples of glazed pottery, excavated in Lapithos and Nicosia (Palaion Demarcheion), and 17 samples of ceramic tripod stilts, coming from a systematic excavation (Nicosia, Palaion Demarcheion) and archaeological survey material research in Lapithos, Lemba (Paphos) and Vasa Koilaniou (Limassol district), were studied by means of micro X-Ray Fluorescence Spectroscopy (m-XRF) and Powder X-Ray Diffraction Spectroscopy (PXRD), for the determination of the elemental and mineralogical composition of the ceramics.

The experimental results of the chemical and mineralogical analysis and the application of statistical analysis (PCA), indicate the differentiation of Lapithos glazed ceramics and tripod stilts samples from Nicosia samples giving significant clues for the existence of a workshop in the area of Nicosia. Also, Lemba and Vasa Koilaniou tripod samples differentiate from the rest of the samples, creating one group, justified from the fact that the two areas belong to the same geological zone of Mamonion, on South-West Cyprus.

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Some considerations regarding the glass vessels from the East-Carpathian Dacian settlements (2nd century B.C.- 2nd century A.D.)

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In this study the authors aim to present a series of considerations regarding the distribution and circulation of imported glass vessels in the east-Carpathian territory. The main sources of analysis are represented by the **dava** fortified settlements like Poiana, Barboşi, Răcătău, Brad and Bîtca Doamnei, which were in that period the cores of political authority but also, strong centers of commercial demand. Thus, the Dacian elite were continuously supplied by merchants and craftsmen with Roman-type luxury goods, among which can also be counted the glass vessels. Although the edited glass fragments are until now quite scarce and the most important group of glass fragments comes from Poiana (about 98 fragments) nevertheless, some important observations can be made. Analyzing the data provided by the glass fragments, we can notice the high values of the tableware (especially all types of bowls, beakers and cups) compared with the small amount of unguentaria, which are widespread in large quantities mainly in funerary contexts, throughout the Roman Empire. This situation is somehow similar in terms of percentage, with that encountered in the free-Germans area, reflecting the taste of the barbarian elite for luxury goods of daily use. Another observation can be made on what's concerning the origin of these goods. According to shape and decorative techniques it seems that the great majority of the vessels have an oriental origin (Syro-palestinian and Asiatic workshops) although we cannot deny also an Italic provenance at least for some types of beakers and bowls. Their ways of penetration in the east-Carpathian territory are not easy to trace but we can assume that they came either from the North Black Sea region in the case of oriental products, or following the main water routes from the Danube to the Siret River. The hypothesis of a local production, by itinerant craftsmen can also be taken into consideration due to the high percentage of demand.

Still, the panorama is far from being complete. We hope that the future study of the unpublished archaeological material lying in the Museum collections will throw a new light in this matter.

Early Byzantine Glass from Eleutherna Pyrgi (Sector II)

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The site of the ancient Greek city of Eleutherna (Central Crete) has been explored since 1985 by the University of Crete. The Pyrgi hill has always been, through the ages, the acropolis of the ancient city. Its central plateau has been excavated by Th. Kalpaxis and is now being excavated by Ch. Tsigonaki.

The excavation has brought to light the Early Byzantine phase of occupation: a settlement organised around a church which begins in the 7^{th} century and continues through the 8^{th} century A.D.

Amongst the material, many glass fragments have been found, mostly from goblets and lamps. The chronological range of the glass material is quite restricted in the Early Byzantine period (the study has just started and is still in progress).

The most important feature is the presence of some pieces attesting the existence of glassworking. This is quite interesting as until now glassworking activity has only been recognized in two Cretan sites: at Knossos, for the Roman period, and Gortyn, for the Roman and Early Byzantine period. In fact, the glass found in Crete is not well known at all. Only the material from the two sites aforementioned has already been extensively published. It is worth mentioning that these happen to be the two most important cities of Crete in the Roman period, Gortyn being the capital city of the province. That is why a study of the glass material from the smaller city of Eleutherna will greatly complete the picture we have on Cretan glass, and especially for the yet not well known Early Byzantine period. Furthermore, it will be interesting in the future to compare the material from Sector II with that from Sector I, currently studied by K. Nikita.

Roman glass as the ritual object and its iconography

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Background: Glass in ancient time was very cheap and accessible material, it is obvious that it was used also during rituals. In this lecture I will discuss its use as the ritual object especially with the connection of contemporary iconography and literature. I will show images of glass vessels on mosaics and frescoes and also mention descriptions of such glass at ancient authors. Mainly glass lamps are shown this way but we can also find other objects.
Results: There are several mosaics and frescoes that show us the usage of glass vessels in ritual context. Most of them are dated to the 3rd century AD and later. They are both pagan and christian, as well as we can find some minor mentions with the connection of jewish religion. As for the literary sources, they mainly refer to the lighting of christian churches. Also amount of images of glass lamps show us the importance of light in late ancient world. It was important both for pagan population (e.g. lighting the deceased during burials) and christians (e.g. everlasting light in the churches).
Conclusion: We can suppose that glass had its role during the rituals in ancient Rome. There are only a few iconographical and literary sources but these pieces prove this presumption.

