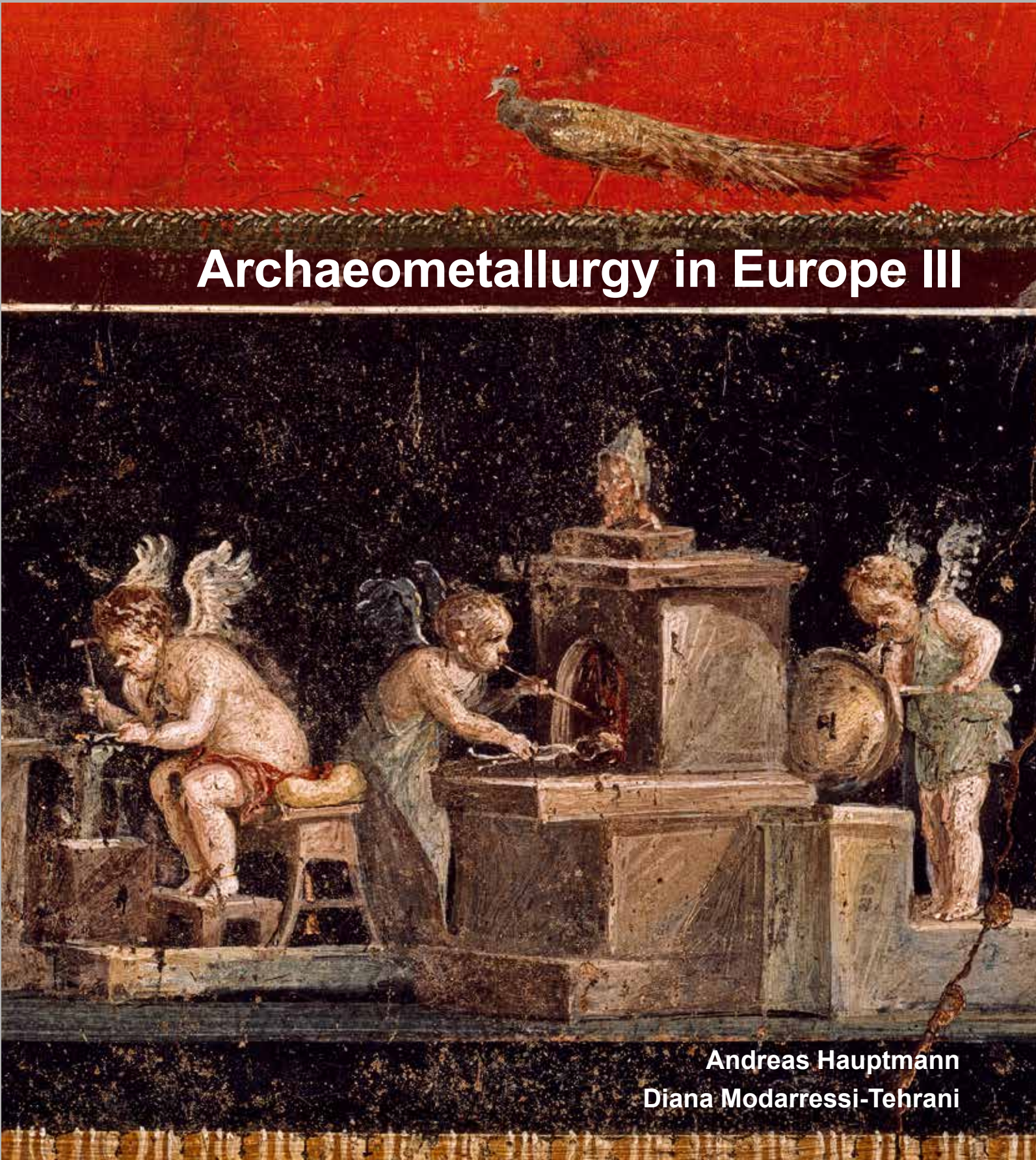


DER ANSCHNITT

ZEITSCHRIFT FÜR KUNST UND KULTUR IM BERGBAU

BEIHEFT 26

Archaeometallurgy in Europe II



Andreas Hauptmann
Diana Modarressi-Tehrani

Archaeometallurgy in Europe III

Archaeometallurgy in Europe III

Proceedings of the 3rd International Conference
Deutsches Bergbau-Museum Bochum

June 29 – July 1, 2011

Editors
Andreas Hauptmann
Diana Modarressi-Tehrani

Bochum 2015

Montanhistorische Zeitschrift

Der ANSCHNITT. Beiheft 26

= Veröffentlichungen aus dem Deutschen
Bergbau-Museum Bochum, Nr. 202

The conference Archaeometallurgy in Europe III
was supported by



Keyence



Analyticon



MLS GmbH



Zeiss



Thermo Scientific



Springer Verlag Berlin Heidelberg
New York

Redaktion

Diana Modarressi-Tehrani, Andreas Hauptmann

Layout

Rolf Krause

Titelgestaltung

Karina Schwunk

Druck

Grafisches Centrum Cuno GmbH & Co. KG

Bibliografische Informationen der Deutschen Bibliothek

Die Deutsche Bibliothek verzeichnet diese Publikation in der
Deutschen Nationalbibliografie; detaillierte bibliografische Daten
sind im Internet über <http://dnd.ddb.de> abrufbar.

ISBN 10: 3-937203-74-5

ISBN 13: 978-3-937203-74-4

Cover

Domus Vettiorum / Casa dei Vettii, Pompeii (Campania, Italy, 63-79 BC), which was excavated in 1894. Section of a Pompeii-style scenic fresco showing Eros and Psyche in a gold assay laboratory. In the left corner, scales for weighing gold are put on a table. Next to it, one of the Erotes is working with a small hammer on an anvil. On the right side, an assay furnace is shown. Another of the Erotes is holding a small crucible with pincers with the right hand while using a blowpipe with his left hand, supplying the fire with air. The large bellow for the assay furnace is driven by the third of the Erotes.

DER ANSCHNITT

Herausgeber:

Vereinigung der Freunde von Kunst und Kultur im Bergbau e.V.

Vorsitzender des Vorstands:

Prof. Dr. Karl Friedrich Jakob

Vorsitzender des Beirats:

Bergassessor Dipl.-Kfm. Dr.-Ing. E.h. Achim Middelschulte

Geschäftsführer:

Museumsdirektor Prof. Dr. rer. nat. Stefan Brüggerhoff

Schriftleitung:

Dr. phil. Andreas Bingener M.A.

