

Results of Magnetic Prospection in Connection with the Archaeological Excavation Finds of Late Antique and Early Mediaeval Iron Production Sites Velike Hlebine and Dedanovice in The Podravina Region, Croatia

Mušič, Branko; Horn, Barbara; Sekelj Ivančan, Tajana

Source / Izvornik: **Secrets of iron - from raw material to an iron object, Proceedings of the 7th International Conference of Mediaeval Archaeology of the Institute of Archaeology Zagreb, 2022, 20, 39 - 50**

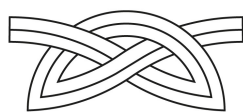
Conference paper / Rad u zborniku

Publication status / Verzija rada: **Published version / Objavljena verzija rada (izdavačev PDF)**

Permanent link / Trajna poveznica: <https://um.nsk.hr/um:nbn:hr:291:553569>

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Download date / Datum preuzimanja: **2024-11-19**



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KNJIGA
VOLUME **20**

SECRETS OF IRON - FROM RAW MATERIAL TO AN IRON OBJECT

Zagreb, 2022.



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Proceedings of the 7th International Conference of Mediaeval Archaeology of the Institute of Archaeology
Zagreb, 10th – 11th September 2020

Zagreb, 2022

ZBORNIK INSTITUTA ZA ARHEOLOGIJU
SERTA INSTITUTI ARCHAEOLOGICI
KNJIGA / VOLUME XX

PUBLISHER

Institut za arheologiju / Institute of Archaeology
Zagreb, Croatia

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Miljenko Gregl, artistic impression of iron ore smelting process

PRINTED BY

Tiskara Zelina d.d., Sv. I. Zelina

CIRCULATION

100

Financially supported by the Ministry of Science and Education of the Republic of Croatia

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CIP zapis dostupan u računalnom katalogu Nacionalne i sveučilišne knjižnice u Zagrebu pod brojem 001160084

A CIP catalogue record for this book is available in the Online Catalogue of the National and University Library in Zagreb as 001160084

ISBN 978-953-6064-66-3

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Foreword

The International Scientific Conference entitled “Secrets of iron - from raw material to an iron object” was organized by the Institute of Archaeology in cooperation with the Archaeological Museum in Zagreb as the seventh in a series of meetings of experts on topics related to medieval archaeology, but also other archaeological and historical periods. The gathering took place in Zagreb on the 10th and 11th of September 2020 in the Gallery of the Archaeological Museum in Zagreb at 6 Pavao Hatz Street, with an all-day program. The Organizing and Scientific Committee consisted of scientists from the Institute dealing with the medieval period: Tajana Sekelj Ivančan, PhD. Tatjana Tkalčec, PhD. Juraj Belaj, PhD. Siniša Krznar PhD. and doctoral student Tena Karavidović. A total of 62 colleagues participated, of which 44 international and 18 Croatian, who presented 16 international and 11 local presentations and/or posters.

Although we live in challenging and unstable times caused by the pandemic of Covid-19 virus, but also by the earthquake in Zagreb which, in the spring of 2020, significantly damaged the city centre, the intention to address issues related to iron production and the manufacture of iron objects in the pre-industrial era was successfully realised. The scientific conference was organized as a hybrid event, with presentations held at the Museum Gallery and via the web platform, all broadcasted live with the active involvement of participants in discussions through the web platform *Crowdcast*. Posters of the participants who were not able to attend the conference in person were printed out and available online on the Institute of Archaeology website during the conference. The official languages of the conference were Croatian and English.

Several lectures and presentations from the conference were prepared for these Proceedings. The received papers cover multiple archaeological and historical periods, from the Early Iron Age up to the Modern Age, while geographically covering almost the entire European area and beyond. The Proceedings are interdisciplinary and include papers with various methodological approaches and sub-topics that permeate and complement each other. The sixteen papers collected in the publication present the results of non-invasive research methods on sites with remnants of ironworks activities, the geological study of the potential for ore formation within a lowland landscape, studies of ore sources and mining, the results of archaeological excavations of preserved furnaces, workshops and ancillary facilities, as well as insights on archaeological finds of slag and technical ceramics and iron objects, as well as discussion on long-term iron production and knowledge transfer and the results of conducted analyses from the spectrum of natural sciences which define the types of materials and technology of iron production and production of iron objects, as well as methods of approach to chemical profiling of archaeological samples. The afore-mentioned papers are signed by thirty-five (co)authors, scientists from Slovenia, Austria, Germany, the Czech Republic, Romania, Poland, Latvia, the Russian Federation and Croatia, who, each in their own way, open a new perspective and contribute to our understanding of iron production and processing.

