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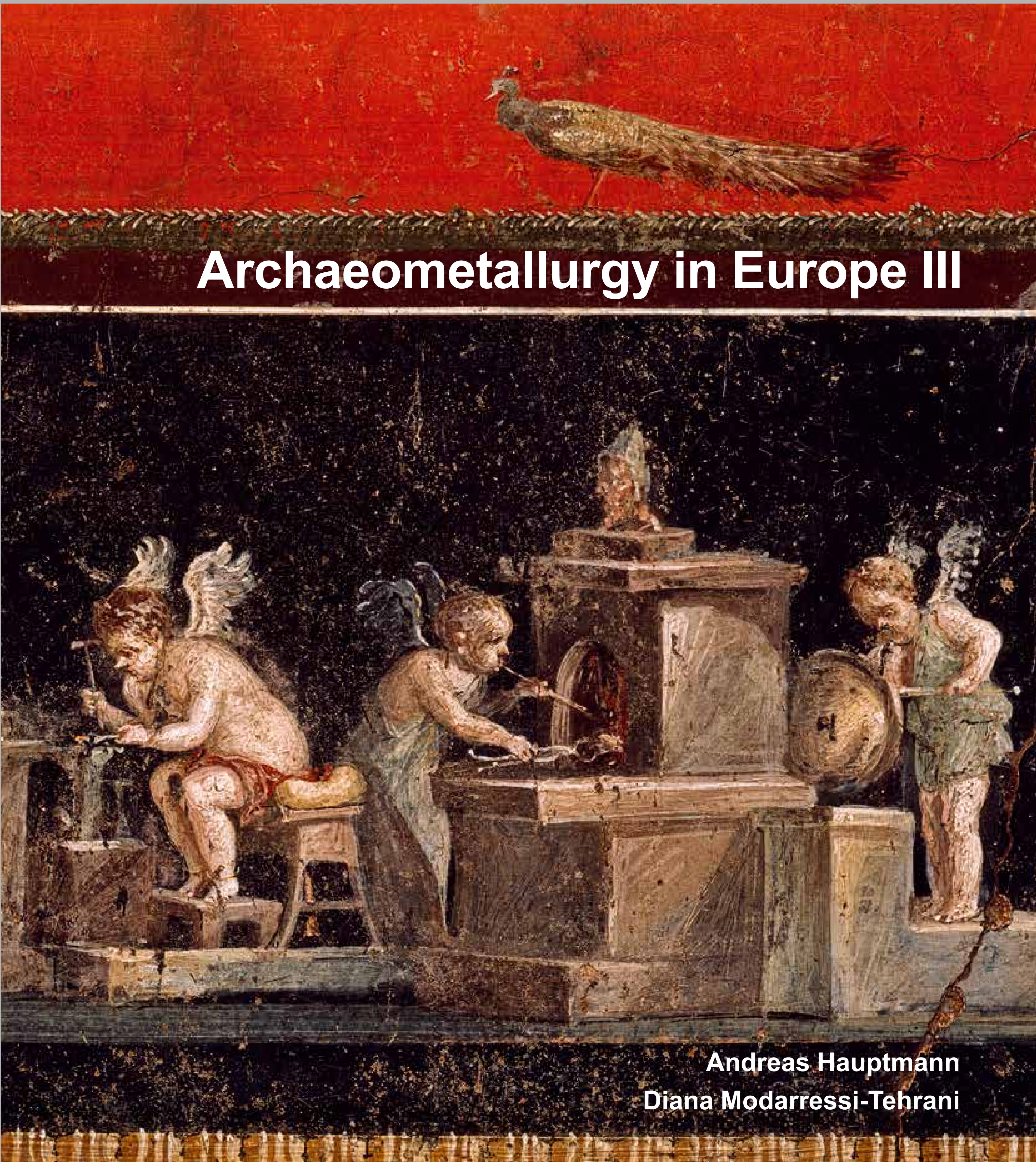
Archaeometallurgy in Europe III



Andreas Hauptmann
Diana Modarressi-Tehrani

Archaeometallurgy in Europe III

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

June 29 – July 1, 2011

Editors
Andreas Hauptmann
Diana Modarressi-Tehrani

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Domus Vettiorum / Casa dei Vettii, Pompeii (Campania, Italy, 63-79 BC), which was excavated in 1894. Section of a Pompeii-style scenic fresco showing Erotes and Psyches 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.