Editorial Board:

Prof. Dr. Stefan Brüggerhoff, Dr. Lars Bluma, Dr. Michael
Farrenkopf, Prof. Dr. Rainer Slotta, Dr. Thomas Stöllner

Wissenschaftlicher Beirat:

Prof. Dr. Jana Geršlová, Ostrava; Prof. Dr. Karl-Heinz Ludwig,
Bremen; Prof. Dr. Thilo Rehren, London; Prof. Dr. Wolfram
Weber, Bochum

Anschrift der Geschäftsführung und der Schriftleitung:

Deutsches Bergbau-Museum
Am Bergbaumuseum 28 - D-44791 Bochum
Telefon (02 34) 58 77-0
Telefax (02 34) 58 77-111

Einzelheft 9,- €, Doppelheft 18,- €;

Jahresabonnement (6 Hefte) 54,- €;

kostenloser Bezug für die Mitglieder der Vereinigung
(Jahres-Mitgliedsbeitrag 50,- €)

Archaeometallurgy in Europe III

Scientific Advisory Board

Gilberto Artioli, Università di Padova, Italy

Roland Gauß, Fraunhofer-Institut für Silicatforschung,
ISC, Alzenau

Alessandra Giumlia-Mair, Merano, Italy

Gert Goldenberg, University of Innsbruck, Austria

Sabine Klein, J.W. Goethe University of Frankfurt/
Main, Germany

Marcos Martinon-Torres, University College London,
United Kingdom

William O'Brien, University of Galway, Ireland

Vincent Serneels, University of Fribourg, Switzerland

Standing Committee

Yannis Bassiakos, Athens, Greece

Alessandra Giumlia-Mair, Merano, Italy

Andreas Hauptmann, Bochum, Germany

Ivelin Kuleff, Sofia, Bulgaria

Susan LaNiece, London, United Kingdom

Ignacio Montero, Madrid, Spain

Local Organizing Committee

Michael Bode

Andreas Hauptmann

Diana Modarressi-Tehrani

Michael Prange

Ünsal Yalçın

Editorial

This volume comprises a range of articles, which were submitted and selected from all the presentations given on the International Conference "Archaeometallurgy in Europe III", held from the 29th of June to 1st of July 2011 at the Deutsches Bergbau-Museum Bochum, Germany.

The present volume is the third in the series "Archaeometallurgy in Europe", capturing the spirit of the successful series of international conferences on this special theme of research. The first conference "Archaeometallurgy in Europe" had been organized by the Associazione Italiana di Metallurgia and took place in Milano, Italy, from the 24th to the 26th of September 2003. The second conference was held in Aquileia, Italy, from the 17th to the 21st of June 2007. It was also organized by the Associazione Italiana di Metallurgia.

The splendid idea to launch this conference series, a scientific series of meetings limited to the countries of Europe, came from the late Prof. Dr. Walter Nicodemi, formerly President of the Associazione Metallurgia di Italia. Thanks to the efforts of Dr. Alessandra Giunliamair, Merano, these conferences have developed into increasingly productive events with a high scholarly quality. Since then three conferences have taken place and the fourth meeting is at an advanced stage of preparation and will take place in Madrid, Spain, from the 1st to the 3rd June 2015.

The title of the conference series covers a research field which is a distinctive part of archaeometry, and which so far was usually included as one of the topics in the program of the "International Symposium on Archaeometry" (ISA), organized every third year at different locations in Europe and in the United States. However it is our opinion, that in the last decade archaeometallurgy has developed as a very important research field, and we are observing a large number of scholarly activities all over the world. We are convinced that such an important topic needs to be organised and presented in conferences specifically dedicated to this field. Therefore the topic of this conference is the history of metals and metallurgy primarily in Europe, but it also includes other regions of the Old World.

The future prospects of the conference series are promising, especially because "Archaeometallurgy in Europe" constitutes an extremely useful broadening and a regional counterpoint to the well-established and successful conference series "The Beginnings of the Use of Metals and Alloys" (BUMA), which was launched in

1981 by Professors Tsun Ko, Beijing, China, and Robert Maddin, then Philadelphia, USA. The focus of the eight BUMA conferences held so far (the last one was held in Nara, Japan, in 2013) lays on the development of metallurgy in South-East Asia and the Pacific Rim. We firmly believe that the two conferences complement each other very effectively and should therefore continue to exist side by side.

With this special volume of *Der Anschnitt*, we are delighted to publish a selection of the lectures presented at the conference at the Deutsches Bergbau-Museum Bochum in 2011. Many of the authors contributed with very instructive and informative papers, which finally resulted in this volume.

We are very much obliged to all these authors who, with patience and persistence, cooperated with us and helped to shape this volume. We would also like to thank the reviewers who decisively contributed in the improvement of the scientific level of this volume.

Our thanks go first to all those colleagues and friends who helped to organize the conference in 2011. The former director of the Deutsches Bergbau-Museum, Prof. Dr. Rainer Slotta, and the present director, Prof. Dr. Stefan Brüggerhoff encouraged and promoted our efforts to organize this scholarly meeting. Dr. Michael Bode, Dr. Michael Prange, and Prof. Dr. Ünsal Yalçın supported the conference planning and realization in every aspect. Many colleagues of the staff of the Deutsches Bergbau-Museum, and many of the students working in our research laboratory offered their assistance and help.

Finally, our thanks go to Mrs. Karina Schwunk and Mrs. Angelika Wiebe-Friedrich who performed the editorial work, design, and layout for this volume.

Andreas Hauptmann
Diana Modarressi-Tehrani

Contemporaneously to the conference in 2011 a volume with abstracts on every lecture given and every poster presented was published:

2011 HAUPTMANN, Andreas, MODARRESSI-TEHRANI, Diana & PRANGE, Michael (eds.), *Archaeometallurgy in Europe III. Abstracts*. METALLA, Sonderheft 4, 2011.

Table of contents

Early mining and metallurgical innovation stages in Europe

Hans Andersson	
Iron – a driving force in early urbanisation	13
Florence Cattin, Matthias B. Merkl, Christian Strahm & Igor Maria Villa	
Elemental and lead isotopic data of copper finds from the Singen cemetery, Germany – a methodological approach of investigating Early Bronze Age networks	19
Guntram Gassmann, Sabine Klein & Gabriele Körlin	
The Roman mines near Ulpiana, Kosovo	33
Marc Pearce	
The spread of early copper mining and metallurgy in Europe: an assessment of the diffusionist model	
A key-note lecture	45
Ignacio Soriano	
The earliest metallurgy in the north-eastern Iberian Peninsula: origin, use and socioeconomic implications	55
Thomas Stöllner	
Humans approach to resources: Old World mining between technological innovations, social change and economical structures.	
A key-note lecture	63
Simon Timberlake, Tim Mighall & Thomas Kidd	
Newresearch into Roman metal mining in Britain	83

