Latest Results and Examination Methodologies of Pre- and Protohistoric Metals and Other Inorganic Materials

1st International Scientific Conference of the UISPP Commission on Archaeometry of Pre- and Protohistoric Inorganic Artifacts, Materials and Technologies

14th October 2016, Miskolc, Hungary

ABSTRACTS

In view of the success and interest shown for the archaeometry session at the UISPP Congress in 2014 in Burgos it was decided to create a new scientific commission in the field of archaeometry. In June 2015 we established our commission with the aim of discussing and promoting archaeometric approaches to lithic technology, metallurgy, ceramics and glass making in Prehistory and Protohistory.

Aim of the conference is the presentation of the results of archaeometric case studies and the examination of methodologies to be employed on Prehistoric and Protohistoric artifacts made of metals or other inorganic materials.

Programme

10:00 Welcome address by the president of the commission - Scientific presentations – metals

B. Nessel, G. Brügmann, E. Pernicka, D. Berger and C. Frank: Tin isotopy on prehistoric bronzes - state of research from an archaeological point of view

A. Giumlia-Mair and S. Ferrence: Analyses of Cretan metalwork

P. Bray and FLAME: Collating large chemical datasets for early metals: Challenges, benefits, and possible ways forward

Coffee break

M. Emami and M. J. Jafari: Preliminary archaeometallurgical studies on bronze objects from "Lama" (2nd Millennium BC), Iran

B. Török, P. Barkóczy and Á. Kovács: Microstructure analysis on metal artifacts from the Carpathian Basin

J. Hosek: Metallographic examination of iron swords – a few notes and examples

Lunch

14:00 Scientific presentations – other inorganic materials

E. Ben-Yosef and O. Yagel: Calcium (CaO) content in metallurgical slag as a proxy for fuel efficiency of ancient smelting technologies

M. Krueger and D. Brandherm: Chemical characterization via pXRF of early Iron Age pottery from SW Iberia

Coffee break

M. Golitko: PXRF and the potentials of obsidian "Big Data"

C. Duckworth: Latest advancements in the application of analytical science to ancient and historical glass production

16:00-18:00 Visit to the laboratories, for use by the Archaeometallurgical Research Group of the University of Miskolc (ARGUM), of the Institute of Physical Metallurgy, Metalforming and Nanotechnology of the University of Miskolc – show and presentations with ATESTOR - OXFORD INSTRUMENTS

Tin isotopy on prehistoric bronzes - state of research from an archaeological point of view

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Our ERC funded multidisciplinary project "Bronze Age Tin" uses a new geochemical approach where prehistoric archaeology, ancient history and geology are combined to decipher the sources of tin and the origin of bronze technology in the 3rd and 2nd millennium BC. The project aims to expand and substantiate published tin isotope compositions and uses MC-ICP-MS to analyze ore samples from known tin deposits and archeological objects via a multiproxy approach. The results will, combined with archaeological context information, lead to a better understanding of the distribution of raw materials and the production processes of tin bronze. The project analyses cassiterite from different tin provinces in the Old World to get a glimpse of the tin isotopic range of different sources and make them broadly comparable. All analytical procedures are carried out by the Curt Engelhorn Center of Archaeometry in Mannheim, while the archaeological work is carried out at Heidelberg University. When it comes to the tin sources used in the Bronze Age in Central Europe currently Cornwall, the Saxony-Bohemian ore mountains, and the Iberian Peninsula seem to be most likely.

The presentation will summarize and compare the results of four case studies. The first one includes bronzes of the early Bronze Age Únětice Culture in the area of Saxony-Anhalt in Central Germany. The chosen artifacts belong to the larger hoards of Gröbers-Bennewitz, Dieskau II and Dieskau III. A major research question was, if local tin from the Saxony-Bohemian ore mountains was used to produce the items or if tin was imported from a different source, especially since the tin of the contemporary Sky Disc of Nebra seems to have derived from Cornwall according to tin isotope ratios while an import of copper from mines in the eastern Alps is highly likely (Lutz et al. 2011; Pernicka et al. 2016). The measured tin isotope values in the bronzes of the Únětice Culture show a fairly small variation.