With these Proceedings, we aim to encourage some new reflections, present the results of new archaeological and interdisciplinary research and insights that will be useful in further research on specific topics related to iron production and processing, and offer them to the general scientific and professional public.

Tajana Sekelj Ivančan and Tena Karavidović

ADVANCED INSTRUMENTAL METHODS IN CHEMICAL PROFILING OF ARCHAEOLOGICAL SAMPLES

Advanced instrumental analytical methods are adopted as the most helpful tools in the chemical characterization of archaeological artefacts. The most challenging issue of provenancing of archaeological objects is often based on chemical elemental fingerprinting. Spectroscopy methods such as instrumental neutron activation analysis (INAA), proton induced X-ray and gamma-ray emission (PIXE, PIGE), scanning electron microscopy (SEM), X-ray diffraction and fluorescence (XRD, XRF) were employed in wide area of archaeological researches. Notable advantages of atomic spectrometry methods based on inductively coupled plasma source with optical or mass detection and laser ablation coupled to plasma mass spectrometry (ICP-AES, ICP-MS; LA-ICP-MS) lay in reliable and high dimensional quantitative elemental characterization of various materials. A multi-sample and/or multi-method analytical approach has showed to be capable for collection of enough compositional data, which are prerequisite for characterization of findings. An overview of advanced instrumental techniques along with their advantages and disadvantages in specific area of archaeological samples recognition is presented in this work.

Key words: chemical profiling, instrumental analytical methods, archaeometallurgical artefacts

INTRODUCTION

Compositional analysis of archaeological materials by means of mineralogical, petrographic and chemical methods provides valuable information of provenance, technology of production and authenticity of objects and findings (Glascok 2016; Pollard 2007). Analysis of chemical composition usually refers to determination of elemental content that can be repeatedly recognized and it represents a specific chemical signature of the observed material. Therefore, “elemental profiling” and “elemental fingerprinting” of examined samples is a kind of chemical analysis with intrinsic aim to detect as many constituents of sample as possible (Trojanowicz 2008). The most helpful tools in the chemical characterization of archaeological artefacts are advanced instrumental analytical methods. Thus, various spectroscopy methods, such as instrumental neutron activation analysis (INAA), proton induced X-ray and gamma-ray emission (PIXE, PIGE), X-ray diffraction and fluorescence (XRD, XRF), scanning electron microscopy (SEM) and plasma based spectrometry (ICP-OES, ICP-MS, LA-ICP-MS), were employed in wide area of archaeological researches (Pillay 2001; Tandoh et al. 2009; Font et al. 2012; Ganio et al. 2012). A multi-sample and/or multi-method analytical approach has showed to be capable for collection of enough compositional data, which are prerequisite for characterization of findings (Schwab et al. 2006; Misarti et al. 2011).

However, the provenancing of archaeological objects based on elemental fingerprinting is still challenging task. The example of complexity of obtaining the provenancing information, one can find in the area of archaeometallurgical studies (Desaulty et al. 2008; Rehren, Pernicka 2008). For instance, the recognition of types of iron ore used in bloomery smelting processes and reconstruction of technology process belong to such demanding research tasks (Killick, Fenn 2012; Stepanov et al. 2020). Therefore, application of more than one advanced analytical technique in studies of chemically complex artefacts is recommendable. In this work, the overview of advanced instrumental techniques that are commonly used in elemental profiling of archaeometallurgical samples is presented. The aim of this overview is to point out the advantages and disadvantages of presented analytical instrumental methods in acquisition of archaeologically useful and reliable data.