Regional studies in Europe and beyond

Lucile Beck, Elise Alloin, Anne Michelin, Florian Téreygeol, Claire Berthier, Dominique Robcis, Thierry Borel & Ulrich Klein	
Counterfeit coinage of the Holy Roman Empire in the 16th century: silvering process and archaeometallurgical replications	97
Maryse Blet-Lemarquand, Arnaud Suspène & Michel Amandry	
Augustus' gold coinage: investigating mints and provenance through trace element concentrations	107
Velislav Bonev, Boika Zlateva & Ivelin Kuleff	
Chemical composition of fibulae from the Iron Age in Thrace (Bulgaria)	115

Carlo Bottaini, Claudio Giardino, Giovanni Paternoster The Final Bronze Age hoard from Solveira (northern Portugal): a multi-disciplinary approach	125
Jennifer Garner Bronze Age tin mines in central Asia	135
Alessandra Giunlia-Mair, Susan C. Ferrence & Philip P. Betancourt Metallurgy of the copper-based objects from Gournia, east Crete	145
Elisa M. Grassi Roman metalworking in northern Italy between archaeology and archaeometry: two case studies	155
Babara Horejs & Mathias Mehofer Early Bronze Age metal workshops at Çukuriçi Höyük Production of arsenical copper at the beginning of the 3rd millennium BC	165
Rüdiger Krause New horizons: archaeometallurgy in eastern Europe and beyond A key-note lecture	177
Janet Lang The Anglo-Saxon cemetery at Dover Buckland, Kent, UK and the technology of some of the iron artefacts	185
Lene Melheim Late Bronze Age axe traffic from Volga-Kama to Scandinavia?	193
Alicia Perea, Patricia Fernández-Esquivel, Salvador Rovira-Llorens, José Luis Ruvalcaba-Sil, Ana Verde, Oscar García-Vuelta & Fabián Cuesta-Gómez Prehistoric gold metallurgy: the Arqeomeb research project	203
Irina Ravich & Mikhail Treister The mirrors of the early nomads of the foothills of south Urals: a complex archaeo-technological study	211
Irina Segal, Miryam Bar-Matthews, Alan Matthews, Yehudit Harlavan & Dan Asael Provenance of ancient metallurgical artifacts: implications of new Pb isotope data from Timna ores	221
Béla Török, Árpád Kovács & Zsolt Gallina Iron metallurgy of the Pannonian Avars of the 7th - 9th century based on excavations and material examinations	229
Frank Willer, Roland Schwab & Kati Bott Large Roman Bronze statues from the UNESCO World Heritage Limes	239
Vladimir I. Zavyalov & Nataliya N. Terekhova Three-fold welding technology in the blacksmith's craft of Medieval Rus' (concerning Scandinavian innovations)	247

Reconstructing ancient technologies

David Bourgarit & Nicolas Thomas Ancient brasses: misconceptions and new insights	255
Vagn F. Buchwald On the characterization of slags and ancient iron artefacts applying the slag-analytical method	263
Joseph Gauthier, Pierre Fluck, Alessandre Disser & Carmela Chateau The Alsatian Altenberg: a seven-hundred-year laboratory for silver metallurgy	271
Anno Hein, Ioannis Karatasios, Noémi S. Müller & Vassilis Kilikoglou Material properties of pyrotechnical ceramics used in the Bronze Age Aegean and implications on metallurgical technologies	279
Silviya Ivanova, Veselina Rangelova, Deyan Lesigyarski & Ivelin Kuleff Observations on the technology of Bronze Age copper and copper alloy finds from Bulgaria	287
David Killick Archaeometallurgy as archaeology A key-note lecture	295
Steffen Kraus, Christian Schröder, Susanne Klemm & Ernst Pernicka Archaeometallurgical studies on the slags of the Middle Bronze Age copper smelting site S1, Styria, Austria	301
Matthias Krismer, Gert Goldenberg & Peter Tropper Mineralogical-petrological investigations of metallurgical slags from the Late Bronze Age fahlore-smelting site Mauken (Tyrol, Austria)	309
Matthias B. Merkl Some thoughts on the interpretation of the elemental composition of Chalcolithic copper finds from central Europe	319
Nerantzis Nerantzis Experimental simulation study of prehistoric bronze working: testing the effects of work-hardening on replicated alloys	329
Barbara S. Ottaway Experiments in archaeometallurgy A key-note address	337
Alessandro Pacini The Lombard fibula of the Arcisa: a substitution?	347
Salvador Rovira, Martina Renzi, Auxilio Moreno & Francisco Contreras Copper slags and crucibles of copper metallurgy in the Middle Bronze Age site (El Argar Culture) of Peñalosa (Baños de la Encina, Jaen, Spain)	355

Sana Shilstein & Sarel Shalev
Comparison of compositional variations in modern European bronze coins with variations in some ancient coins 363

Elena Silvestri, Paolo Bellintani, Franco Nicolis, Michele Bassetti, Siria Biagioni, Nicola Cappellozza, Nicola Degaspero, Marco Marchesini, Nicoletta Martinelli, Silvia Marvelli & Olivia Pignatelli
New excavations at smelting sites in Trentino, Italy: archaeological and archaeobotanical data 369

Maria A. Socratous, Vasiliki Kassianidou & Gaetano Di Pasquale
Ancient slag heaps in Cyprus: the contribution of charcoal analysis to the study of the ancient copper industry 377

New approaches, new technologies in archaeometallurgy

Gilberto Artioli, Matteo Parisatto & Ivana Angelini
High energy X-ray tomography of Bronze Age copper ingots 387

Elisa Barzagli, Francesco Grazi, Francesco Civita, Antonella Scherillo, Alessio Fossati & Marco Zoppi
Characterization of ancient Japanese sword hand guards through time-of-flight neutron diffraction and scanning electron microscopy 391

The authors 401

Copper slags and crucibles of copper metallurgy in the Middle Bronze Age site (El Argar Culture) of Peñalosa (Baños de la Encina, Jaen, Spain)

Summary

The archaeological site of Peñalosa (Sierra Morena) is one of the most northern settlements of the El Argar Culture. Radiocarbon dating spans approximately from 1850 to 1450 cal BC. Finds recovered from the excavations include archaeometallurgical material, such as minerals, slags, smelting and melting crucibles, moulds, metallic masses, ingots and finished objects. The paper will focus on the scientific study of slags and slagged layers on ceramic vessels.

Copper ores originate from two different mineralisations and two areas of exploitation close to the site have been identified by lead isotope analyses. Complex ores were distinguished. Consequently, the slags have two different compositions, with lead as a discriminating element. Slag composition corresponds to non-equilibrium physical-chemical systems resulting from direct reduction of minerals without added fluxes. A silica-rich matrix was often found in the melted material; metal prills are embedded in this matrix. Mineral relics or their transformation in non-reduced cuprite can be observed. Iron oxide in the gangue led to the formation of delafossite and magnetite. Finally, crystals of hedenbergite, melilite, åkermanite, wollastonite and other silicates were found in the slags. Fayalite was detected only occasionally, and, when present, it was confined to some micro-domains in a slag. The slaggy layers formed on the smelting crucibles reproduce exactly the same pattern we observe in the slags.

