Archaeometry of Pre- and Protohistoric Inorganic Artefacts, Materials and Technologies

L'archéométrie des artefacts et matières inorganiques et leurs technologies en pré- et protohistoire

Internal Meeting and 2nd International Scientific Conference of the UISPP Commission for Archaeometry

Pavia, Italy

22nd - 23rd June, 2017

PROGRAM

22nd June, Thursday

14.30:

2nd Internal meeting of the members of the UISPP Commission for Archaeometry of pre- and protohistoric inorganic artifacts, materials and technologies.

Venue: Dipartimento di Scienze della Terra e dell'Ambiente (Department of Earth and Environment Sciences), Polo "La nave", Via Ferrata 9, Paino G, Sala d. Giunta

Agenda:

- **Latest news about the UISPP (presidency, new commissions, funding, etc.)**
- **Preparation of 18th UISPP World Congress in Paris**
- **Publication of the workshop proceedings**

The meeting was attended by Béla Török (president of the commission), Alessandra Giumlia-Mair (secretary), Maria Pia Riccardi (local main organizer), Bianka Nessel, Bogdan Constantinescu, Dirk Brandherm, Erez Ben-Yosef, Ignacio Montero Ruiz, Jiři Hošek, Marianne Mödlinger, Michal Krueger, Mohammadamin Emami.
Were excused due to various justifications: Peter Bray, Ana Ávila Melo, Cloë N. Duckworth, Jerolyn E. Morrison, Mark Golitko, Raquel Vilaça, Susan Ferrence, Yi-Xian Lin, Jairo Escobar Gutierrez

19.30:

Social dinner at the Ristorante "Il Sagrestano" (Oltrepò Pavese) and trip to the nearby astronomy observatory of Ca Del Monte.

All members of the Commission and the UISPP bureau were invited.

23rd June, Friday

2nd International Scientific Conference of the UISPP Commission for Archaeometry:

LATEST RESULTS AND EXAMINATION METHODOLOGIES OF PRE- AND PROTOHISTORIC INORGANIC MATERIALS II.

Venue: Historical Aula Volta, Palazzo Centrale Università, Corso Strada Nuova 65

Program

10.00:
Welcome address by the organizers, Maria Pia Riccardi and Alessandra Giumlia-Mair
Welcome address by the Pro-rector of the University of Pavia, Prof Antonella Zucchella
Introduction by the President of the Commission, Béla Török

Morning session (Chairperson: Béla Török)

10.30
Michał Krueger[1] and **Dirk Brandherm**[2]
[1]Instytut Archeologii, Uniwersytet im. Adama Mickiewicza w Poznaniu, Poland
[2]School of Natural and Built Environment, Queen's University Belfast, Northern Ireland
Chronology and pXRF at La Cruz del Negro: exploring the beginnings of the Orientalizing Period in Western Andalusia

10.50
Mohammadamin Emami
Department of Conservation and Archaeology, Art University of Isfahan, Iran
Department of Building Material Chemistry, University Siegen, Germany
Celadons: maritime trade along the South coastal route of Asia from China to Iran

11.10
Yotam Asscher
Dept. of Geoscience and CIRCe – Center for the investigation of cement materials, University of Padova,
Identifying and mapping inorganic pigments in ancient wall paintings based on non-invasive XRF and multispectral imaging

11.30
Marco Tizzoni
Formerly Università degli Studi di Bergamo, Italy
The missing mines: sources of copper in the Italian Central Alps

11.50
Marianne Mödlinger
Université Bordeaux Montaigne, Maison de l'archéologie, Pessac, France
Chemical and metallurgical aspects of arsenical bronze: the case of arsenic-loss in prehistoric metal production

12.10
Ignacio Montero-Ruiz[1] and **Raquel Vilaça**[2]
[1]Instituto de Historia, Consejo Superior de Investigaciones Científicas, Spain
[2]Instituto de Arqueologia da Faculdade de Letras da Universidade de Coimbra, Portugal
Between the Atlantic and the Mediterranean: Late Bronze Age copper ingots from the Iberian Peninsula.