The Influence of Dewatering and Carbonation on the Strength of Lime and Cement Mortars

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This work investigates the effects of carbonation on the strength and microstructure of dewatered mortars manufactured from hydrated calcium lime (CL90), natural hydraulic limes (NHL) of classification 2, 3.5 and 5 and Portland cement (PC), with binder/aggregate/water ratios of 1:2:0.78. Dewatering was achieved by placing the mortars on a high porosity brick. Dewatered and non-dewatered mortar specimens were exposed to an atmosphere of nitrogen and nitrogen containing 400 ppm carbon dioxide with a relative humidity of 65%, at 20^{o}C for periods of 14, 28 and 56 days. Following curing compressive strengths were compared to evaluate mechanical performance. Structural morphology was identified using scanning electron microscopy. Results indicated that the CL90 mortars were affected by carbonation but unaffected by dewatering. However, carbonation and dewatering leads to an increase in compressive strength for hydraulic limes and cement mortar mixes. Scanning electron micrographs revealed microstructural differences between the various binders which are associated with strength.

Glass gaming pieces from the Viking-age early urban centre Gnezdovo

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Board games were widely spread in Western Europe, Byzantium and Islamic Orient in the Middle Ages. Archaeological evidence survives for the game of *hnefatafl* played with two sets of counters, one of which defends the king (Murray 1952). Gaming sets containing boards, dice and counters made of bone, antler, clay, stone and amber are known from Anglo-Saxon and Scandinavian graves in England, France, Germany, Northern countries, Poland and Russia (Gabriel, 1988; Korzuchina, 1964; Riddler, 2007). Gaming pieces of glass are much rarer. Gaming sets and single counters were found in the rich graves in Norway, Sweden and Russia. The Russian finds dated to the second half of the 10th century AD come from Kiev and Chernigov in the Middle Dnieper region and from the early urban centre Gnezdovo situated in the Upper Dnieper region. During the Viking Age Gnezdovo was the great centre for merchant travelling between the Baltic and Black seas. The archaeological complex situated near the present city of Smolensk originally consisted of over 4,000 barrow graves dating from the early 10th - to the early 11th century as well as the vast settlement of the same period.

Definite game pieces of translucent purple, turquoise, dark green or green-olive glass were found at Gnezdovo in one of the richest inhumation chamber-grave (13 specimens), in the hoard of dirchams combined with ornaments (1 specimen) and in the cultural layers of the settlement (4 specimens). The pieces are all of similar size (18x24mm) and form, hemispherical but with flat base. Almost all the counters show negative traces of a punty rod slightly chipping the top of hemispherical surface. Molten glass filled the mould first, after that punty was fixed on the top of hot glass and hemisphere was drawn out. In certain cases cavities of punty were decorated by gold foil.

Discussing the origin of the glass gaming pieces we should exclude the small counters of opaque glass produced by the provincial Roman workshops up to the end of the 4th century AD. The earliest Viking-age glass counters from Cunnarshaug (Rogaland, Norway) and grave 624 from Birka (Upland, Sweden) dated to the 9th century (Lindqist, 1984). They are totally different from the Roman gaming sets. Backgammon (nard) was one of the most popular games in Central Asia and Iran since the 4th century AD (Semenov, 2007). Gaming pieces of glass dated to the 9th-11th centuries were found in Iran, Iraq, Afghanistan and Egypt (Kröger, 1995; Carboni, 2001). However, their conical form and mosaic technique differ from the Viking-age glass counters.

Chemical composition of the glass gaming pieces from Gnezdovo probably confirms assumption about their Continental origin argued by H. Arbman in 1937. We have analysed 10 gaming pieces using non-destructive XRF (Tornado spectrometer with Rh-tube, Bruker AXS). All gaming pieces analysed are very low in soda and high in potash and magnesia. The potash-rich composition reflects the use of ashes of inland trees appeared in northwestern Europe from the late 8th – 9th centuries

(Henderson, 1993; Wedpohl, 2003). Counters of turquoise glass show relatively high content of lime and lead. Both components reduced the melting point of glass but made it fragile. Possibly it explains the poor preservation of gaming pieces produced of turquoise glass. Purple items contain high iron, copper and manganese; olive-green pieces are of low lime and lead but they are characterized by extremely high iron.

There is no evidence of the places of glass counters' production in the Viking-age Scandinavia as well as in Carolingian or Ottonian Europe. Evidence for glass working is totally absent in Gnezdovo. High-quality gaming pieces of glass, which are definitely to be classified as luxury goods, available only to the aristocracy and to the richest merchants, came to Gnezdovo from Scandinavia. Their dissemination was probably related to diplomatic exchange rather than trade.

Technological change or consistency: strontium isotope analysis of Egyptian faience from the Middle Kingdom to the New Kingdom.