SELECTION OF ANALYTICAL METHOD

Application of chemical analysis on different types of archaeological samples by use of advanced instrumental methods have specific advantages and disadvantages. Therefore, a selection of an appropriate method for compositional analysis is very important. Before submitting archaeological samples to an analytical laboratory, consultation on the types of analysis would be advantageous. This interdisciplinary project counselling should presuppose the answers to the crucial following questions (Glascock 2016; Price, Knudson 2019):

1. Which analytical method is the most appropriate for the specific archaeological material?
2. Will the elements measured be able to answer the archaeological questions?
3. Is the sensitivity of method adequate for the determination of elements of interest?
4. Are the measurements precise and accurate?
5. Is the applied method invasive or non-invasive for sample?
6. How much sample is required for the specific analytical method?
7. Does the laboratory have previous experience with the archaeological samples?
8. Is there any disposable database for comparative purposes?
9. Are the measured data from applied methods comparable to data from other studies?
10. What are the costs of the applied methods?

Beside the most important answers, additional instructions on collection, preparation and delivery of samples to the analytical chemistry laboratory should be provided, too. Such previous mutual arrangements between archaeologists and chemists may avoid collection of unessential data, especially in the case of large and expensive analytical experiments.

ACTIVATION ANALYSIS (NAA) AND PARTICLE INDUCED EMISSION TECHNIQUES (PIXE, PIGE)

Neutron activation analysis (NAA) is an instrumental method for the determination of elemental concentrations in a wide variety of samples including various archaeological materials in solid state. Generally, this method might be non-invasive for small-sized samples, but very often samples must be grounded into powder before analysis. The method involves exposition of samples to the flux of neutrons that causes many elements in the sample to become temporarily radioactive. The radioactive decay of elements into stable forms produce gamma rays of different energy levels, which are characteristic for the specific element (Fig. 1). This phenomenon allows many elements to be identified and measured simultaneously (Tandoh et al. 2009). Nuclear reactors with high fluxes of neutrons obtained from uranium fission give the best sensitivity for the most of the examined elements. For this reason, NAA method is limited in accessibility.

One of the most powerful methods for identifying the technology processes in archaeometallurgical investigations is particle-induced X-ray emission (PIXE). This technique induces characteristic X-ray radiation by bombarding the surface of the sample with energetic heavy charged particles such as protons. Because of its low detection limits (between 1 and 100 mg kg⁻¹) for samples weights of a few milligrams, and the higher sensitivity obtained compared to standard X-ray fluorescence method (XRF). The method is used to detect trace elements as well as major and minor elements. Thus, it is a technique of great importance in provenance studies (Tuurnala et al. 1985; Pillay 2001). Usually, samples are placed in a vacuum chamber and the most of instruments can accommodate small-sized samples. Further advantages of this technique are that the instrument can be modified, separating the vacuum system from the sample chamber, permitting examination of specimens without sampling or charging. The penetration depth of incident radiation takes several microns, and it can indicate the bulk sample composition if surfaces are polished to remove tarnish, patinas, or weathering crusts prior to analysis. In the case of complementary technique such as particle induced gamma ray emission (PIGE), emitted gamma rays are of particular interest as their energies are characteristic for the element. Therefore, it is used to fingerprint elemental composition while yields are used to quantify elemental concentrations (Mateus et al. 2007). However, ion beams for PIXE and PIGE techniques which produced by accelerators are expensive, and thus there are limited instruments that are available in specific research laboratories (Fig. 2).

X-RAY DIFFRACTION (XRD) AND X-RAY FLUORESCENCE (XRF)

X-ray diffraction (XRD) is a non-destructive technique for analysing the structure of materials at the atomic or molecular level. It works best for materials that are crystalline, but is also used to study non-crystalline materials. The method has been traditionally applied for phase identification, qualitative analysis and the determination of structure imperfections. Generally, incident X-ray beam encounters the regular three-dimensional arrangements of atoms in a crystal. The most of