The site

The archaeological site of Peñalosa is located in the province of Jaén (Fig. 1), and it extends over the Rumbiar River valley, now partly submerged by the waters of a reservoir with the same name (Fig. 2).

As one of the northernmost settlements of the expansion of El Argar Culture (2nd millennium BC) looking to exploit Sierra Morena's mining resources (Contreras 2000; Contreras & Cámara 2002), this site played an important



Fig. 1. Location of the archaeological site of Peñalosa.

role in the cultural valorisation of the Bronze Age on the Iberian Peninsula. The main expansion of Peñalosa (Phase IIIA) dates around 1750 cal BC, after which it was eventually abandoned around 1450 cal BC (Contreras et al. 2004: 35).

Archaeometallurgical record

The archaeological record is rich in metallurgical findings that allow fairly accurate reconstructions of the metallurgical processes' chaînes opératoires carried out at the settlement, particularly those relating to copper production. When we published the preliminary study of these materials (Moreno et al. 2010), more than 600 pieces of metal ores and numerous slagged ceramic fragments had been recorded—suggesting the existence of about 200 metallurgical vessels, nearly 150 pieces of slag, several copper ingots, moulds and metal objects. At present, the number of these findings has significantly increased after the discovery of a waste dump with abundant metallurgical debris, excavated in summer 2011.



Fig. 2. Aerial view of Peñalosa.

In general, slags were scattered in the archaeological layers but no quantitatively important accumulation was located. The slags usually are small nodules or globular masses, several centimetres in size, often showing signs of fragmentation (Fig. 3). Ceramic vessels related to metallurgy are also widely represented in all areas of the site. A multivariate morphometric study was performed on the largest sherds and whole vessels, resulting in two basic types of crucibles: deep (Fig. 4a) and flat ones (Fig. 4b) (Contreras & Camara 2000).

The number of ceramic moulds recovered at the site is also abundant and includes some complete specimens. It is worth mentioning a particular kind of mould with a more or less prismatic shape and straight walls, possibly employed for the production of ingots (Fig. 4c). The minerals used as temper on these ceramics are predominantly quartz accompanied by feldspar, mica and plagioclase.

Copper ores

70 copper ore samples were analyzed by XRF-ED (Metrox XMET-920 spectrometer with 20mCi ^{241}Am source) in the Laboratory of the National Archaeological Museum of Madrid (Spain).



Fig. 3. Slag nodules from Peñalosa.

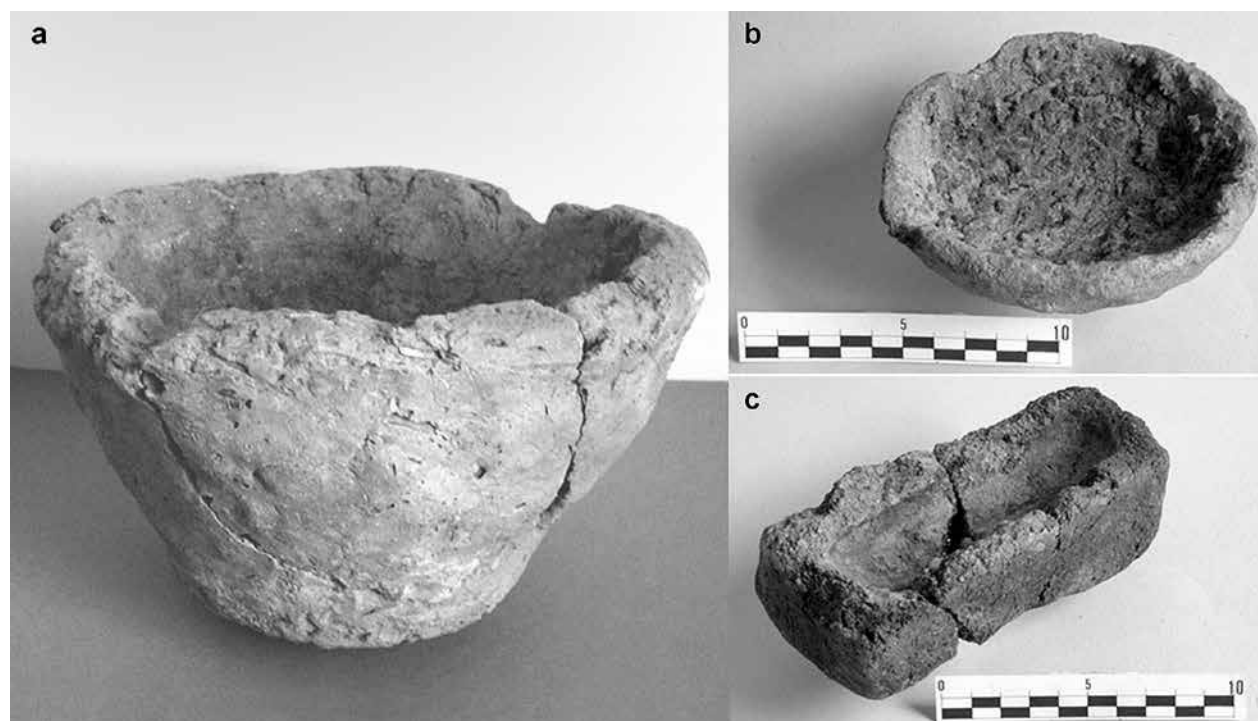


Fig. 4. Crucibles and ingot mould from Peñalosa.

As shown in table 1, they are polymetallic ores with two main components: copper and lead. Although some samples contain noteworthy amounts of iron in the gangue, they are generally poor in mineral iron compounds. The predominant gangue contains quartz and silicates.

These ores can be divided fairly accurately into two groups: ores in which copper compounds are the predominant minerals, and copper-lead ores with significant amounts of lead (galena or its corresponding oxidized compounds). The exploitation of copper-lead ores in the Middle Bronze Age is an important finding within the metallurgical landscape of the Iberian Peninsula documented so far.

The presence in many samples of metal sulphides, together with oxidized compounds, suggests the use of “fahlore” metallurgy (Craddock 1995: 28). This kind of metallurgy has been only indirectly documented during this chronological phase and it has been traditionally considered exceptional and unplanned, as in the case of a few samples recovered from the Chalcolithic levels at Almizaraque (Cuevas del Almanzora, Almería) (Müller et al. 2004: 48, 51) and a large smelting crucible from La Ceñuela (Mazarrón, Murcia) (Rovira 2002a: 90-91).