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Faience is considered to be the first 'high-tech' non-clay ceramic (with a chemical composition of soda-lime-silica) and has been produced for over 6,000 years. The overall objective of this research is to understand how the technology and chemical composition of faience in Egypt changed from the Middle Kingdom (2040-1640 BC) to the New Kingdom (1570-1070 BC) by analyzing beads from tombs at Abydos. This includes developing a methodology for determining the raw material sources utilized in the production of faience, specifically the colorant, silica and alkali sources using several different analytical methods (SEM-EDS, CL, and EBSD). However, these methods brought up several other questions regarding the alkali and after reviewing several successful cases of strontium analysis on ancient soda-lime-silica glass this research set out to recreate this success with Egyptian faience.

This is the first time strontium isotope research has been conducted on faience and will form an integral part of the development of a scientific methodology for studying faience no matter where it is found in the world or from what time period. As part of this process the project aims to investigate the alkali and silica sources utilized in the production of ancient Egyptian faience. By investigating the origin of the basic raw materials it will be possible to discuss if local faience production was possible or whether there were distinct regions that specialized in this material. Changes in the source of the raw materials may also indicate different choices made by the producers and may be indicative of broader social or economic issues. This analysis also has the potential of providing information useful to other fields of research concerned with, for example, production strategies, trade and exchange, as well as other forms of interaction that involve the movement of materials.

Strontium isotope analysis has the potential to provide significant information on the provenance of silica and alkali sources used in the production of faience.

This project tested two hypotheses: whether the significant differences in strontium isotopes determined in soda-lime-silica glasses can also be determined in faience (a material of similar composition) and that the differences identified are attributable to the same basic reasons; the different origins of the soda and the lime. The second hypotheses tests whether the origins of the soda and lime in Egyptian faience differ between samples of faience made during the Middle Kingdom and faience made in the Second Intermediate Period and the subsequent New Kingdom. This will be vital data for discussions about the nature of social and economic change in Ancient Egypt and the surrounding areas.

Glass of Amenhotep II from Tomb KV55 in the Valley of the Kings

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In 1907 Theodore Davis and Edward Ayrton discovered a tomb which they published in 1910 as the "Tomb of Queen Tiyi". It has subsequently become one of the most discussed and disputed tombs in Egypt's Valley of the Kings and is now better known as tomb KV55. Recent work on the human remains found in the tomb suggests that it may actually be the burial place of the 'heretic pharaoh' Akhenaten (1352-1336 B.C.).

Amongst the finds from this puzzling tomb comes a piece of white glass bearing the cartouche of Amenhotep II. The fragment has a brown wavy line running through the opaque white and the cartouche is made up of blue, red and yellow. The fragment is now in the Swansea Museum in South Wales and we are indebted to them for permission to sample the fragment.

Kate Bosse-Griffiths, writing in 1961, believed the sherd to be a missing piece from a vessel discovered in 1898 by Victor Loret in the tomb of Amenhotep II (1427-1400 B.C.) (tomb KV35). That vessel is now in the Cairo Museum and unavailable for analytical study, so the opportunity to examine an important fragment of glass from it and dating to the period before the first excavated glass works at Amarna is a welcome one.

This paper reviews the evidence for the discovery of this Amenhotep II fragment and examines its composition, thus allowing it to be compared with known compositions from some of the earliest Egyptian glass, that from the reign of Thutmose III (1479-1425 B.C.), father of Amenhotep II. This earliest glass has been the subject of renewed interest in recent years but analytical studies of the glass of Amenhotep II are less common.

The sample offers the opportunity to examine the compositions of the blue, brown and white sections of the glass. The compositional data is used to establish the likelihood that the glass was manufactured in Egypt and whether local mineral sources might have been used for colouring the glass.

A preliminary study of Roman Glass Fragments from Thessaloniki Agora

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In this paper we studied 12 samples of Roman glass, using the analytical techniques of micro X-ray Fluorescence Analysis (m-XRF), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Flame Atomic Absorption Spectrometry (FAAS).

The samples come from old excavations of the Roman Forum of Thessaloniki, which is currently located between the streets, Olympou and Philippou, and started being built during the second century AD. It occupied an area of about two hectares in the heart of the city. The samples were provided by the Archaeological Museum of Thessaloniki.

The study of the samples and their experimental results give answers to questions concerning the origin of the samples as well as the manufacturing technology of glass.

The high concentrations of sodium oxide ($N\alpha_2O$) and calcium oxide (CaO) indicate that all the samples belong to the category of soda-lime glasses. The relatively low concentrations of potassium oxide (K_2O) and magnesium oxide (MgO) support the view that natural soda was used as alkaline material. Its origins cannot be determined precisely, it is either natron of Egypt or it comes from the region of Macedonia.

The study concerning the colours of the samples showed that cobalt oxide (CoO), even at very low concentrations, is responsible for the blue color. Moreover, copper oxide (CuO), in conjunction with cobalt oxide (CoO) is responsible for the blue-green colour. Chromium oxide (Cr_2O_3) is responsible for the amber colour. The white opaque is probably due to dispersion in the mass of glass of tin oxide (SnO), used as an opacifier. The purple colour is due to the high concentrations of manganese oxide (MnO).