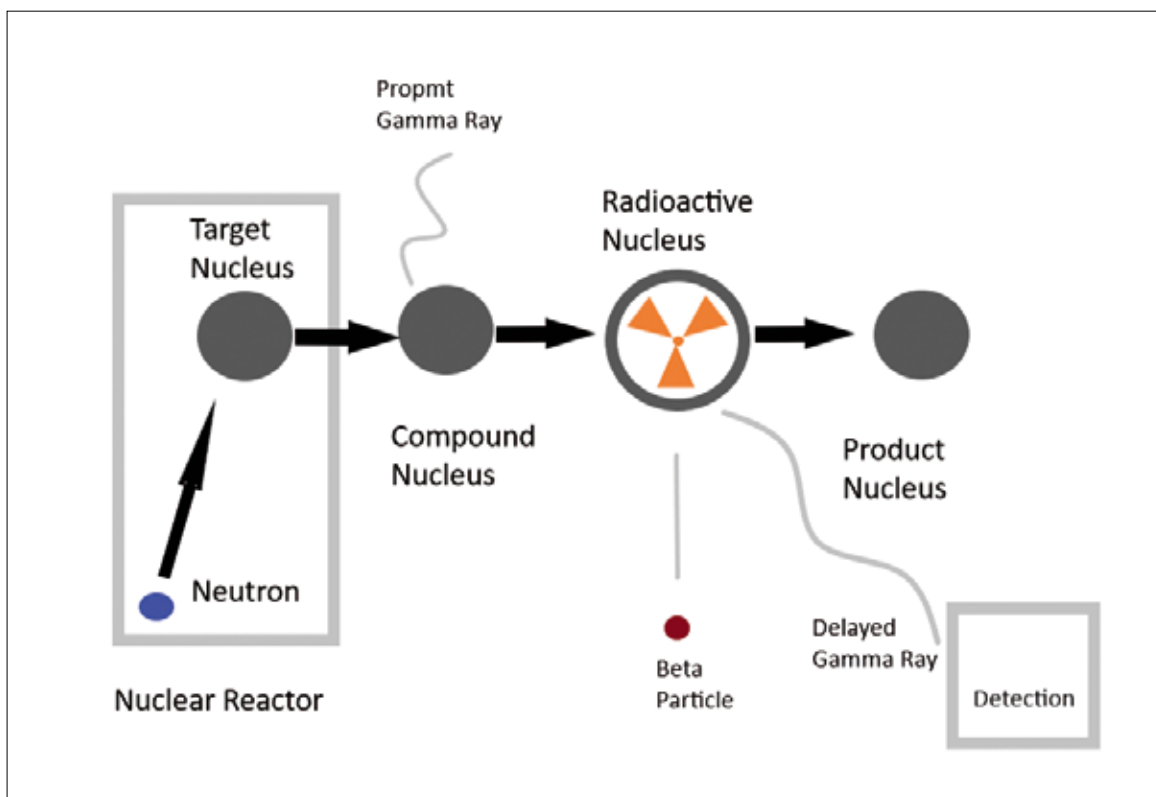


Fig. 1 Schematic presentation of NAA method (made by: S. Rončević)