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Archaeometallurgy in Europe III

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 Assoziazione Metallurgia di Italia. Thanks to the efforts of Dr. Alessandra Giumlia-Mair, 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 belief 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

Reconstructing ancient technologies

Steffen Kraus, Christian Schröder, Susanne Klemm & Ernst Pernicka

Archaeometallurgical studies on the slags of the Middle Bronze Age copper smelting site S1, Styria, Austria

Summary

The copper smelting site S1 in the Eisenerzer Ramsau Valley, Styria, is the largest Bronze Age copper smelting site excavated in the Eastern Alps. The site was almost completely excavated from 1992 to 2006 and ten roasting hearths, six double furnaces, a number of pits of variable size, form and function, and three separate slag dumps have been recorded. The use of this smelting site covers the whole period of the Middle Bronze Age from the 16th to the 13th century BC and might extend as far as the 11th century BC. The aim of this archaeometallurgical study is the reconstruction of the smelting process at this site and the discovery of possible diachronic changes or developments in the technology of smelting during the different phases of use. Therefore slags of the different archaeological phases were analysed for their chemical and mineralogical composition. A few slags were analysed with Mössbauer spectroscopy to obtain further information about the conditions during the smelting process.

The results of the analyses show that nearly all slags belong to one particular step of the smelting process which was the production of raw copper or copper matte under reducing conditions at temperatures around 1250 °C.

Introduction

During the Bronze Age copper ores were mined and smelted in many areas of the Eastern Alps, where copper sulphides (chalcopyrite) and fahlore are found in the ore mineralisations of the greywacke zone. In Styria, an extensive prehistoric copper mining area has been in the process of being recorded in the Eisenerzer Alps since the 1950s (Klemm 2003; Klemm 2006; Klemm 2010). The largest Bronze Age copper smelting site excavated in the Eastern Alps – the copper smelting site S1 – is situated in the north-eastern part of those Alps, close to the mining town of Eisenerz.

The focus of the archaeometallurgical study is the chemical and mineralogical investigation of the slag material and associated finds. The aim of the archaeometallurgical investigation is to reconstruct the technology of the smelting process at this Bronze Age site. Furthermore, our intention was to discover possible diachronic changes or developments in the technology used for smelting copper ores during the different construction phases of the site.

The archaeological excavation

The stratigraphic excavation at the copper smelting site S1 from 1992 to 2006 has revealed about 80% of this complex Bronze Age site (Fig. 1). The remains of ten roasting hearths, six double furnaces, a number of pits of variable size, form and function, and three separate large slag dumps have been recorded (Klemm 2003; Klemm, in preparation). The use of this smelting site covers the whole period of the Middle Bronze Age from the 16th to the 13th century BC and might extend as far as the 11th century BC.

In accordance with all other smelting sites in the Eastern Alps, the Middle Bronze Age copper-works consist of two furnaces and one roasting hearth. In the north-western part of the site three different construction phases for these have been revealed. The double furnaces 9/10 with roasting hearth 7 date back to the earliest phase of the smelting site. In the following phase these furnaces were levelled and the double furnaces 4/5 with roasting hearth 4 were built to the north of these early furnaces. The latest phase is represented by the double furnaces 1/2 with the roasting hearths 1, 2 and 3. The stratigraphy of the central and eastern part of the site is more complex. This is partly due to extensive disturbances which resulted from the construction of a large pit for charcoal production at the end of the 13th to the early 15th century AD, the late mediaeval period (Klemm et al. 2005); the Bronze Age features in this central and eastern area of the site cover a period from the 15th to the 12th century BC.