Finally, we observed the combined use of two decolorizers manganese oxide (MnO) and antimony oxide (Sb_2O_3), which is related to geographical, chronological and technological factors. There was a deliberate addition of antimony in the melt to produce a more bright glass, or antimony glass was used as an additional filler material for the production of glass that was discolorised by manganese (Mn).

Archaeological Glass Weathering and Resulting Implications to Analytical Glass Studies

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Analytical and technological study on archaeological glass was undertaken with emphasis placed upon non-destructive approaches. Scanning Electron Microscopy (SEM) coupled with an EDX analyzer was applied for the detection of the major elements and for the study of samples' topography and X-Rays Fluorescence (XRF) was used for tracing the minor and trace elements present in the glass batch. Various assemblages of Mycenaean glass have been studied analytically in an attempt to tackle specific archaeological questions. The assemblages comprise glass beads and relief plaques from excavation contexts at the sites of Palaia Epidavros, Kazarma, Ancient Asini, Mycenae and Pylos. In the course of the research a set of 70 samples was subjected to scrutiny. A major hindrance readily arose from the beginning of the examination, since various alteration effects were detected. In some cases the signs of deterioration were readily visible in hand specimen, whereas, in others, glass degradation was detected only microscopically, as already presented in literature. Weathering of excavated archaeological glass surface is the results of an acidic attack occurring sometime during the burial period, usually ending up to a surface layer depleted in alkaline and alkaline earth oxides.

In the course of the analytical investigation a variety of corrosion patterns was detected in the overwhelming majority of the samples, forming three major categories of implications: alkaline leaching, uptake of environmental pollutants and distinctive areas of inhomogeneity. These implications to the technological investigation of archaeological glass caused by alteration effects are discussed in the present study along with all the analytical problems stemming from the poor preservation state of the artifacts. Caution to sampling strategies and analytical tackling is drawn. Additionally, an attempt is made to measure the expected deviation with respect to the corrosion state of the artifacts by means of comparing 'healthy' glass areas to weathered ones. Overall, the study aspires to contribute to our knowledge of corrosion phenomena on glass objects and suggest ways of dealing with the analytical problems arisen by means of a proposed protocol of investigation and approach.

Raman spectrometry investigation and identification for natural and ancient glasses

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Raman spectroscopy allows a non-destructive remote analysis for crystalline and amorphous phases can be identified. Last-generation instruments are portable, which allows “in situ’ examination in museums, on archaeological sites, in the geological open field etc.

This paper gives an overview of the potential of the Raman-spectrometry technique to analyze both natural mineralogical samples and ancient glasses. The ancient glasses came from the Jewellery collection of Byzantine and Christian Museum and dated in 7th cent. A.D. The investigated archaeological samples are two golden earrings pair, with olive green glass beads and blue glass beads respectively, from the Treasure of Krateghos (Mytilene).

Selected natural glasses are Libyan Desert Glass (Impact Glass), Thailandite Tektite (Impact Glass), Moldavite (Impact Glass) as well as, Obsidian samples from Nisyros, Melos and Eastern Turkey (Kars). Were we performed to show the capability of Raman spectroscopy for answering archaeometric questions?

$\delta^{18}O$ and chemical measurements of Roman glass from Greece

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Archaeologists have argued that in Greek antiquity glass was not made but the vitreous material was imported from different areas of the East Mediterranean coast. Especially in the Greco-Roman age, glass artefacts in Greece are considered to have been manufactured using raw glass made with sand and natron, and produced in Egyptian and Near East glass-making factories. These factories probably produced only batches of raw glass and not necessarily vessels or other objects. The importation of raw glass complicates more the existing problem regarding the identification of the origin of the basic components of glass and the fusion processes. Thus, it is of utmost importance to distinguish the origin and composition of 'Roman' age glasses from glasses imported from other provenances. In this study chemical and isotopic methods, were employed for the identification of the fingerprint of Roman glasses manufactured in Greece, for distinguishing the different raw materials and fluxes used and for defining the production technology.

Two groups of glass samples of the Roman period (first to sixth century) from Thessaloniki were studied by $\delta^{18}O$ and chemical analysis.
The isotopic results obtained from the Greek glass ($\delta^{18}O$=15.5‰ vs SMOW) of the Roman period, first group (10 samples), are very close to those obtained from the Italic Roman glass suggesting, in accordance with Pliny, that probably the raw glass of these finds was made using natron and sand, respectively from Egypt and Belus or Volturnus.

The isotopic composition of the second group (7 samples) defines a very widespread area of data (from 15.2 to 22.6‰ vs SMOW) that is not consistent with the supposed origin of their raw materials, their composition and their age. In particular, the analysed glass samples differ in the type of flux and production technology. Chemical results suggest two different groups of glasses: soda-lime silica and soda plant ash glasses.