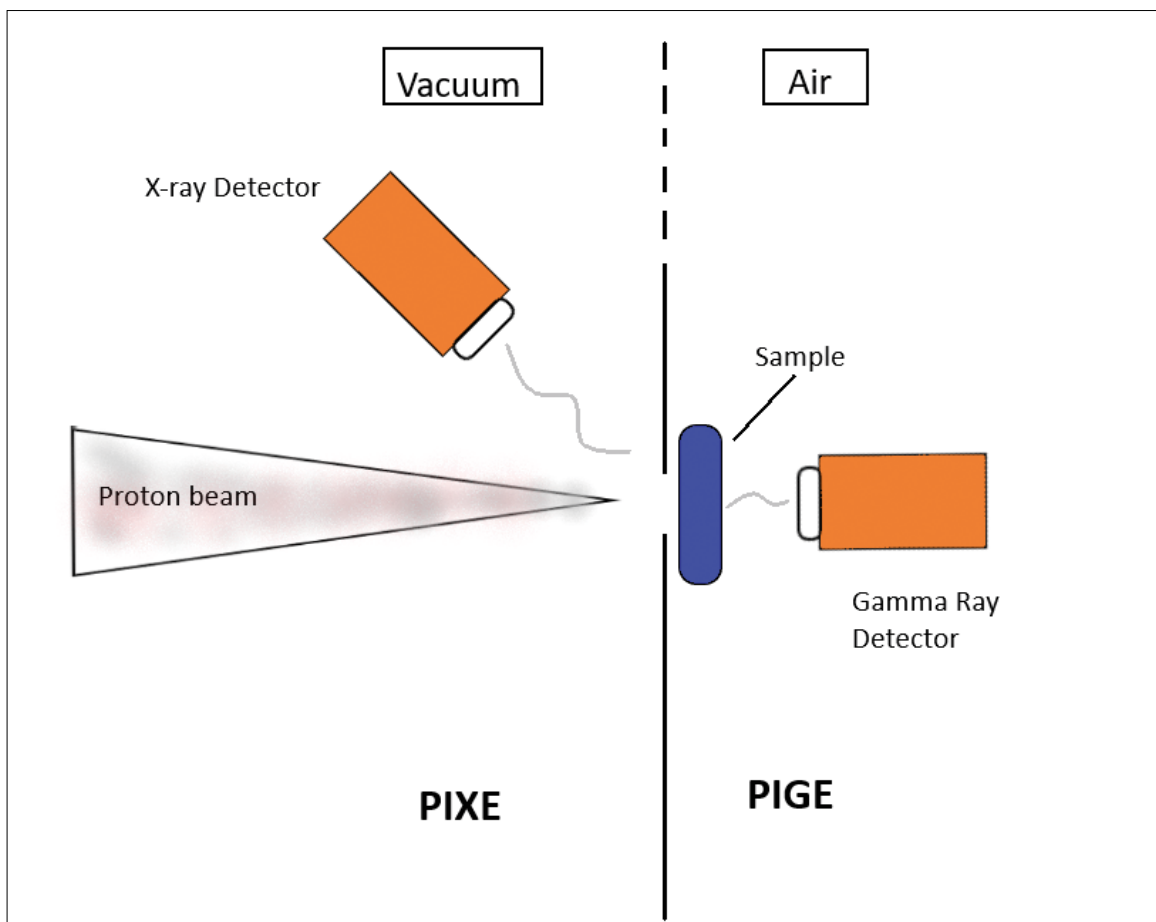


Fig. 2 Schematic presentation of PIXE/PIGE method (made by: S. Rončević)

the X-rays will destructively interfere with each other and cancel each other out, but in some specific directions, the X-ray beams interfere constructively and amplify one another. The diffracted X-rays produce the characteristic X-ray diffraction pattern that is used for crystal structure determination.

In recent years, applications have been extended to new areas, such as the determination of moderately complex crystal structures and the extraction of three-dimensional microstructural properties (Artioli 2019). Various kinds of microcrystalline materials may be characterized from X-ray powder diffraction (XRPD), such as inorganic, organic compounds, minerals, catalysts, metals and ceramics. For most applications, the amount of information, which can be extracted, depends on the nature and magnitude of the microstructural properties of the sample, the complexity of the crystal structure and the quality of the experimental data. Since the method is one of the few that detect and quantify minerals, it can be used to measure the different minerals in iron ores (Young 2012; Stepanov et al. 2020). This usually can enhance the classification of ores and clarify the elemental variation of main constituents.

X-ray fluorescence (XRF) spectrometry is a well-known, well-established and widely applied technique in the determination of many major elemental compositions of geological, environmental and metallurgical materials. By this technique, solid samples are analysed non-destructively through X-radiation. The physical principles of XRF are simple: electronic transitions can be induced in the inner shells of the atoms by electromagnetic radiation or charged particles of suitable energy (Fig. 3). Such transitions result in the emission of X-rays whose energy and intensity are related to the type and abundance of the atoms involved by the interaction. In practice, there are limitations in detecting light elements with the low fluorescence yield and the attenuation of X-rays by the detector window for elements lighter than sulphur ($Z = 16$). Due to attenuation in the matter, only the X-rays emitted in the first layers under the surface can reach the detector. Portable XRF instruments that can perform non-destructive analysis of examined material are of great importance due to their high applicability. Their importance has been recognised in the archaeometric field where art historians, conservators and restorers perform analyses on art works without causing any damage and without the need to move the objects to specialized laboratories (Shackley 2018). This enables qualitative and quantitative information on chemical composition of the objects of interest. It should be keep in mind that quantitative analyses can be performed only in cases when the sample is homogeneous and its surface material is the same as in the rest of the object (Bitay et al. 2020).