Discussion

13.00: Lunch break

Afternoon session (Chairperson: Marco Tizzoni)

14.30
Bianka Nessel[1,2], **Gerhard Brügmann**[3], **Ernst Pernicka**[1,2,3] and **Janeta Marahrens**[3]
[1]Institute of Earth Sciences, Heidelberg University, Germany
[2]Institute of Prehistory, Protohistory and Near-Eastern Archaeology, Heidelberg University
[3]Curt-Engelhorn-Center Archaeometry gGmbH, Mannheim, Germany,
How did tin trade in southeast Europe work? Considerations about long distance networks and raw material exchange

14.50
Erez Ben-Yosef[1] and **Omri Yagel**[1]
[1]Department of Archaeology and Ancient Near Eastern Cultures, Tel Aviv University, Israel
Copper-based artifacts of Iron Age metalworkers at Timna: Does the shoemaker's son go barefoot?

15.10
Alessandra Giumlia-Mair[1] and **Maria Pia Riccardi**[2]
[1]AGM Archeoanalisi, Merano (BZ), Italy
[2]University of Pavia, Dipartimento di Scienze della Terra e dell'Ambiente, Italy
Analyses of Iron Age cauldrons with cross-attachments (Kreuzattaschenkessel)

15.30
Bogdan Constantinescu
National Institute for Nuclear Physics and Engineering, Bucharest, Romania
XRF analyses of Roman and Dacian bronze artifacts from Romanian museums

15.50
Béla Török
Institute of Physical Metallurgy, Metalforming and Nanotechnology, University of Miskolc, Hungary
Materials testing of iron slag samples from Late Iron Age sites in Hungary – complex investigations

16.10
Jiři Hošek[1] and **Rastislav Korený**[2]
[1]Institute of Archaeology of the CAS, Prague, Czech Republik
[2]Hornické muzeum Příbram, Czech Republik
Metallographic examination of two Roman scythes from Dobříš, Czech Republic

Discussion

ABSTRACTS

Chronology and pXRF at La Cruz del Negro: exploring the beginnings of the Orientalizing Period in Western Andalusia

M. Krueger and D. Brandherm

La Cruz del Negro is one of the most important sites of the orientalizing period in western Andalusia. It occupies the northern part of the Los Alcores area, a region with very fertile soils. La Cruz del Negro has been excavated since 1895; more then one hundred graves have been discovered there. It is the eponymous site for a special type of urn of clearly Phoenician inspiration, the so-called "Cruz del Negro" urn. This paper has two aims: one is to present the complete results of portable XRF analysis of pottery from La Cruz del Negro, including a considerable number of "Cruz del Negro" urns.
This is the first time that these have been submitted to spectrometric analysis. This study also demonstrates that it is possible to establish clear chemical markers which allow a distinction between pottery from different Early Iron Age sites. The second objective of this paper is to present new chronological data for burial assemblages containing Cruz del Negro urns from the site, based on C14 determinations from cremated human remains. These seem to hint at a potentially earlier start date for the type than conventionally accepted.

Celadons: maritime trade along the South coastal route of Asia from China to Iran

M. Emami

Celadons are ceramic wares first mentioned in the Han Dynasty (206 BC–220 AD) in China. The ceramics defined with the widely accepted term proto-celadon are documented in the Shang Dynasty (c.1600-1046 BCE). This kind of ceramics had an enormous distribution through maritime trade between the China Sea and the Persian Gulf. The South Persian coastline has been a very dynamic region for many centuries with abundant marine export/import of goods. Chinese celadons with a very smooth green-grey surface reached this coastal line in around 1100-1500 AD. The ancient maritime trade of celadons was described by Arab travellers such as Ibn Battuta and Al-Masudi in the 10th century. Celadons trade from China and through Iran was also reported in East Africa, on the Swahili coast (Manda) and toward to the East coast of Tanzania (Kilwa).
Seven pieces of celadon from a recent excavation in the historical ruins of the ancient port of Harireh on the Kish Island in Iran were submitted for petrological and chemical investigations in order to determine their technology. Based on archaeological data, the investigated samples belong to the Saljuq dynasty (11th-14th centuries). Investigations were carried out on the body as well as on the glaze of the celadons. Celadon samples were investigated petrologically and chemically by polarized light microscopy (LM), environmental scanning electron microscopy (ESEM), quantitative X-ray diffraction with