Sample set II includes bronzes from southeastern Europe. It comprises of 16 objects from Romania from five hoards, including Apa, Sinaia, Borleşti, Maglavit and Predeal, two settlements in Braşov and Truşeşti, as well as third artefact from the Hajdúsámson hoard in Hungary. A dagger and an axe from Crete also belong to the investigated bronzes. Here a major research question was, if the tin isotope values differ from the bronzes of Central Europe and/or if they differ from each other. In general the tin isotope values in this sample set show a larger variation than the Únětice bronzes. The Cretan objects from the beginning of the 2nd millennium BC show tin isotope values, which are higher than those of the southern European sample set. This suggests that different sources might have been used to manufacture the bronzes.

A third sample set includes tin objects of the end of the 3rd and the 2nd millennium BC with different functions from several locations in Europe. Their variation in tin isotope values is higher compared to those of previous sample sets. The same applies to a fourth sample set including Near Eastern bronzes from the 3rd millennium BC, which were found in graves and hoards of Ur, Tell Asmar, Tell es-Suleimeh and Khafajah. The presentation will discuss if the determination of tin isotope ratios suggests the usage of one or more ore sources to produce the bronzes of the different regions in question and how much the sources differ in their isotopic signatures.

Analyses of Cretan metalwork

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This paper presents an overview of the data obtained at this stage of research from the metal objects from various Cretan sites dated to different periods, analysed by X-ray fluorescence spectrometry (XRF) in the frame of an INSTAP project on the metallurgy of Bronze Age Crete, sponsored by the Institute for Aegean Prehistory.

Objects made of copper-based alloys, lead, silver, and gold from various Cretan sites are under study, but this paper focuses on the results obtained from the metal finds from Hagia Photia, Livari, Petras, Gournia, and Mochlos, as sites representative for different periods.

A number of metal finds made of copper-based alloys and silver alloys from Livari Skiadi, Hagia Photia, and Petras can be dated to the Early Minoan IB period (ca. 3000–2900 BC), a time of changes and innovations. The analytical data demonstrate that in the field of metallurgy there were important discoveries and experimentation with alloys and technologies. A number of daggers show very high arsenic contents that induces inverse segregation (or arsenic sweat) on the surface, creating a silvery sheen on the blade surface. The aim of the metal artisans was the production of silver-coloured daggers to be used for ritual purposes only. This is confirmed by the fact that also silver-alloy daggers have been identified.

Gournia is a Late Minoan I settlement (ca. 1625–1450 BC), excavated in 1901–-1904 by Harriet Boyd Hawes. The objects analysed belong to the collection of the University of Pennsylvania Museum of Archaeology and Anthropology (Penn Museum). The analyses showed that many of the copper-based alloys contain both arsenic and tin. The objects with the highest tin content are daggers and knives, while many of the everyday tools and implements are made of unalloyed copper. The copper employed for decorative or representative objects is better purified, while the copper used for small parts, such as for example rivets, contains more trace elements. Tweezers and so-called weaving hooks seem to have been considered decorative and representative status symbols in the society of the time. Gournia must have been a metallurgical centre, as new excavations discovered furnaces and metallurgical residues.

The Late Minoan I–III town of Mochlos was an important port of trade, and the excavations brought to light a large number of metal objects of all kinds, a few of which date to the middle part of the Late Minoan III period (ca. 1310–1200 BC). Several finds are of particular interest and indicate clear Egyptian influence.

Collating large chemical datasets for early metals: Challenges, benefits, and possible ways forward

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Over the last twelve years the research laboratory at Oxford (RLAHA) has slowly been building a large digital archive of chemical analytical sets for early metallurgy. Based primarily upon existing 'legacy' datasets of published and private work, our archive now amounts to scientific data on almost 100,000 artefacts, stretching from the earliest metallurgy to the Industrial Revolution. This paper will briefly describe the aims and intentions behind this effort.

Collating, checking, and organising this mass of data is a significant database challenge. What may appear to be obscure, mundane questions such as 'what does a blank cell represent' have major interpretative implications. Finding duplicates, mistakes and errors is time consuming and sometimes practically impossible. Designing a flexible and powerful database structure has taken many years and currently involves a series of information specialists, and links with CIDOC-CRM community.