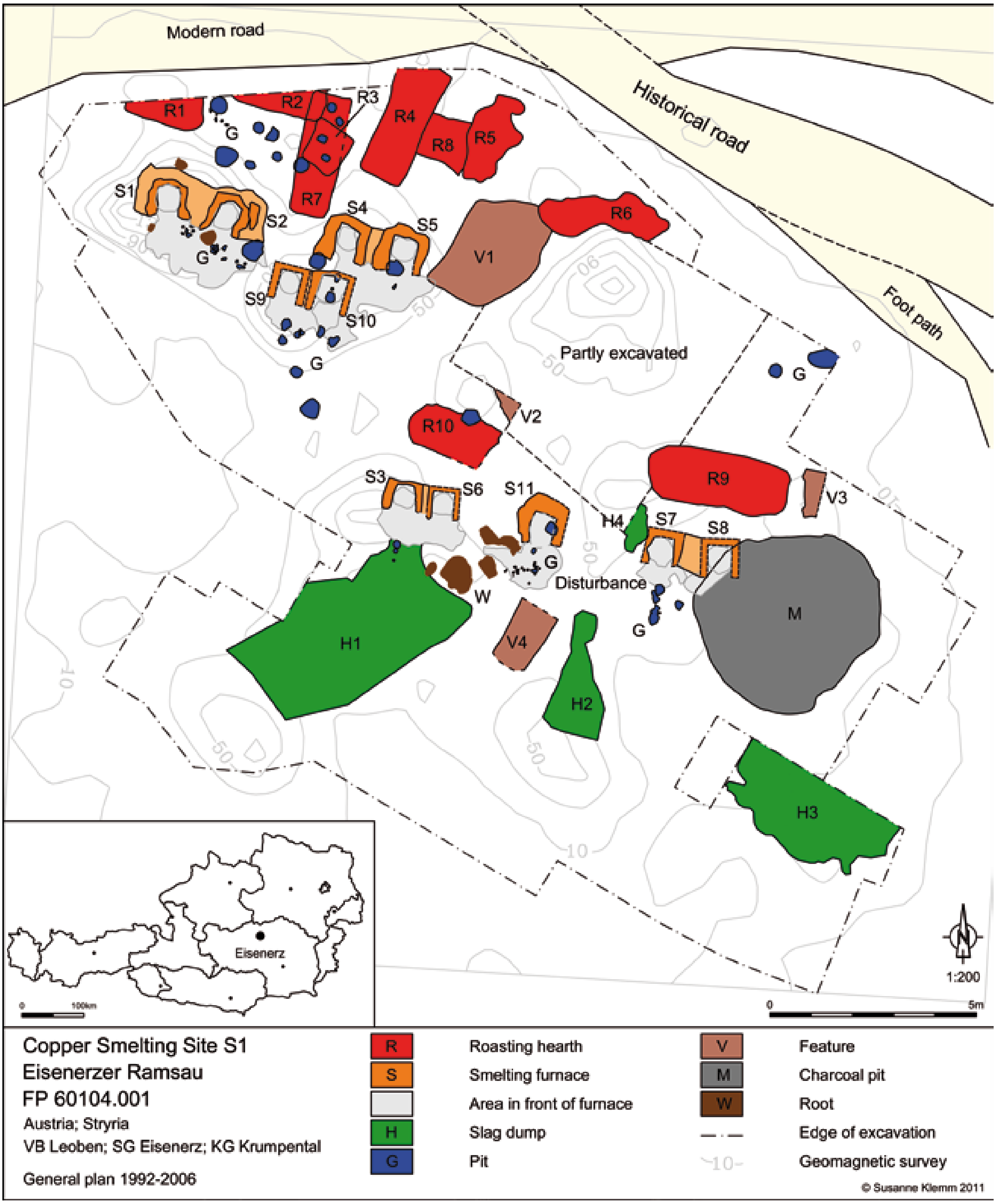

Fig. 1: General plan of the Bronze Age copper smelting site S1, Eisenerzer Ramsau, Styria. (S. Klemm, U. Schuh)

Archaeometallurgical study

Research objectives and methods

The mineralogical investigation included macroscopic analysis as well as optical microscopy in reflected and transmitted light enhanced by scanning electron microscopy which also allows the semiquantitative chemical analysis of small areas or particles. The chemical bulk composition of the slags was determined with wavelength-dispersive X-ray fluorescence analysis. In addition some slags from the double furnaces 9/10 and samples of the slag lining from the double furnaces 4/5