Rietveld refinement (QXRD), X-ray fluorescence (XRF) and simultaneous thermo-analytic (STA) in order to understand their manufacture. The amount of FeO as the main glaze constituent and K in the body is quantitatively calculated for possible modelling of the technology as essential know-how. The mineralogical composition of the pottery proves that the firing temperature of celadon was about 1050-1100ºC. The matrix is fired clay and basically similar to the Chinese ware

Chemical and metallurgical aspects of arsenical bronze: the case of arsenic-loss in prehistoric metal production

M. Mödlinger

The chemical composition of ancient copper-based metal changes over time due to repetitive recycling and mixing of old metal. Prehistoric copper usually contains impurities from the copper ores themselves, and some have been used as evidence of anthropomorphically induced chemical change. Research into these changes has historically relied upon the assumption of element loss linearity, which in fact varies with a multitude of factors. To illustrate the complexity of such losses for prehistoric alloys, several arsenical bronze (Cu-As alloys) was selected for study. The mass loss of several Cu-As-alloys were measured by DTA/TGA.
From the comparison of the experimental results to thermodynamic calculations and literature data, it was unclear whether weight losses were solely caused by the volatilization of arsenic. However, a prolonged time temperature-cycling run demonstrated that mainly arsenic volatilizes, hence the non-linear mass loss from the alloy can be directly attributed to arsenic.

Between the Atlantic and the Mediterranean: Late Bronze Age copper ingots from the Iberian Peninsula.

I. Montero-Ruiz and R. Vilaça

The study of the copper ingots by elemental analysis (pXRF and some ICP-LA-MS) and Lead isotope Analysis (MC-ICP-MS) try to understand the bronze production in the Late Bronze Age Iberia. This bronze metallurgy show a very homogeneous composition characterised by a very low amount of impurities in metal, what it could be expected to find in the copper ingots. However, lead isotope analysis draws a very different picture than homogeneity in provenance. Although some main sources as Linares could be detected, some others results are not yet identified and great provenance diversity are found even in the same deposit or hoard.
Another interesting feature is the detection of copper-lead ingots. We try to link this alloy with the production of high leaded bronzes in the NW of Iberian during 7^{th}-6^{th} century BC.
XRF analyses of Roman and Dacian bronze artifacts from Romanian museums

How did tin trade in southeast Europe work? Considerations about long distance networks and raw material exchange

B. Nessel, G. Brügmann, E. Pernicka and J.Marahrens

Recent research makes it is more and more likely that tin sources in western and central Europe supplied large parts of the Continent with tin (Nessel et al. 2015).
The presentation will focus on tin and lead isotopic data of southeastern European bronzes from the end of the Early and beginning of the Middle Bronze Age. The sample set comprises bronzes from hoards, graves, and typologically well-dated single finds from Slovakia, Hungary, Romania, Bulgaria, Serbia and Aegean bronzes from the first half of the 2nd millennium BC.
We will discuss the analytical determination of tin isotopic compositions and the possible use of tin from different ore sources, as well as the potential distribution of tin through exchange networks between the Carpathian Basin, the Aegeo-Balkan-Complex and tin bearing regions in Central and Western Europe. Analyses of Aegean bronzes from the beginning of the 2nd millennium BC have higher tin isotope ratios than the southeastern European sample set. Therefore different tin sources might have been used to manufacture these bronzes. The presented analyses will shed new light to this problem and on a possible reorientation of exchange routes during the 2nd millennium BC.
Tin isotopic ratios of southern European bronzes display a broad range of tin isotopic compositions compared to those of the central European Únětice Culture. This might be due to the chronological difference of at least one hundred years between the finds. However, it also reflects specific trade networks and exchange partners. Specifically, the sampled bronze ingots indicate connections through continental Europe during the Early and the beginning of the Middle Bronze Age. The combined approach of archaeological methods and tin and lead isotopic data provides a glimpse of how and where trade networks were established and extended over a period of 500 years.