How to interpret this mass of data is again a challenge; requiring statistical, presentational, archaeological, chronological, and GIS innovations. My paper will briefly introduce the ERC-supported *FLAME* (FLow of Ancient Metal across Eurasia) project as a case study. This is a five-year effort to investigate first and second millennium B.C. metallurgy across the full extent of Eurasia, from Iberia to the Pacific Coast of China.

By reusing legacy data, and building a rich and diverse database we argue that we can leave behind the restrictions of a 'provenance' hypothesis and move towards a 'characterisation' hypothesis. Large datasets contain structures that reveal relationships beyond ore – artefact - deposition point. Though difficult, we aim to write histories of the flow of metal on multiple-scales. This requires and leads to new relationships between laboratory, field and museum based archaeologists.

The *FLAME* team:

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Preliminary archaeometallurgical studies on bronze objects from "Lama" (2nd Millennium BC), Iran

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Lama Cemetery is located in the west of Zagros orogeny, 25 km northwest of Yasuj, in Kohgiluyeh and Boyerahmad Province. The cemetery was discovered in 1999 while being excavated for construction of the Yasuj-Isfahan Road. Unfortunately, many of structures were destroyed. Archaeological expedition carried out in this region in order to undertake a rescue project. The teams began the excavation and restoration in 2012. During six months of field working 53 prehistoric cemeteries were discovered. The next season of excavation was started in August-September 2008, through which 8 new tombs were discovered. The most common structural feature of graves includes stone structures with different sizes. The other objects include; potteries, bronze objects, rings made of silver and iron tools scattered inside and outside of the grave cavity. Buff and red pottery with continuous painted lines and triangular decors, inclusive different metal tools were the main evidence for dating cemetery to Middle Elamite II, III and neo Elamite I (1400-800 B.C).

The use of tin bronzes at the Iranian plateau seems to start about 500 years later than in Mesopotamia. One explanation could be that at the Iranian plateau, there was no direct access to tin sources until the 2nd millennium BC. The found included 33 needles, 11 beads, 42 rings, 13 bracelets, 18 arrow points, 2 lance points, 3 unknown tools and one bronze rivet. It seems that most of the artifacts were decorative, while some may have been used as weapons. A few of the objects have geometrical carved patterns.

The objects are analyzed with respect to their chemistry and mineralogy by means of different techniques such as ICP-OES, OM and SEM-EDX in order to have representative results. The results show high verities concerning the Cu/Sn ratio in the metallic core of the objects.

The variety of tin content proves that the objects have not been made by a particular alloy proportion to reach a homogenous bronze composition such as adding a separate amount of tin to copper and melting them, but an uncontrolled process is used to produce tin bronze alloy, such as co-smelting, cementation, recycling or smelting copper-tin containing ores.

Further, the use of arsenical copper and tin bronze together in a single vessel marks the phase of transition from an accidental/deliberate Cu–As alloy/alloying to deliberate Cu–Sn alloying in the Bronze Age of south-western Iran. The smelting of copper sulphide ores to produce copper alloy objects is another significant aspect of the results of these analyses.

Microstructure analysis on metal artifacts from the Carpathian Basin

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To able to analyse the microstructures of metallic artefacts, have a great impact on archaeological research. The main task is to identify the special features of the raw material and the process technology by microstructure analysis and metallography. This information could give a great support to able to describe how the metal working and trading happened in the ancient live, etc. Therefore, the accurate measurements, and correct technical interpretation are very important.

In this field, there are several hazards. To avoid these, the metallographer has to perform the tests carefully. The interpretation of the results also needs deep knowledge on metallography and metallurgy. This means special methodology has to be used in the metallographic examination. Present days several physical methods are developed in the field of microanalysis. However, ARGUM uses the classic methods and equipment for their own research.

These methods are the optical microscopy, micro-hardness measurement, scanning electron microscopy with EDS or WDS microanalysis. The usage, accuracy and the limits of these methods are well known, which has a great importance during the interpretation.