The glasses (5 samples) appertaining to the soda-lime silica type were produced with siliceous feldspars, or calcareous sand. The range of $\delta^{18}O$ values is between 15.2 and 18.6‰. Excluding the more enriched values (18.6‰ and 17.3‰) the rest of the values present a mean isotopic value (15.5‰) that is quite similar with the Roman glass according to the literature. The high isotopic value (18.6‰ and 17.3‰) and the significant isotopic difference (1.3‰) suggest that these glass-objects were manufactured from different raw materials.

The basic raw material used in the soda plant ash glasses (2 samples) was probably siliceous sand or quartz pebbles. The $\delta^{18}O$ of these plant ash glasses was "particular" because it is very high (22.5‰ vs SMOW) and also higher than plant-ash glass as suggested from the bibliography (<15‰ vs SMOW). Probably this oxygen isotope composition indicates that these glasses were imported and not produced with sand from the famous sources of Belus or Volturnus. Also it is suggested that these glasses were made at different factories and with different production technologies.

Evaluation of archaeological glass samples from the archaeological site of Vergina via a combination of analytical techniques *(μ-XRF, ICP-AES, AAS)* and subsequent statistical analysis

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The chosen subject falls within the domain of archaeometry and focuses on the study of archeological glass from the site of Vergina (Macedonia, Greece) using a combination of analytical techniques. Our goal was to answer certain archaeological queries regarding the provenance of the samples and, additionally, to investigate the necessary steps for organizing a holistic research approach for similar analytical problems and the ways of extracting the maximum amount of information from our results. A total of 18 samples from the excavation of Vergina were examined, including 17 glass fragments and glass paste samples as well as a clay matrix sample.

The techniques chosen for the analysis of the samples were micro – X Ray Fluorescence Spectroscopy (μXRF), atomic emission spectroscopy using inductively coupled plasma (ICP-AES) and, finally, atomic absorption spectroscopy (AAS). The statistical analysis of the results included a Student t-test for the determination of the correlation between the μ-XRF and ICP-AES/AAS techniques, as well as the application of hierarchical classification algorithms, cluster analysis and principal component analysis (PCA). Finally, regarding the clay matrix sample, we employed a three dimensional laser scanning technique in order to obtain an accurate digital model of its inner surface. One of the most important conclusions we reached was the determination of the site Pikrolimni (Macedonia, Greece) as the source of natron in the glass making process, based on the samples' K_2O and MgO ratios. The high concentrations of Al_2O_3, Fe_2O_3 and MgO of the glass paste samples suggests they constitute by-products of the glass making process and also support the employment of recycled materials. Furthermore, sample 008, the only one exhibiting intense coloring, was found to owe its blue coloration to the high concentrations of Co (0,080%) and Cu (0,021%), elements known as common coloring agents in glass.

Additionally, the statistical analysis of the elemental compositions before and after the cleaning of the glass fragments was keen in classifying the samples according to their prior proximity within the excavation site and also their state of corrosion. Finally, regarding the results of the clay matrix, we reached the conclusion that it was used for the smelting of small glass items, probably decorative elements or jewels. The inner surface of the molds did not exhibit any signs of modulation targeted in engraving certain pictorial elements onto the resulting item's surface.

Mycenaean Glass Finds from S.W. Peloponnese Sites

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Twelve glass finds (beads and plaques) displayed in the Archaeological Museum of Kalamata were studied within the context of Mycenaean luxury items from Nestor Palace and nearby archaeological sites of the S.W. Peloponnese. Emphasis was placed upon blue glasses. The items were examined by means of Optical Microscopy (OM), X-Ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM-EDAX). No clear systematic compositional trends arose from this study an observation which may be attributed to the non local production of the items; nevertheless, the fact that these glasses span a period of four centuries (15th-11th century BC, which coincides with the early glass experimentation in the area) suggests that compositional variations may be a reflection of early technological evolution.

The study reports on the technological characterization of the collection and also a comparison to other parallel glass finds excavated from the same areas and published in scientific literature, is attempted.

The discovery of cobalt colourant raw materials as inclusions within Anglo-Saxon glass beads

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Cobalt is one of the earliest colourants used in ancient vitreous material production. Its use can be traced from the 3rd millennium BC until the present day. However, identifying the specific cobalt raw materials used in ancient glass production has been a problem for archaeological scientists for decades. Many analytical studies of cobalt-blue glasses have used the presence of minor or trace elements, or increased levels of major elements, to suggest the raw materials that may have been used. These sources range from minerals associated with silver ores found in Central Europe to the use of cobalt-rich alums in New Kingdom Egypt [1,2]. However, some studies have discussed the compositional analysis of cobalt-containing inclusions actually found within glass objects to provide a direct means of identifying the raw material sources used [see 3]. Further discoveries of cobalt-rich raw materials in similar primary contexts that directly link them to glass production are therefore of great importance to the study of ancient glasses.

Using a combination of scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) and X-ray fluorescence (XRF) glass vessels and beads from the Anglo-Saxon site of Ringlemere, Kent, have been analysed. Bulk compositional analysis was able to identify variations in the recipes used to produce the glasses. In particular the use of different cobalt colourant raw materials can be suggested by significant differences in the minor element composition of blue glasses. Various additions are made to the basic raw materials of glasses to alter their physical or chemical qualities. Occasionally these materials will not fully dissolve in the glass batch. This can be an intentional result, in the case of some opacifiers, or unintentional, in the case of most colourants and impurities in the basic raw materials. Where it is unintentional it will often be the result of insufficient temperature resulting in incomplete melting of the batch.