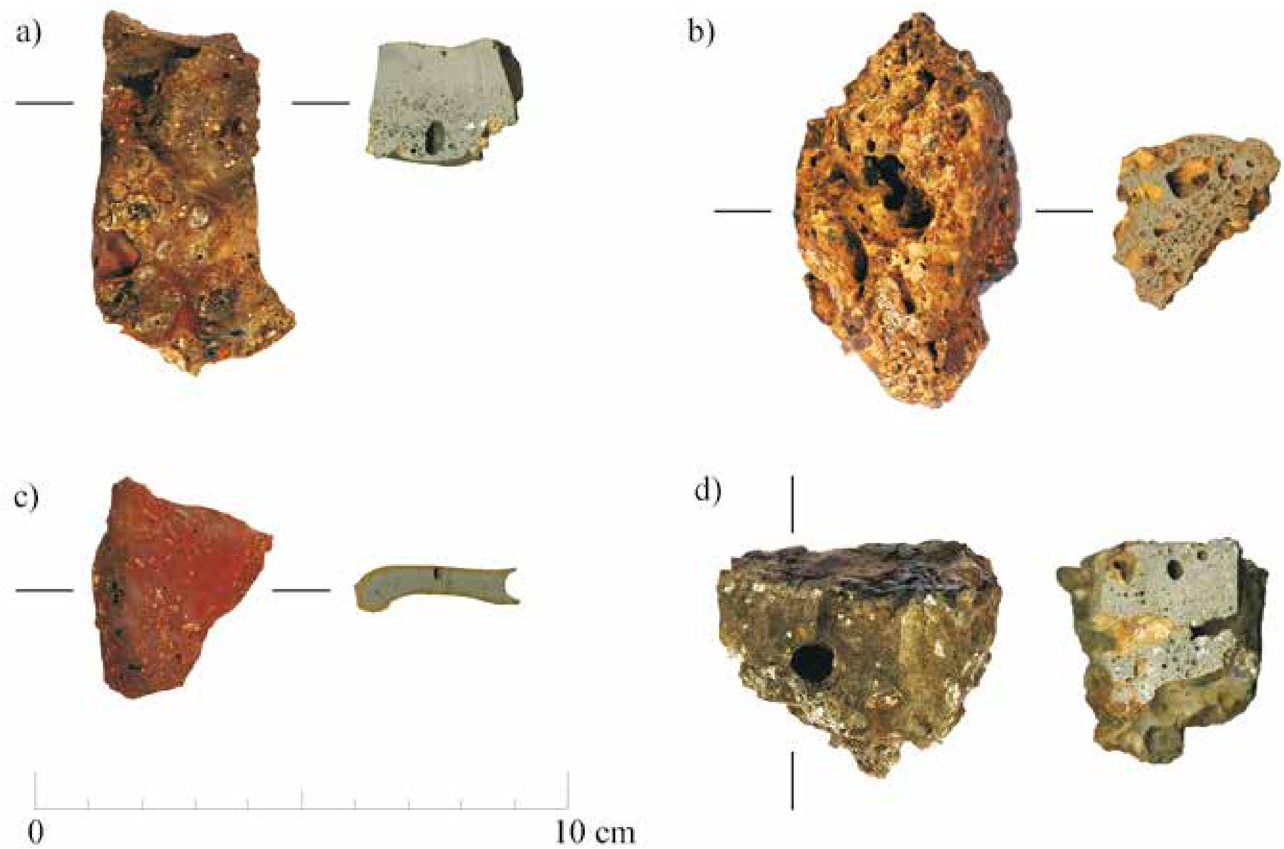

Fig. 2: Types of slags found at the copper smelting site S1: a) 'Laufschlacke' (type A); b) 'Blasenschlacke' (type B); c) 'Plattenschlacke' (type C); d) slag type A+B. (S. Kraus)

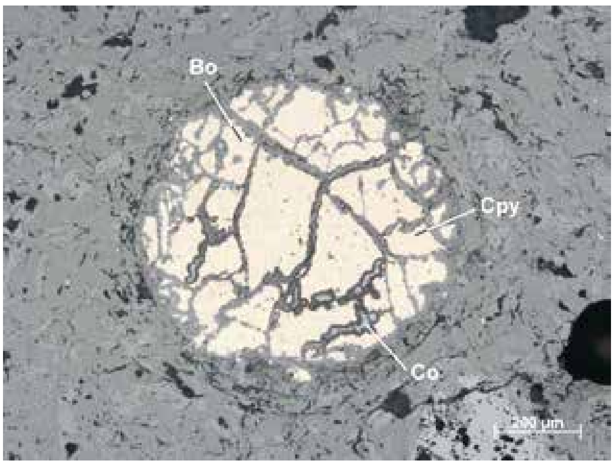

Fig. 3: Copper matte inclusion (Bo = bornite, Co = covellite, Cpy = chalcopyrite). (S. Kraus)

were analysed with Mössbauer spectroscopy to determine Fe^{2+}/Fe_{total} ratios and the abundance of Fe-bearing minerals. With this information it was possible to establish the temperature, oxygen partial pressure and cooling rate during the smelting process (Moesta et al. 1984; Moesta et al. 1989; Hauptmann 2000).

Results

Following Doonan et al. 1996, the slags were divided into three different types according to their macroscopic properties (Fig. 2): 'Laufschlacke' (type A), 'Blasenschlacke' (type B) and the characteristically thin 'Plattenschlacke' (type C). Mostly slags of types A or B or combinations of these (types A+B) and occasionally type C slags were found at the site.

Under the microscope the slag types A 'Laufschlacke' and B 'Blasenschlacke' show similar structures of short prismatic to lath-shaped olivines and prismatic clinopyroxenes. The only differences between these two slag types are the higher porosity of type B 'Blasenschlacke' and the increased occurrence of unmelted quartz inclusions in it. Some of these quartz inclusions contain the remains of Cu/Fe-sulfides. These are mainly iron-rich sulfides which consist of agglomerates of copper bearing pyrrhotin and chalcopyrite. In contrast, the structure of 'Plattenschlacke' consists of thin, long fayalite needles in a glassy matrix. Nearly all slag samples contain matte inclusions (Fig. 3) of varying copper concentrations.