Another important task is the sampling. There are a several question about the sampling. During the sampling, it had to take into consideration the assumed processing technology. It is important to take the relevant sample, to achieve the maximum of results. This show, that the best way, when the metallographer helps to take it with the restorer.

As it mentioned earlier the deep knowledge in metallography and metallurgy is important during the whole investigation. There is basic difference between copper and iron based alloys. Copper alloys from the middle Bronze-Age are in a near equilibrium state. So the equilibrium phase diagrams can give a great help to analyse the micrographs. Extends to the micro-hardness measurement, it is possible to perform a good phase-analysis. Beside this "classic way" the SEM-EDS methods quickly can prove these results. Besides that, there are several phenomena which are needed to take into consideration in a full study. In the case of iron alloys, which is not really the focus of the present study frequently can meet with non-equilibrium states, where the seconder microstructure shows several aspect of the processing steps.

Pre- and protohistoric iron artefacts, as well as the medieval ones, do not show any metallic remains on the surface, but only corrosion products, so that the surface and the areas are close to that, could not be used for metallographic examination. The best useable way to investigate their microstructure is that, after an X-ray examination, the finds are sampled by cutting, and embedded in epoxy-resin. The cut surfaces are grounded and mechanically polished. After polishing the samples are etched with nital and iron-chloride.

The metallographic investigations of iron artefacts aimed at answering the major questions: Were the objects made of one or multiple types of raw materials? Can similarities be revealed with regards to the technology of production, forging and the possible heat treatment of the artefacts?

The basic processing steps can often be described, based on the nature and the occasional heterogeneity of the microstructure. The grain size, the distribution of inclusions and the position of layers containing different volumes of perlite served information about the technology of forming.

SEM-EDS examinations of the shape, microstructure and chemical composition of the inclusions in the iron samples provide information which help to identify their origin from processing point of view (remains of smelting or forging).

In our presentation, we will explain to you the used methodology through some selected examples; you also will understand why the knowledge in metallography and metallurgy is so important in this research area. When we selected the samples and results, we considered that we would present as much different examples as possible in this lecture. The main samples have been taken from axes from different places and quarries in Carpathian-Basin. Besides the axes we choose other artefacts also to show the whole picture about this problem.

Metallographic examination of iron swords – A few notes and examples

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Four books dealing wiht ancient and medieval swordsmithing technology have been published in last four years (Williams 2012; Košta-Hošek 2014; Żabiński–Stępiński–Biborski 2014; Moilanen 2015). This reflects the increasing interest of scholars in research into swords and techniques of their manufacture in the past. One can expect that modern metallurgist will become interested in this issue as well, and they will start with metallographic examination of sword, albeit rather with individual pieces than whole sets.

Therefore, a few notes on examination of swords and few examples of result recently obtained will be presented. Also recent reassessment of two swords from the Great Moravian site of Staré Město will be introduced. All this could help the newly involved scholars in basic orientation in the issue and prevent them to publish incorrect results.

References:
Williams A. 2012: The Sword and the Crucible: A History of the Metallurgy of European Swords up to the 16th Century (Brill: Leiden-Boston).
Košta, J.- Hošek, J. 2014: Early Medieval Swords from Mikulčice (Brno: Studien zum Burgwall von Mikulčice, Band X).
Żabiński, G. – Stępiński, J. – Biborski, M. 2014: Technology of Sword Blades from the La Tene Period to the Early Modern Age: The case of what is now Poland (Archaeopress Archaeology).
Moilanen, M. 2015: Marks of Fire, Value and Faith: Swords with Ferrous Inlays in Finland during the Late Iron Age (ca. 700–1200 AD), (Archaeologia Medii Aevi Finlandiae XXI).

Calcium (CaO) content in metallurgical slag as a proxy for fuel efficiency of ancient smelting technologies

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While analysis of slag material is essential in reconstructing ancient smelting technologies, the interpretation of the analytic data might be challenging. In this paper we address a particular question, namely the interpretation of calcium (CaO) content of copper smelting slag, based on a new and substantial analytic dataset (ICP-MS) of multiple slag samples from the copper ore district of Timna Valley (southern Israel).