Analysis of Iron Age cauldrons with cross-attachments (Kreuzattaschenkessel)

A. Giumlia-Mair and M. P. Riccardi

Caudrons with cross-attachments (Kreuzattaschenkessel) have been in use from the Late Bronze Age until the Early iron Age. Different shapes can be recognized. The main differences are found in the types of attachments for the handles. Type A displays triangular attachments with two lateral rings for rivets, and is considered the prototype of cross-attachment cauldrons. Type B comprehends decorated and undecorated vessels with twisted or smooth handles, and short and broad cross-shaped attachments. These can be cast in one piece, and have the shape of a double cross or, in case of Type B2, two separate cross-shaped attachments on each side. Cauldrons of type C show elongated cross-attachments. The distribution of the various types is rather different.
The earliest analyzed pieces, cauldrons of type B, come from Mušja Jama (the Flies Cave), near Škocjan in Slovenia (Trampuž et al. 2016) and contain around 8-9% of tin. Several cauldrons of type C from Trentino have been analyzed in the past by one of the authors (Giumlia-Mair 2002; 2014), have different characteristics and contain up to

15% of tin. The analytical results of more cross-attachment cauldrons, belonging to the Naturhistorisches Museum in Vienna, from Býči Skála, in Moravia, Czech Republic, and from Toplice and Šmarie**,** both in Slovenia, will be presented in this study. Early cross-attachment cauldrons A to B2a seem to come from Transylvania and the Carpathian area until the 7th century BC. After the end of the 7th century BC the production in the Carpathians seems to stop, but new shapes are produced around the Eastern Alps. The different metallurgical traditions can be recognized, and seem to depend on the trade routes and the different metal supplies.

Giumlia-Mair A., 2002, *Studi tecnici sui reperti dell'età del ferro in leghe a base di rame provenienti dalla Val di Non*, in D'Amico C. ed., Atti del congresso nazionale di Archeometria, Bologna, 20 gennaio-1 febbraio 2002, Patron Editore, Bologna, 683-694.

Giumlia-Mair A., 2014, *Bronzi di Sanzeno nella* koinè *alpino-orientale dell'età del Ferro*, in Roncador R. and Nicolis F., *Antichi popoli delle Alpi. Sviluppi culturali durante l'età del Ferro nei territori alpini centro-orientali*, Atti della giornata di Studi internazionale, 1 maggio 2010, Sanzeno, Trento, Provincia autonoma di Trento, Soprintendenza per I beni architettonici e archeologici, Ufficio Beni archeologici,183-197.

Trampuž Orel N., Heath D.J., Orel B., 2016, *Chemical composition of bronze objects in the hoard from Mušja Jama near Škocjan*, in Teržan B., Borgna E., Turk P., *Depo iz Mušje Jame pri Škocjanu na Krasu / Il ripostiglio della Grotta delle mosche presso San Canziano del Carso*, Narodni Muzej Slovenije, Karalogi in Monografije 42, Ljubljana, 301-344.