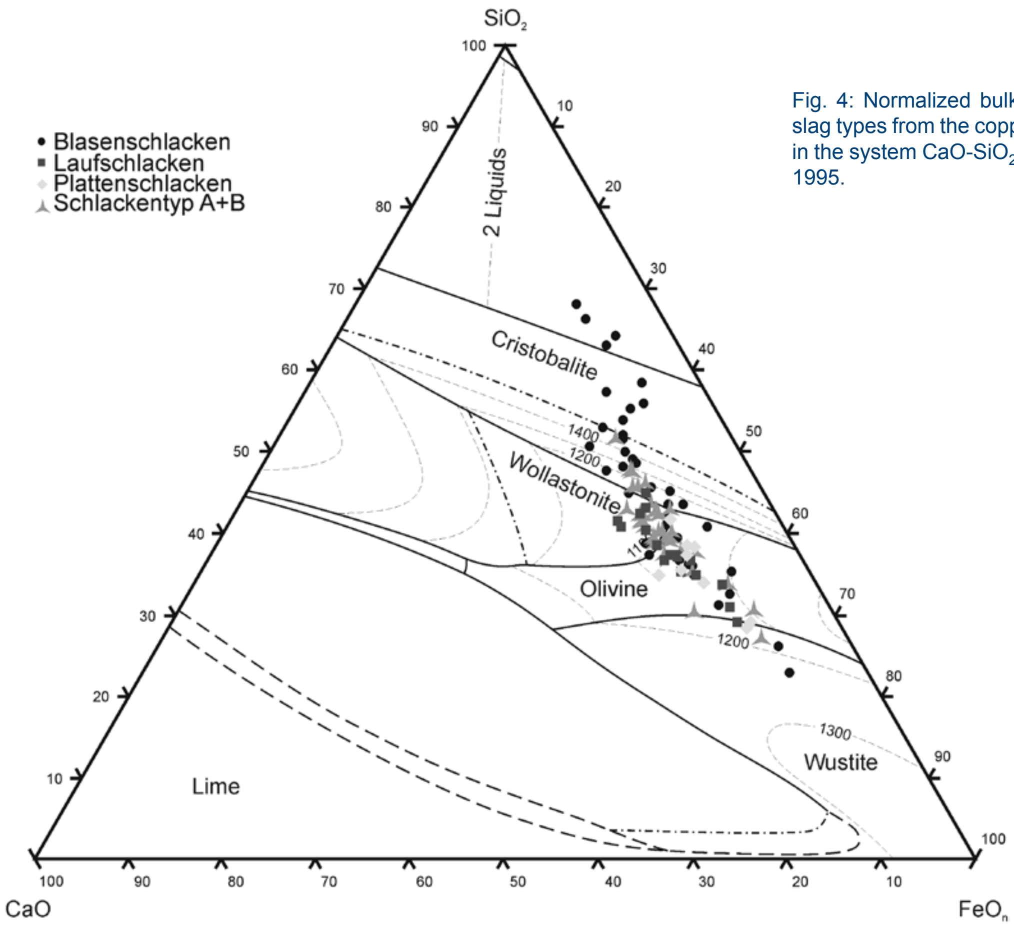

Fig. 4: Normalized bulk analyses of the different slag types from the copper smelting site S1 plotted in the system CaO-SiO_2-FeO_n after Kowalski et al. 1995.