It was possible to observe and analyse a large number of inclusions in prepared sections of many of the coloured beads from Ringlemere using SEM-EDX. They include many impurities added along with the basic raw materials, high in calcium, aluminium, titanium and magnesium, but also occasional cobalt-rich inclusions. These inclusions have been found in translucent blue beads with mottled opaque red decoration, a type which is believed to have been traded into the UK from the Continent [4]. The inclusions are characterised by high levels of iron (60 wt.% FeO), cobalt (20 wt.% CoO) and aluminium (15 wt.% Al_2O_3). Further analysis using Raman spectroscopy was carried out to identify these inclusions.

The discovery and characterisation of these inclusions located within a glass object provides a definitive means of identifying an actual raw material used in Anglo-Saxon cobalt-blue glass production. The sources for the raw materials used in the glasses found at Ringlemere are diverse and as such provide a means of establishing trade patterns across Europe. This poster will present the findings of this analytical study and how they fit into the wider picture of technology and trade in first millennium AD glass production.

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A radioactive shamanic apron: analysis and conservation

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A late 19th shamanic apron produced in Siberia was selected for display at the British Museum. The apron, made from reindeer hide, is heavily adorned with free moving amulets, metal rings and tassels threaded with colourful glass beads. Prior to a scheduled display in the Museum galleries this object was assessed by conservators. This assessment highlighted that some of the beads showed signs of deterioration. Initially it was thought this damage may be physical, caused by adjacent heavy ornamental metal rings. After further examination under a visible light microscope two factors indicated that the deterioration was the result of the phenomenon commonly referred to as glass disease; uniform cracks or crizzling could be seen across the surface of the translucent yellow beads. Small fragments of these beads were sacrificed for scientific analysis to discover how their chemical composition may have contributed to this deterioration.

Compositional analysis using scanning electron microscopy with energy dispersive x-ray spectrometry (SEM-EDX) confirmed that an unstable composition was the cause of deterioration in the yellow beads. This instability is caused by high levels of alkali (potassium and sodium) and low levels of stabilising components (calcium, magnesium and aluminium). As it was not possible to identify the compositional reason for the beads' yellow colour using SEM-EDX, surface X-ray fluorescence (XRF) analysis was carried out. The wider spectral range of the XRF analysis allowed the identification of uranium. Although the uranium does not affect the stability of the glass it has the potential to be harmful to health so its presence was investigated further. Uranium generally produces green or yellow when used alone as a glass colourant, but many other colours are achievable when combined with other metal oxides [1]. It was therefore decided that beads of all other colours on the apron should be checked using ultraviolet (UV) light and a Geiger counter. None were found to fluoresce under UV light or to be emitting radiation above background levels. The results of the analytical project posed two important questions:

Firstly, what conservation options are there to reduce the rate of glass deterioration and enable this object to go on display? Due to practical limitations and resource constraints it was not possible to house the apron in a location with the climatic conditions necessary to greatly slow the deterioration of the beads. This being the case, an interventive approach was chosen. Localised consolidation was carried out to impart temporary strength to deteriorating beads in the knowledge that they will continue to deteriorate. The apron will be displayed with the recommendation that regular monitoring is carried out. This decision was taken to allow maximum access to this unique object before the yellow beads, intrinsic to the object, fragment beyond repair.

Secondly, will the levels of radiation emitted by the object pose a danger to Museum staff and visitors? The levels of radiation emitted by the yellow beads were assessed using a dose rate and contamination meter. The results identified radiation emission at levels only slightly above background. These levels do not represent a serious danger to museum staff and the public will be at no risk when the object is on display in the showcase. However, safety precautions must still be observed, as prolonged or repeated exposure would lead to a cumulative danger.

This poster will outline the analytical and conservation work carried out, and the recommendations for display and handling of this unique object. The conclusions drawn from this study are of importance to scientists and conservators working on a wide range of multi-media museum objects that are either actively deteriorating or pose a potential threat to museum staff or the visitors.

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Chemistry, Structural and Technological Examination of a Greek Glass Archaeological Collection Spanning from the Mycenaean to Roman Period probed by SEM/EDS, IR and Raman Spectroscopy

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A series of archaeological glass fragments from Greece were studied by Infrared and Raman spectroscopy. The historic samples included:

[1] Blue vitreous relief fragments from the Mycenaean Period (Palaia Epidavros, LBAIIb-IIIa)

[2] Blue glass beads and vessel fragments from the Classical Period (both Thebes, 5th century BC)

[3] Mostly colorless, but also blue fragments of Roman vitreous tableware (Thessaly, 3-4th century A.D.) Some fragments exhibited pale, translucent to transparent colors ranging from yellow to brownish, or greenish to turquoise and light blue.