XRF analyses of Roman and Dacian bronze artifacts from Romanian museums

B. Constantinescu

Fragmented bronze sculpture is a category of numerous finds from Roman settlements of Dacia. We concentrated on 30 fragments found in Racari – castrum and civil settlement from South-West of Romania, situated approx 100 km north to Danube and to border between Moesia Superior and Moesia Inferior. XRF measurements were performed using a X-MET-TX3000 portable spectrometer – Oxford Instruments. We determined the alloy composition, especially the proportion of lead and tin, which is from 6% to 48% for lead and from 2% to 11% for tin. The observed technique of gilding was leaf procedure (approx 5 microns thickness), gold being very pure (most probably from contemporary gold coins – aurei). We also found remnants of lead on the inner part of some fragments, suggesting lead was used as a solder. The destruction of the bronze statues (e.g. by Christians) and their use as scrap metal is also important. The possibility of a local workshop with itinerant masters specialized in statues foundry is discussed. Our results are compared with the results of German specialists Frank Willer, Roland Schwab and Kati Bott on fragments found on UNESCO world heritage Limes – Germania Superior, Germania Inferior and Raetia.

We also analyzed two bronze Tabulae containing legal status of Troesmis Municipium (in Dobroudja, on Danube) recuperated by authorities from treasure hunters. Compared with bronze Roman military diplomae, the Tabulae have strong in-homogeneities in the alloy, suggesting a local workshop with a reduced metallurgical experience.

Dacian bronze artifacts found in Sarmizegetusa – the ancient capital of Dacia – were also measured. The most spectacular is the case of “positive” monetary dies used to mint Roman denarii (“pirate” emissions), dies based on a very hard high-tin bronze (approx 30%). Most probably these dies were used to produce real “negative” dies from iron.

Materials testing of iron slag samples from Late Iron Age sites in Hungary – complex investigations.

B. Török

Among archaeological finds, many sporadic and hardly classifiable materials are gathered and unearthed. Slag type materials make up a significant group within such sporadic findings, usually paid less attention to. On these findings even the definition of fundamental characteristics is a frequent problem. Besides, if the material has been identified to be slag, other questions are raised, such as determining the processes which once lead to the melting, then solidification of the material. On the other hand, a crucial task is the slag classification by chemical, microstructural and mineralogical investigations. Also, these investigations must be optimally used to unfold the physical and chemical characteristics of related technological processes.
The experts of the Archaeometallurgical Research Group of the University of Miskolc (ARGUM) have been investigating over 100 slag samples from Protohistory, Antiquity and Middle Ages, regarding their chemical and mineralogical compositions, together with their textural analysis. The main analytical techniques are ICP-OES complemented with C and S determination (moreover using titration for separating the Fe^{2+} and Fe^{3+}), SEM-EDS and XRD. Chemical investigations can be supplemented by pXRF.
Numerous slag samples and a piece of slaggy bloom from excavations of Celtic settlements (La Téne B2-D2) at Ordacsehi (S-W Hungary), Jászberény (Great Hungarian Plain) and Szilvásvárad (N-E Hungary) were examined. The main objectives of the investigations were to study the material and structural properties of the slag specimens, the definition of the metallurgical functions of the different pieces of slag.
Some slag samples can be originated from the purification hammering process where in an oxidizing atmosphere intended to separate the slag from the iron after reheating the bloom or during the forging. Some of the samples with fine dendrites remind metallurgical slag, although there have not been found traces of bloomery at the excavation sites. The examined slaggy bloom-fragment interlocks to the beginning of the technological line of forging as the first (by)product after the smelting formed in the bloomery. The examined samples are by-products of Celtic smithy workshops, which were not organized in a centred structure, but were rather conducted at the households with the required professional experience that would satisfy the local needs.
Heterogeneous structures and compositions of the slags provide a good possibility for comparison of the usability of various chemical analytical methods (XRF, ICP, EDS).

Metallographic examination of two Roman scythes from Dobříš, Czech Republic.

J. Hošek and R. Korený

Across Europe, numbers of Roman iron objects of various types were metallographically examined so far. Not surprisingly, the majority of the items studied are weapons, cutlery and craftsmen tools. Concerning agricultural tools, it seems they are out of interest of archaeometallurgists, although even they had to meet certain criteria in terms of quality. This is well demonstrated by results of a metallographic examination of two long Roman scythes, which come from the period of the 1st to 3rd centuries AD as suggested by their typological determination. Results of the examination will be widely discussed within the presentation.

Photographs of the events