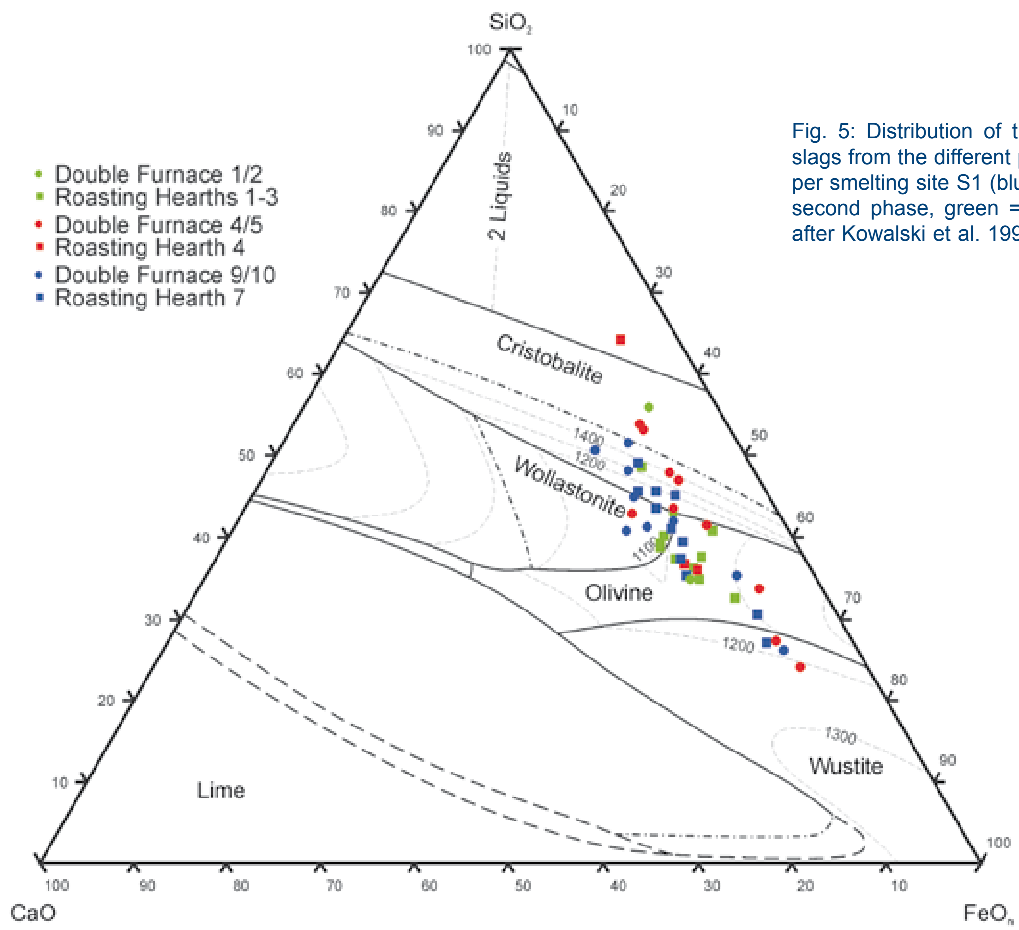

Fig. 5: Distribution of the main components for slags from the different phases of use of the copper smelting site S1 (blue = earliest phase, red = second phase, green = latest phase). (modified after Kowalski et al. 1995)

Table 1: Mössbauer model parameters, Fe oxidation state and mineral phase identification for samples MA-092862 and MA-101407 ([1]isomer shift relative to α-Fe at room temperature, [2]quadrupole splitting (ΔE_Q; doublet subspectra) or quadrupole shift (ε; sextet subspectra), [3]internal magnetic field, [4]Gaussian distribution of Voigt-based lineshapes; in mm/s (doublet subspectra) or T (sextets), [5]area ratio; proportional to Fe content in mineral phase).

δ[1]	**ΔE_Q** or ε[2]	B_{hf}[3]	**σ**[4]	A[5]	Fe ox.	Mineral
[mm/s]	[mm/s]	[T]	[mm/s or T]	[%]		
MA-092862						
1.18	2.35	-	0.2	24	Fe^{2+}	Pyroxene
1.17	2.85	-	0.2	25	Fe^{2+}	Olivine
0.33	1.03	-	0.2	9	Fe^{3+}	Paramagn. Fe^{3+}
1.18	1.93	-	0.2	20	Fe^{2+}	Pyroxene/glass
	1.23	-	0.2	6		
0.25	1.90	-	0.2	4	Fe^{3+}	Glass
0.37	0.10	51.8	1.0	3	Fe^{3+}	Hematite
0.26	0.00	49.2	1.0	5	Fe^{3+}	Magnetite
0.67	0.00	46.1	1.0	4	$Fe^{2.5+}$	Magnetite
MA-101407						
1.14	1.93	-	0.3	7	Fe^{2+}	Pyroxene
1.04	2.75	-	0.2	5	Fe^{2+}	Olivine
0.40	0.80	-	0.2	11	Fe^{3+}	Paramagn. Fe^{3+}
0.40	0.32	-	0.2	1	Fe^{3+}	Delafossite
0.37	-0.1	51.8	1	6	Fe^{3+}	Hematite
0.32	0.01	49.3	0.5	22	Fe^{3+}	Magnetite
		47.5	0.5	6		
0.62	0.01	46.3	0.5	16	$Fe^{2.5+}$	Magnetite
		44.7	0.5	11		
		42.9	0.5	6		
		40.2	0.5	3		
		48.1	0.5	5		