The new data indicate a decrease in the average calcium content in slag between the Late Bronze Age (~12th century BCE) and the Iron Age (~10th century BCE), from 2.38±1.65 wt.% (n=27) to 1.17±0.91 wt.% (n=15) respectively. Based on several lines of argument we suggest that this difference represents primarily an improvement in fuel efficiency (i.e., less fuel per smelting cycle while similar [or larger] quantity of Cu was produced), rather than a change in the smelting charge (flux, ore, or charcoal species) or furnace structure. In addition, we discuss our results in light of previously published analytic data from Timna Valley and the Arabah, and reassess previous interpretations of Ca content in slag from this region.

Chemical characterization via pXRF of Early Iron Age pottery from SW Iberia

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The main aim of this paper is to present the results of archaeometrical analysis of Tartessian pottery recently undertaken in the Lower Guadalquivir region (western Andalusia, Spain). A non-invasive portable X-ray fluorescence spectrometer (pXRF) has been used to determine the chemical composition of the pottery sherds from seven archeological sites dated to the Early Iron Age. The purpose of this research was to create a database of Tartessian pottery in order to help establishthe provenance of the ceramics.

The settings used for the measurements were as follows: energy 15 kV, current 25 μA, no filter, 15 s per analysis. All the measurements were done with the help of a vacuum pump. Their accuracy has been verified by means of comparison with a key sample with known chemical composition. All specimens were measured at least two times on a flat, external surface of the sherd. The spectrometer was normally set up in laboratory position, so the distance between the detector and a sample was the same. During the analyses, MajMudRock calibration, provided by the manufacturer of the device was used.

The adopted method to categorize pottery due to differences in its chemical composition was the potassium-titanium test established in the provenance determination of clay cuneiform tablets by Y. Goren, H. Mommsen and J. Klinger. However, other elements, especially Ba, Fe and Ca, have been taken into account in the interpretation of the results as well.

An additional part of this study was the experimental examination of samples of local clay sources and raw material obtained from sites surroundings in order to create a reference database of local clay. The samples were fired in oxidizing atmosphere at several, gradually increasing temperature levels, starting from 600ºC and ending at 850ºC, after which they were examined by pXRF.

The data obtained through the pXRF analyses are generally coherent with the results of the previously completed petrographic examination. The portable XRF device appears in the context of this study as a very useful tool for primary, quick investigation of archaeological material deposited in museum storage rooms or acquired during an archaeological field survey. With some exceptions there is no clear correlation within the investigated sites in terms of ceramic production. On the other hand, the pottery items normally classified as Phoenician imports seem to be local imitations of Eastern Mediterranean products.

PXRF and the potentials of obsidian "Big Data"

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The volume of data generated from archaeological studies of obsidian has rapidly increased in the last decade, largely driven by widening availability of relatively inexpensive portable XRF devices. These instruments are generally capable of distinguishing between obsidian sources in most areas of the world, and archaeologists have used them to analyze thousands of individual artifacts in some studies.

However, questions remain about the quality of data generated as access to instrumentation expands beyond specialist laboratories and practitioners. Challenges also exist in collating and combining older studies with new data, constructing useable databases, making these data available to the broader archaeological community, and developing models and methods to tie these data to archaeological questions and theory.

This paper examines the new era of obsidian "big data," including discussion of methods such as network analysis that can be used to draw meaningful archaeological conclusions from obsidian source determinations.

Latest advancements in the application of analytical science to ancient and historical glass production

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The analysis of past glass production has advanced significantly in recent years, including new work into the use of various isotopes in order to trace the geological origins of glassmaking ingredients, the building up of chemical datasets, the increasing application of trace element analysis to understand the nuances of glass production and recycling, and the application of analytical techniques to questions about glass production, dating, and circulation.

I shall present a summary of the latest research and findings, including advancements in established analytical techniques. I shall then present some projects I direct or am personally involved with, which apply novel analytical techniques, the construction and interpretation of large datasets, and new fieldwork methodologies. It will be shown that, while we have come a long way in the analysis of ancient glass, much exciting work still lies ahead.

ORGANIZATION

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