Lead isotope analyses of some mineral samples point to three possible mining resources used at the site (Hunt et al. 2011). Two of them correspond to mines situated in the Peñalosa area – Jose Palacios Mine (copper) and Mina Polígono (lead-copper) – while a third one has not yet been isotopically characterized.

Copper ores (wt. %)	Copper-lead ores (wt.)
74.9 – 2.06 Cu	43.2 – 7.10 Cu
3.16 – nd Pb	69.2 – 24.5 Pb
14.8 – nd Fe	2.68 – nd Fe
4.79 – nd As	1.56 – nd As
0.80 – nd Sn	0.03 – nd Sn
0.22 – nd Sb	0.17 – nd Sb
0.242 – nd Ag	0.64 – 0.023 Ag

Table 1: Copper ores analyses (XRF-ED analyses, summarized). Abbreviations: nd = not detected

Copper slags

45 slag samples have been analyzed by XRF spectrometry to gain a first insight into their elemental composition. Like the copper ores exploited at Peñalosa, slags are also divided into two groups: those that do not contain significant amounts of lead and highly leaded slags. This preliminary analysis indicates that the different type of raw material processed, reflected in the slags' composition, provide tentative evidence of direct ore-reduction technology.

Among the analysed slags, 18 samples were selected for further study by scanning electron microscopy (Fei Inspect, equipped with detectors for secondary and backscattered electrons and with an Oxford Instruments Analytical-Inca microanalysis system) in the Laboratory

Analysis #	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	TiO ₂	CaO	MnO	FeO	CuO	ZnO	BaO	PbO	SO
BE26171/3	nd	4.48	46.7	nd	1.98	nd	0.63	0.53	44.7	0.91	nd	nd	nd	nd
PA13595/6	nd	2.58	51.5	nd	1.46	nd	1.55	nd	40.4	0.85	nd	1.66	nd	nd
PA13597/1	4.98	2.46	44.3	4.10	nd	nd	8.98	0.54	33.9	0.78	nd	nd	nd	nd
PA13598/01	2.44	1.15	39.9	4.50	0.41	nd	5.33	0.50	42.9	0.58	nd	2.28	nd	nd
PA13599/2	nd	4.94	29.0	8.37	0.36	nd	1.17	nd	51.4	4.75	nd	nd	nd	nd
PA13601/3	1.64	1.79	47.7	nd	0.91	0.50	5.51	2.34	18.0	21.5	nd	nd	nd	nd
PA13604/2	4.50	1.63	24.9	18.2	nd	nd	11.6	0.75	30.1	nd	nd	8.19	nd	0.13
PA13943/1	6.07	2.69	51.3	nd	0.86	nd	10.2	0.62	25.2	1.51	nd	1.55	nd	nd
PA14058/1	1.73	1.72	46.0	nd	nd	nd	9.55	nd	40.0	1.00	nd	nd	nd	nd
PA14059/1	nd	nd	37.5	nd	0.44	nd	1.53	nd	54.0	6.49	nd	nd	nd	nd

Table 2: Composition of the melted matrix in copper slags (SEM microanalyses, wt. %). nd = not detected

of the National Natural Sciences Museum (CSIC) of Madrid, Spain. These investigations proved in all cases that we are dealing with immature slags characterised by an heterogeneous composition and containing plenty of free silica (quartz), remains of minerals or their immediate transformations into oxides (i.e., cuprite). The molten material is a complex silicate (Tab. 2), in which many metal prills are embedded. Delafossite, magnetite and crystals of hedenbergite, melillite, åkermanite, wollastonite and other silicates have also been identified. These results are shown in figures 5 and 6. Fayalite is rarely detected, and wherever present, it is confined to few microdomains within the slag matrix.

All these microstructural phases are characteristic of immature slags, a type well known in Spain and elsewhere in the Old World since the Chalcolithic period,

and indicate a primary metallurgical production of raw copper using open fires and smelting crucibles as reactors. In this thermal and chemical environment, redox conditions are variable; occasionally they are oxidising, causing, e.g., the formation of magnetite and delafossite (if enough iron is available in the system). At other times redox conditions are reducing and allow a successful reduction to metal.

Components in the slag such as delafossite, chalcocite and cuprite are also excellent thermal indicators: delafossite is stable at a temperature of about 1,150 °C and both chalcocite and cuprite melt at about 1,200 °C, so, their presence in the slag (see Figs. 5 and 6) indicates that such high temperature had been reached in the pyrometallurgical structure.

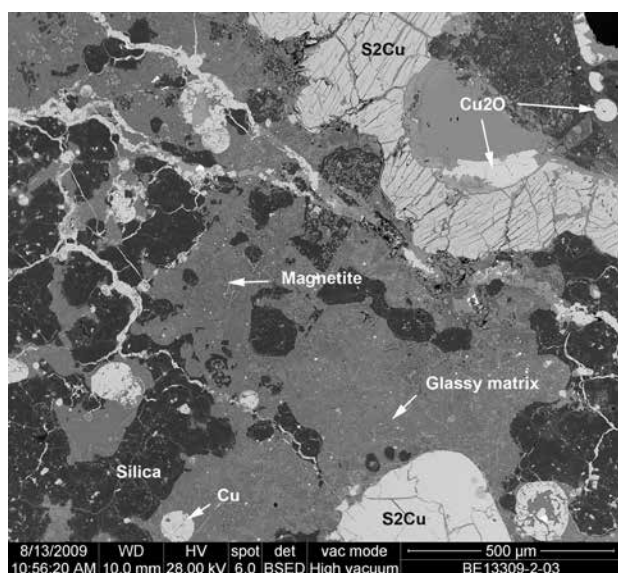


Fig. 5. Complex structure of slag sample BE13309-2 (PA14060). SEM image, backscattered electrons.

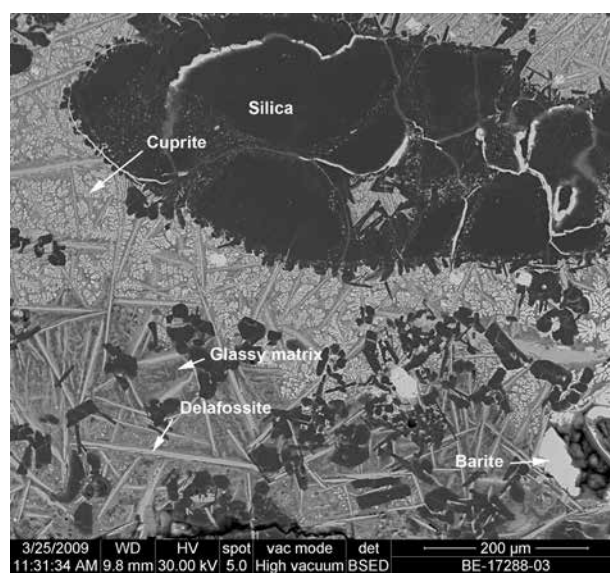


Fig. 6. Complex structure of slag sample BE17288. Silica is being progressively transformed to tridymite-cristobalite. SEM image, backscattered electrons.