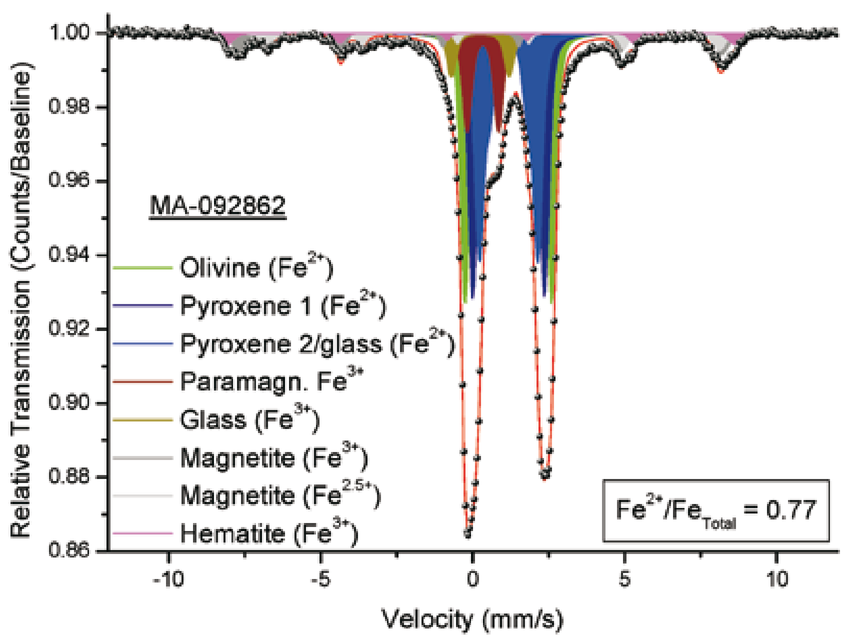

Fig. 6: Mössbauer-spectrum collected at room temperature of a 'Laufschlacke' (sample MA-092862) from the double furnace 9/10. The iron, made up of fayalite and pyroxene and very little magnetite with Fe^{2+}/Fe_{total} = 0.77, suggests a slow cooling of the melt within the furnace. (Graphics: C. Schröder)

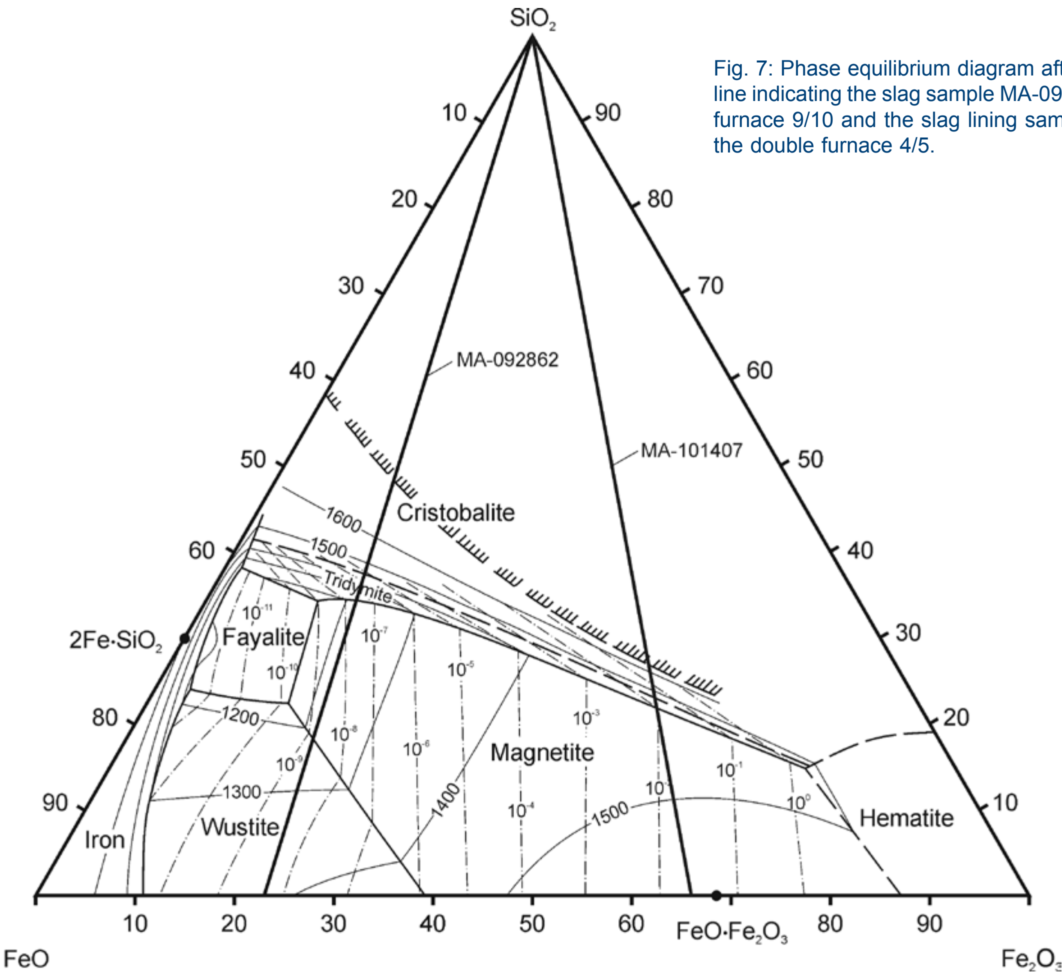

Fig. 7: Phase equilibrium diagram after Muan 1955 with a line indicating the slag sample MA-092862 from the double furnace 9/10 and the slag lining sample MA-101407 from the double furnace 4/5.

Figure 4 shows the distribution of the major components of the slag types in the ternary diagram CaO-FeO-SiO_2. It is obvious that macroscopically different slags show no significant differences in their chemical composition. These are mainly fayalitic and silicate slags formed during the smelting of roasted chalcopyritic ores. Some slags of type B show higher concentration of SiO_2 which is due to several inclusions of quartz. The smelting temperatures of the slags which can be derived from their chemical and mineralogical composition were between 1150 °C and 1250 °C.