The chemical composition of most samples was available from SEM/EDS and XRF studies.

The deep blue color of the Mycenaean and Classical samples was either due to CuO (0.1-0.52 wt%) or a combination of CuO and CoO (0.09-0.38 wt%).

The three blue classical vessel fragments all contained decorative layers. One exhibited white lines, one white and yellow decoration, and a tiny fragment a white layer of undisclosed geometry. These decorative layers were analyzed by micro-Raman and micro infrared spectroscopy and four different pigments could be identified. The yellow coloring was due to Naples Yellow, a lead antimonate $Pb_2Sb_2O_7$, embedded in a silicate-based glaze. In the two samples with white decorative lines the white color was due to the opacifier $CaSb_2O_6$, which was also found in the yellow decorations. The third sample with white decorations showed in addition to $CaSb_2O_6$ the typical Raman signatures of rutile TiO_2 and Calcite $CaCO_3$.

The Roman samples are basically all soda-lime silica glasses but belonged either to the high iron manganese titanium (HITM) or the Levantine composition, although recycled, although mixed compositions were present as well.

Raman spectroscopy was hindered by a strong fluorescence in the Roman samples, but the Q^n speciation of the different tetrahedra with "n" bridging and "4-n" non-bridging oxygen atoms was determined from the infrared spectra. The Q^n distribution could be correlated to the glass composition, the state of weathering, and to changes in the fictive temperature T_f encountered by the samples during glass production. The last point is based on the disproportionation reaction:

$Q^3 \xrightarrow{t_f} Q^4 + Q^2$ for which the equilibrium is shifted to the right as the melting and annealing temperature of the glass sample is increased.

The problems of fluorescence encountered in the Raman measurements of the Roman samples did not extend to the older Mycenaean and Classical glass samples.

The Mycenaean Relief fragments deviated in the infrared spectra from all other measured samples as the spectra resemble rather those of a weathered low alkaline borosilicate glass than the expected soda-lime-silicate glass composition. However, spectra taken on relative fresh cuts are consistent with soda-lime-silicate glasses. Measurements on the cross sections show that only a very thin layer of several microns on the front and back of the sample are of the borosilicate type. White spots on the sample surface showed infrared spectra typical of vitreous silica. Because of the thinness of the layers boron could not be detected by SEM/EDS, though reflectance infrared measurements were not influenced by the bulk glass composition. Possible boron sources and chemical reaction mechanisms leading to the formation of the outer layer will be discussed.

Lefkandi's vitreous beads at the beginning of a new tradition of vitreous materials in the Aegean

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In this paper I would like to present the vitreous beads (glass, faience, frit) of especially the Toumba cemetery of Lefkandi, and place them in the framework of the wider Eastern Mediterranean. Not only Greece but also many areas in the East saw an end of glass and faience production, or at least a severe crisis, in the 12th and 11th centuries BC at the end of the Bronze Age. Beads were the first objects which started being made and distributed again in the Early Iron Age. Lefkandi on the island of Euboea occupies a special position as its beads belong to the earliest beads from the Aegean after the breakdown of the Mycenaean bead culture and its decline and eventual disappearance in LH IIIC. Furthermore, the quantities of vitreous beads used as burial gifts surpass all contemporary find places of the Early Iron Age Aegean. The use of beads in the Early Iron Age differs a lot from the Late Bronze Age bead culture. The only visible connection to the past is found in the necklace of the female burial in the Toumba Building. Otherwise, the beads should be connected rather with the contemporary East. But the people of Lefkandi were quite selective in their choice of beads. This resulted in differences of the Aegean bead culture to the Eastern Mediterranean.

A glass-making technology study used in Amathouda (Cyprus), 5th - 6th century A.D. by Micro X-ray Fluorescence Spectroscopy (μ-XRF), Inductively Coupled Plasma Emission Spectroscopy (ICP-AES), Flame Atomic Emission Spectroscopy (FAES)

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This dissertation is on the subject of the technology of glass-making that was used in Amathouda (Cyprus) during the 5th – 6th century A.D. For this purpose twenty two samples of glass were analyzed, twenty of which were fragments of glass vessels and two were fragments of glass windows of Amathouda Episcopal Christian Basilica (Cyprus). Initially, the samples were photographed, observed under a stereoscope in order to identify the alteration products and analyzed using a micro x-ray fluorescence spectrometer (μ-XRF). Then the samples were pulverized, dried and dissolved by acid attack using HF - HNO_3 – HCl, which was carried out in a microwave oven. Inductively coupled plasma emission spectroscopy (ICP-AES) and flame atomic emission spectroscopy (FAES) were used for the determination of major and minor glass constituents as well as the trace elements. All the samples were found to be silica - soda - lime type of glass. The fusing agent for these types of glass seems to have been natron (a mineral deposit that is found in the delta of the river Nile in Egypt). A change was observed in the silica source, indicated by the Ti content variation. The samples with superficial black crust have the greater content of K_2O. The hues of the colours mainly develop in glass due to the presence of Fe^{+2} and Fe^{+3} ions, which are found in different ratios. The manganese was used as the decolorizing agent. The elements Cu, Cr, Co, Pb, Ni were not added intentionally to the initial fuse but were introduced as contaminants from the raw materials. This type of glass which is comprised of high iron, manganese and titanium (HIMT) content, was in common use but is of uncertain origin up to the present day.