Analysis #	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	TiO ₂	CaO	MnO	FeO	CuO	ZnO	BaO	PbO	SO
BE28275-2/1	nd	6.87	47.9	nd	3.07	nd	0.63	nd	11.3	4.22	nd	nd	25.9	nd
PA13668/5	nd	1.68	39.0	nd	0.66	nd	3.71	nd	24.9	0.98	nd	8.56	20.5	nd
PA13759/01	nd	6.98	41.8	nd	1.44	nd	6.94	nd	17.0	nd	nd	2.51	23.3	nd
PA13759/08	nd	5.83	42.9	nd	2.05	nd	7.90	nd	19.7	nd	nd	2.23	19.3	nd
PA13760/3	nd	2.68	42.6	nd	0.57	nd	2.16	nd	16.1	0.46	nd	16.3	19.2	nd
PA13943/9	2.07	2.5	51.8	nd	1.23	nd	5.09	nd	28.9	3.45	nd	1.40	3.49	nd
PA14052/01	nd	2.36	36.5	nd	0.88	nd	5.06	nd	17.1	nd	nd	17.4	20.7	nd
PA14055/3	1.34	4.83	43.2	nd	1.41	nd	1.96	0.30	40.9	nd	1.49	nd	4.59	nd
PA14055/8	1.40	10.5	52.4	nd	2.32	nd	3.81	nd	19.4	2.59	1.09	nd	6.54	nd
PA14055bis/5	0.94	4.14	47.2	nd	0.95	nd	2.25	0.33	29.8	9.39	0.97	nd	4.08	nd
PA14057/06	nd	4.51	44.0	2.40	1.32	nd	0.74	nd	8.66	nd	nd	nd	38.4	nd
PA14060/2	0.79	2.94	47.1	nd	1.10	0.52	2.21	nd	33.9	7.83	nd	nd	3.58	nd

Table 3: Composition of the melted matrix in copper-lead slags (SEM microanalyses, wt. %). nd = not detected

However, what makes Peñalosa metallurgy truly original and innovative is the exploitation of copper-lead ores from the Sierra Morena outcrops. The matrix of copper-lead slags is characterized by a molten material that corresponds to a lead-rich complex silicate (Tab. 3). Crystals of the pyroxene andremeyerite ($\text{BaFe}_2\text{Si}_2\text{O}_7$) were detected in the slags (Fig. 7) and their formation is due to high barium contents present in the gangue of the mineralizations.

Lead behaves in two different ways during ore reduction. In some cases, almost all of it goes into the slag forming a lead-rich glassy matrix. In other cases, one part of the lead goes into the slag and the rest is reduced to metal and alloyed to copper, forming bimetallic nodules or masses with abundant segregates of lead due to immiscibility between copper and lead (Tab. 4). This is shown in Figure 8, where binary Cu-Pb-alloys are embedded in a silicate slag. In fact, although lead is the major element in some prills, no pure lead was found.

Peñalosa slags retain a high amount of copper, both as metallic copper and as mineral compounds. XRF analyses indicate metal losses ranging from 0.51 to 31 % Cu. It is possible that slags were crushed to recover the entrapped metallic inclusions and were then recycled in subsequent smelting operations, explaining the small amount of leftover slags found at the site. Overall, the microstructure and composition of Peñalosa slags point to primitive metallurgical processes for obtaining copper (Rovira 2002a; Hauptmann 2003).

Smelting crucibles

A typical feature of Iberian prehistoric metallurgy is a reluctance to use proper furnaces until well into the Iron

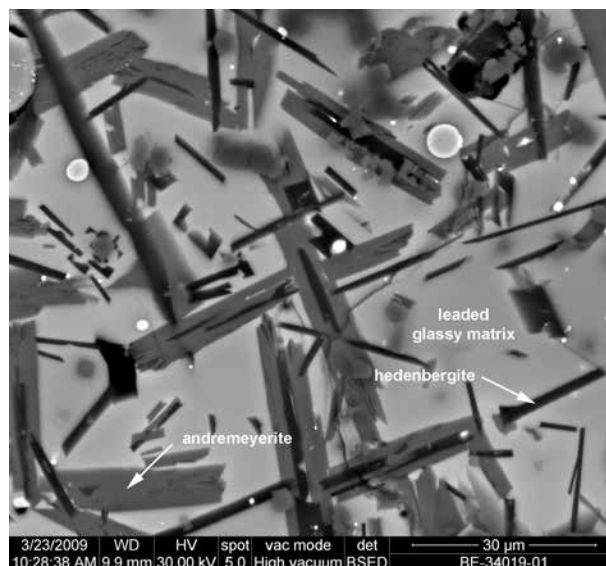


Fig. 7. Detail of the structure of slag sample BE34019. White spots are metal prills. SEM image, backscattered electrons.

Age (Rovira 2002b: 8). Before that time and even during the Iron Age, ceramic smelting crucibles were used to reduce copper ores.

The content of these vessels is usually formed by the reduced ores, accompanied by their gangue and the ash resulting from the combustion of the charcoal used to heat the system and to provide the carbon monoxide needed for the reduction. Chemical reactions and interactions take place between the abovementioned materials and the silicates forming the ceramic of the crucible, leading to the formation of a slaggy layer on the interior wall of the reactor. The chemical and mineralogical composition of this layer has many similarities with the slags resulting from the reduction described in the previous

Analysis #	Cu	Pb	Fe	Ni	As
PA13668/2	91.8	6.6	1.62	nd	nd
PA13668/3	88.0	9.54	2.46	nd	nd
PA13668/4	94.3	3.99	1.67	nd	nd
PA13759/03	69.1	6.3	3.26	0.66	16.9
PA13760/2	96.4	nd	nd	nd	2.54
PA13760/4	96.8	nd	0.56	nd	1.94
PA13760/5	96.3	nd	0.62	nd	2.34
PA14052/04	16.6	83.4	nd	nd	nd
PA14052/05	76.5	23.5	nd	nd	nd
PA14052/06	93.7	6.3	nd	nd	nd
PA14052/07	94.8	4.1	nd	nd	nd
PA14055/4	97.6	1.48	0.91	nd	nd
PA14055/5	91.9	1.65	2.59	nd	nd
PA14055/7	98.5	1.06	0.44	nd	nd
PA14056/4	95.4	4.41	nd	nd	nd
PA14057/08	97.5	nd	2.47	nd	nd
PA14057/10	99.4	nd	0.57	nd	nd
PA14060/3	96.4	nd	3.63	nd	nd
PA14060/4	93.9	1.92	4.13	nd	nd
BE28275-2/2	99.0	nd	0.98	nd	nd
BE28275-2/3	98.5	nd	1.48	nd	nd
BE28275-2/7	98.9	nd	1.07	nd	nd

Table 4: Chemical analyses of metal prills embedded in the slags' matrix (SEM microanalyses, wt. %). nd = not detected

section. The presence in this slag of remains of copper ores provides strong evidence to consider these vessels smelting crucibles.