In order to discover possible diachronic changes or developments in the technology used for smelting copper ores, the chemical composition of the slags from the different archaeological phases of the copper smelting site S1 were compared as shown in Figure 5. It was found that the slags from the latest period (from furnaces 1 and 2) were lower in SiO_2 content but higher in CaO content which corresponds well with the mineralogical results which showed that there were fewer inclusions of unmelted quartz in those particular slags. It can be assumed that in the later periods of use of the copper smelting site S1 the smelting process was performed without or with less quartz than in the previous periods. Nevertheless no evidence has been found of changes in the technique used for the smelting process. To obtain further information about the processing parameters, some slags were analysed with Mössbauer spectroscopy. Figure 6 shows the spectrum of a slag of the sample type 'Laufschlacke' and its associated Fe^{2+}/Fe_{total} ratio, which was used to deduce the oxygen partial pressure (pO_2) relating to the system FeO-Fe_2O_3-SiO_2 developed by Muan 1955 (Fig. 7). Therefore a line from the SiO_2-top was drawn to a point on the FeO-Fe_2O_3 axis representing the measured Fe^{2+}/Fe_{total} ratio. For the 'Laufschlacke' the pO_2 was found to lie between 10^{-9} and 10^{-8} atmospheres. The drawn line also shows the range of temperature to be between 1200 to 1300 °C which is in accordance with the temperatures that were estimated on the basis of the chemical composition.

In contrast to the slag sample from the double furnaces 9/10, the slag lining sample from the double furnaces 4/5 shows a different spectrum (Fig. 8). The slag lining sample derives from the northwest corner of furnace 5 at a height of approximately 20–25 cm from the bottom. The deduced pO_2 is between 10^{-2} and 10^{-1} atmospheres indicating oxidizing conditions at this height in the furnace during the smelting process.

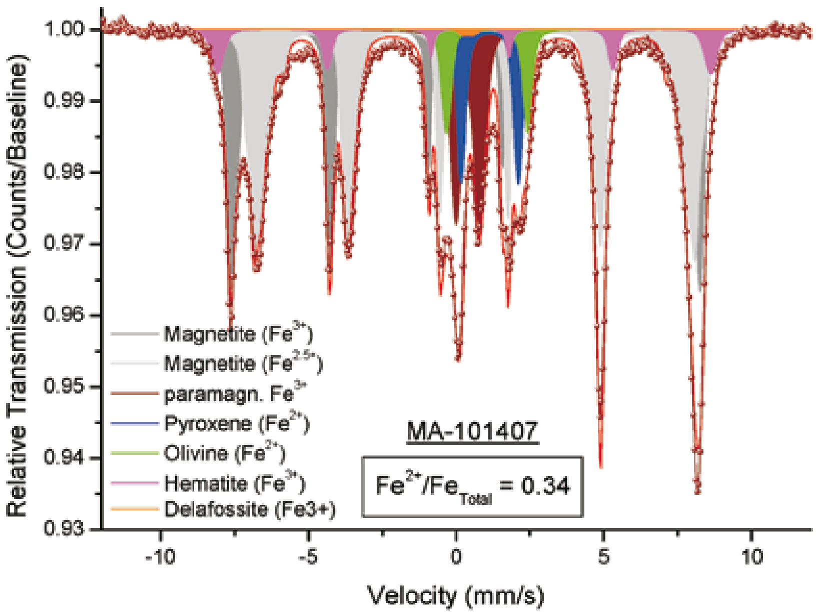

Fig. 8: Mössbauer-spectrum collected at room temperature of a 'Blasenschlacke' (sample MA-101407) from the double furnaces 4/5. The low Fe^{2+} / Fe_{total} = 0.34 suggests more oxidizing conditions. (Graphics: C. Schröder)

Discussion

The macroscopically different slags found at the Copper Smelting Site S1 show no significant differences in their chemical composition so it seems that they belong to the same step of the smelting process. Based on the composition of the copper matte inclusions that were found in nearly all the analysed slags, it can be assumed that the slags derive from a particular step of the production process such as the production of raw copper or copper matte. The pO_2 of 10^{-9} to 10^{-8} atmospheres indicates reducing conditions while smelting. The temperatures during the smelting process were determined to be between 1150 °C–1250 °C. The results of the Mössbauer spectrometry of the slag lining sample indicate oxidizing conditions in the lower part of the furnaces. Currently, there is no evidence of diachronic change or development in the smelting technology which means that throughout the Middle Bronze Age a most sophisticated metallurgical process was used to produce metallic copper at the site S1 and in this part of the Eastern Alps.

Acknowledgements

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