Glass votive offerings in the Great Rhodian sanctuaries

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A significant number of metal votive zoomorphic small objects dated from the late ninth century BC to the early Hellenistic period (early 3rd c. B.C.), was found in the pan-rhodian sanctuary of Zeus Atavyrios at the top of the homonymous higher mountain of Rhodes; a small part of this group is currently exhibited in the archaeological exhibition for the "2400 Years of Rhodes' in the Grand Master's Palace at the medieval town of Rhodes.

The zoomorphic metal objects were found in the *sacred apothetes* or *bothroi* of the sanctuary, part of which was excavated for a short period in 1927 by the then Italian Archaeological Service. Although the excavation of the sanctuary has not yet been completed, the area has been extensively looted, until recently, due to the remoteness and to the impeded accessibility of its region.

These votives are mainly bronze zoomorphic figurines, mostly animals in a variety of shapes (bulls, buffaloes, oxen, bison, etc.), or models of insects (grasshoppers, etc) with particular morphological features related to the nature of the cult of Zeus Atavyrios in Rhodes, which also, suggest the existence of a local metal-workshop where they were manufactured. Among those of particular interest are the bronze plates in the shape of an ox, which were worthless offerings, substitutes for most precious solid or hollow zoomorphic figurines, some of which have dedicatory inscriptions of their owners.

The current paper refers to matters of chronology and typological classification of these offerings, as well as to interpretation issues associated to the cult and the cult practice in the Zeus Atavyrios sanctuary from the early historical times until the Roman imperial period.

Islamic Glass of X – XV cc in Eastern Europe

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During XX century systematization was determined, regional peculiarities, development periods were defined, chronology was developed, chemical composition and major centers of Islamic glass manufacture were investigated by the works of C. J. Lamm, P. J. Riis, E. V. Sayre, R.W. Smith, F. Bass, Van Doorninck, G. T. Scanlon, von Saldern, R. N. Brill, S. Carboni, D. Whitehouse, J. Henderson, J. Kroger.

In Soviet archaeology, due to the studies made in1960s-1980s by F.D. Gurevich, R. M. Dzhanpoladyan, M.V. Malevskaya, N.N. Busyatskaya, M. D. Poluboyarinova, A. A. Abdurazakov, M. A. Bezborodov, Y. A. Zadneprovskyi, oriental glass has gained a status of incredibly informative source highlighting, first of all, international connections and characteristics of Eastern Europe urban culture. During recent decades geography of the finds has been significantly extended and their quantity has risen (on Middle Volga, in Volga Bulgaria, new Islamic glassmaking center was found (Valiulina, 2005), that gives an opportunity to reconsider former conclusions.

In IX – beginning of XIII cc Islamic glass was commonly represented in Caucasus, in the monuments of Volga Bulgaria and in some Lower Volga cities and towns. In the beginning of X century Volga Bulgaria became a Muslim state. Judging by the materials of the burials, it can be concluded that during X – XI cc Islam spread on the whole territory of the state. True masterpieces of Islamic glassmaking in Bolgar monuments of that age are represented by single finds such as miniature inkwells of colorless glass with carved and overhead ornament which were art wares of Nishapur workshops of IX – X cc and obviously came to Volga not as goods for sale but as items for presents and personal items of merchants or ambassadors.

Finds of Mesopotamian clay tableware with lustre paintings of IX – X cc mark the route of Islamic art works to Eastern Europe at that time – through Transcaucasia (Dvin, Ani) by the Volga-Baltic highway: Sarkel – Bilyar – Ladoga.

It took some time to Bolgar society to realize a need in the fragile and expensive non-essential goods. From XI to XV cc glass tableware, lamps, window glass became a mass component of Bolgar culture and in the capital – Bilyar – its own glass manufacture appeared that was a part of Islamic glass manufacture by its morphological and technological features.

Glass lamps, bottles, glasses with golden and enameled paintings of the mid XIII till XV cc are commonly found not only in towns and burial complexes but also in all major cities of Russ – in Moscow, Novgorod, Turov, Vladimir, Suzdal, Ryazan, Tver, Yaroslavl, Nizhny Novgorod. These finds were a part of Russian aristocratic life.

At that time Islamic glass came to Russ both from West and East through the Golden Horde and the latter was a primary source of this glass.

Orientalism of Eastern Europe of the mid XIII – XV cc has a principal distinction from the Western orientalism: wide acceptance of oriental elements by material and spiritual culture (fabrics, glazed and glass tableware, metal art wares, weaponry, etc.), oriental motifs in Russian architecture and art reflect the initial stage of the formation of unified Eurasian Russian culture. Islamic glassware finds marked on the map of Eastern Europe of mid XIII – beginning of XV cc are another bright illustration of this process.

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