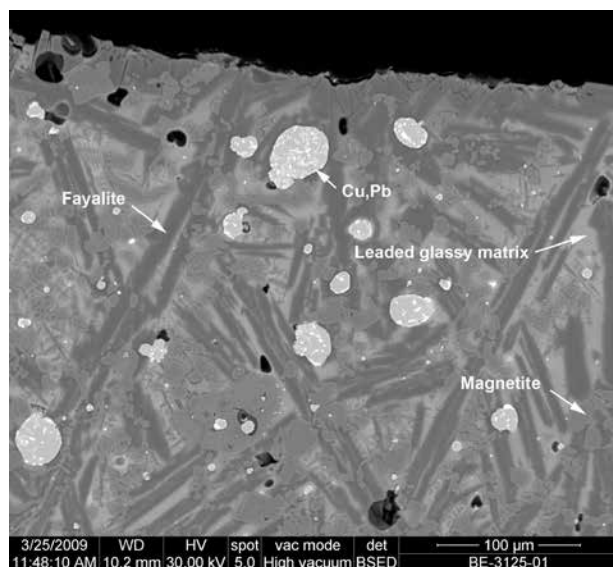


Fig. 8. Many copper-lead prills in slag sample BE3125. SEM image, backscattered electrons.

Although in some cases there may be doubts about whether we are dealing with a crucible for smelting mineral or for melting metal, it should be noted that the duration of a reduction process is much longer than that to melt metal, as demonstrated by numerous experiments (e.g., Rovira 1999: 109). In the first case, the ceramic vessel is exposed to high temperatures for much longer than in the second one, thence it is more likely that chemical reactions occur between the vessel's charge and the reactor. In other words, we can expect more significant alterations in smelting crucibles than in melting ones.

About 50 slaggy ceramic fragments were selected for analyses by XRF spectrometry and 10 of them have been also investigated by SEM. Slaggy layers on smelting crucibles have a microstructure and composition similar to copper slags: some of them show that the processed ore contained only copper, while some others are characterised by copper-lead components. The mineral compounds detected in these slagged crucibles are the same ones identified in the slags (Fig. 9).

Melting crucibles

Based on the composition of metallic inclusions found in the slags, it could be assumed that metal objects from Peñalosa were made of natural alloys of copper with other impurities (mainly arsenic) and copper-lead. However, this is not the case.

As shown in table 5, one single lead-rich copper melting waste has been identified (Tab. 5, PA13967A). In the other metallic items lead is present at rates below 1 % Pb. Consequently, most of the lead must have been eliminated during the process for copper refining. The

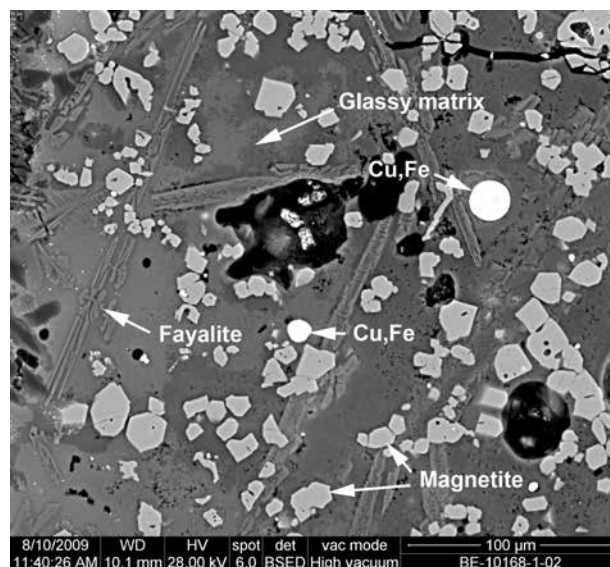


Fig. 9. Smelting crucible slag, sample BE10168. SEM image, backscattered electrons.

Analysis #	Object	Cu	Pb	As	Sn	Fe	Ni	Zn	Ag	Sb
PA13632	Flat axe	99.7	nd	0.31	nd	nd	nd	nd	nd	nd
PA13967A	Raw copper prill	88.1	11.0	0.24	0.03	0.12	nd	nd	0.414	0.098
PA14032	Awl	98.7	0.58	0.66	0.04	nd	nd	nd	0.049	0.018
PA14033	Arrow head	97.8	nd	2.12	0.02	nd	nd	nd	0.016	nd
PA14034	Dagger	85.2	0.13	14.7	0.01	nd	nd	nd	0.016	0.016
PA14036	Awl	97.6	0.61	1.70	nd	0.12	nd	nd	nd	nd
PA14047	Dagger	96.3	nd	3.55	nd	0.10	nd	nd	nd	0.027
PA14048	Awl	98.6	nd	1.41	nd	nd	nd	nd	tr	nd
PA14049	Dagger	97.4	0.12	2.30	0.03	0.10	nd	nd	tr	0.001
PA14051	Dagger	97.3	0.20	2.37	0.03	0.12	nd	nd	nd	nd
PA14053	Awl	97.3	0.91	1.45	0.04	0.27	nd	nd	0.003	0.010
PA14061	Metal lump	97.8	0.17	1.76	0.03	0.17	nd	nd	0.030	0.011

Table 5: Chemical analyses of metal objects (XRF-ED analyses, wt. %). nd = not detected

slaggy layers formed on the inner wall of some melting crucibles provide a reasonable explanation for this lack of lead in the final products.

The matrix of these slaggy layers consists of leaded glasses. As show in table 3, the raw copper obtained after reduction of copper-lead ores in some cases retains appreciable amounts of lead. Lead is virtually insoluble in copper at any temperature, so it is always segregated. Its melting temperature is relatively low (327 °C), compared to 1,083 °C needed to melt copper. If the crucible is charged with droplets, prills and fragments of metallic copper-lead and it is heated to get a melt, once 327 °C has been reached, copper begins to sweat off the lead it contains. Lead easily oxidises at high temperature and the resulting lead oxide (litharge) reacts with the crucible clay producing a lead silicate; this characteristic of lead is the basic principle of the cupellation process. Once the crucible reaches the melting temperature of copper, a great part of the lead has been transformed into a leaded glass adhered to the crucible's wall. The result is a copper with a low lead amount. Figure 10 shows a section of a crucible sherd in which the surface layer of leaded glass is clearly visible.

Conclusions

Peñalosa is a Middle Bronze Age site that was dedicated to copper production for nearly 400 years. The debris related to these metallurgical activities is found scattered throughout the entire settlement, without any evidence of specialized areas or workshops so far.

The analyses of some copper ore indicate the exploitation of two different types of mineralisation, clearly differentiated by their lead content. The exploitation of

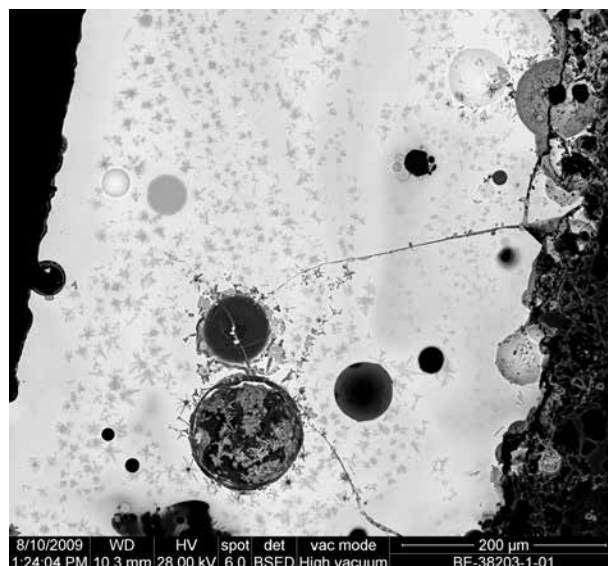


Fig. 10. Leaded glass in the melting crucible BE38203. Light grey small dendrites correspond to cuprite. SEM image, backscattered electrons.

copper-lead ores documented at Peñalosa constitutes an important novelty in the metallurgy of this chronological period.

The reduction process was carried out in smelting crucibles, probably with little slag production. Both the analyses of slags and crucibles faithfully reproduce the nature of the two types of ores used. We did not observe mixtures of these minerals in the same subproducts, suggesting that the resources available were not processed simultaneously. This hypothesis should be proved by the chrono-stratigraphic sequence of the materials that is still underway.

The chemical and mineralogical composition corresponds to immature and highly viscous slags; in these materials the presence of free silica is abundant and much copper is retained as metal or as non-reduced mineral. These characteristics allow us to classify the slags as subproducts of a primitive technology for obtaining copper by direct ores reduction, without the addition of fluxes. Under these conditions, the amount of slag is limited and in any case dependent on the mineralogy of the minerals exploited.

Acknowledgements

This work was part of the research project I+D: Mining in the Upper Guadalquivir: methods of historical reconstruction of antiquity examining the production, consumption and distribution of metals [*La minería en el Alto Guadalquivir. Formas de construcción histórica en la antigüedad a partir de la producción, consumo y distribución de metales*] (HAR2011-30131-C02-01). It was financed by the Ministry of Science and Technology. We are very much obliged to Marta M. Furio and Laura Torro for the investigations at the scanning electron microscope.

Bibliography

CONTRERAS, F. (coord.):

2000 Análisis histórico de las comunidades de la Edad del Bronce del Piedemonte meridional de Sierra Morena y Depresión Linares-Bailén. Proyecto Peñalosa. Arqueología, Monografía 10, Sevilla, Dirección General de Bienes Culturales.

CONTRERAS, F. & CAMARA, J.A.:

2000 El poblado de la Edad del Bronce de Peñalosa (Baños de la Encina, Jaén). 4. La cerámica. In F. Contreras (coord.), Análisis histórico de las comunidades de la Edad del Bronce del Piedemonte meridional de Sierra Morena y Depresión Linares-Bailén. Proyecto Peñalosa. Arqueología, Monografía 10, Sevilla, Dirección General de Bienes Culturales, 77-128.

CONTRERAS, F. & CAMARA, J.A.:

2002 La jerarquización social en la Edad del Bronce del Alto Guadalquivir (España). El poblado de Peñalosa (Baños de la Encina, Jaén). BAR International Series 1025, Oxford, BAR.

CONTRERAS, F., CAMARA, J.A., MORENO, A. & ARANDA, G.:
2004 Las sociedades estatales de la Edad del Bronce en el Alto Guadalquivir (Proyecto Peñalosa. 2ª Fase). V Campaña de Excavaciones (2001). Anuario Arqueológico de Andalucía 2001, II, 24-38.

CRADDOCK, P.T.:

1995 Early Metal Mining and Production, Edinburg, Edinburg University Press.

HAUPTMANN, A.:

2003 Rationales of liquefaction and metal separation in earliest copper smelting: Basics for reconstructing Chalcolithic and Early Bronze Age smelting process. In: International Conference Archaeometallurgy in Europe. 24-26 September 2003. Milan, Italy. Proceeding. Vol. 1, Milan, Associazione Italiana di Metallurgia, 459-468.

HUNT, M., CONTRERAS, F. & ARBOLEDAS, L.:

2011 La procedencia de los recursos minerales metálicos en el poblado de la Edad del Bronce de Peñalosa (Baños de la Encina, Jaén). In: J.M. Mata, L. Torro & N. Fuentes (eds.), Actas del Quinto Congreso Internacional sobre Minería y Metalurgia Históricas en el S.E. Europeo (León 2008), Poblado de Segurs, SEDPGYM, 195-206.

MORENO, A., CONTRERAS, F., RENZI, M., ROVIRA, S. & CORTES, H.:

2010 Estudio preliminar de las escorias y escorificaciones del yacimiento metalúrgico de la Edad del Bronce de Peñalosa (Baños de la Encina, Jaén). Trabajos de Prehistoria 67 (2): 306-322.

MÜLLER, R., REHREN, TH. & ROVIRA, S.:

2004 Almizaraque and the early copper metallurgy of Southeast Spain: New data. Madrider Mitteilungen 45, 33-56.

ROVIRA, S.:

1999 Una propuesta metodológica para el estudio de la metalurgia prehistórica: el caso de Gorny en la región de Kargaly (Orenburg, Rusia). Trabajos de Prehistoria 56 (2), 85-113.

ROVIRA, S.:

2002a Early slags and smelting by-products of copper metallurgy in Spain. In: M. Bartelheim, E. Pernicka & R. Krause (eds.), Die Anfänge der Metallurgie in der Alten Welt/The Beginnings of Metallurgy in the Old World, Rahden/Wetf., Marie Leidorf.

ROVIRA, S.:

2002b Metallurgy and society in prehistoric Spain. In: B.S. Ottaway and E.C. Wager (eds.), Metals and Society, BAR International Series 1061, Oxford, BAR, 5-20.