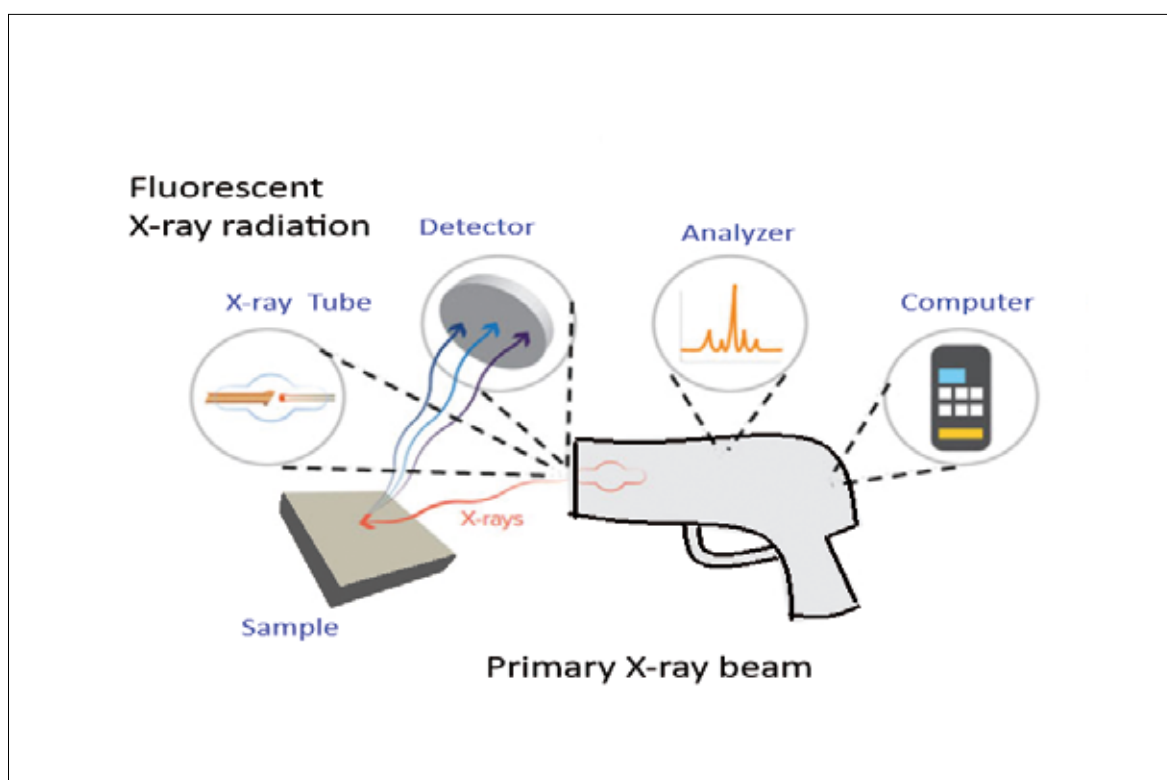


Fig. 3 Schematic presentation of portable XRF instrument (made by: S. Rončević)

There are limitations regarding the age and calibration of instruments, costs of setting up, matrix effects and the sets of available standards. However, XRF laboratory analyses remain the most acceptable technique for providing high-quality data analyses in the investigation of main and minor elemental fraction of archaeometallurgical samples.

SCANNING ELECTRON MICROSCOPY (SEM)

Scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX) is an excellent tool in many fields of science. It has found many applications in archaeological fields like ceramic material studies, pigment analysis, archaeometallurgical tracking of ores, and human remains studies (Froh 2004; Shah et al. 2019; Stepanov et al. 2020).

The scanning electron microscope allows the observation of very fine details of sample morphology with a resolution down to the order of about a nanometer. To obtain a scanning electron image, the sample surface is scanned with a focussed beam of high-energy electrons (Fig. 4). The interactions of these primary electrons with the sample surface give rise to the emission of electrons and photons. They are mostly secondary electrons, backscattered electrons and X-rays. The characteristic X-rays emitted when the target is subdued to electron beam, yield element analyses for selected spots on the target surface. They can be used to produce images of the distribution of certain elements in the selected area of sample.

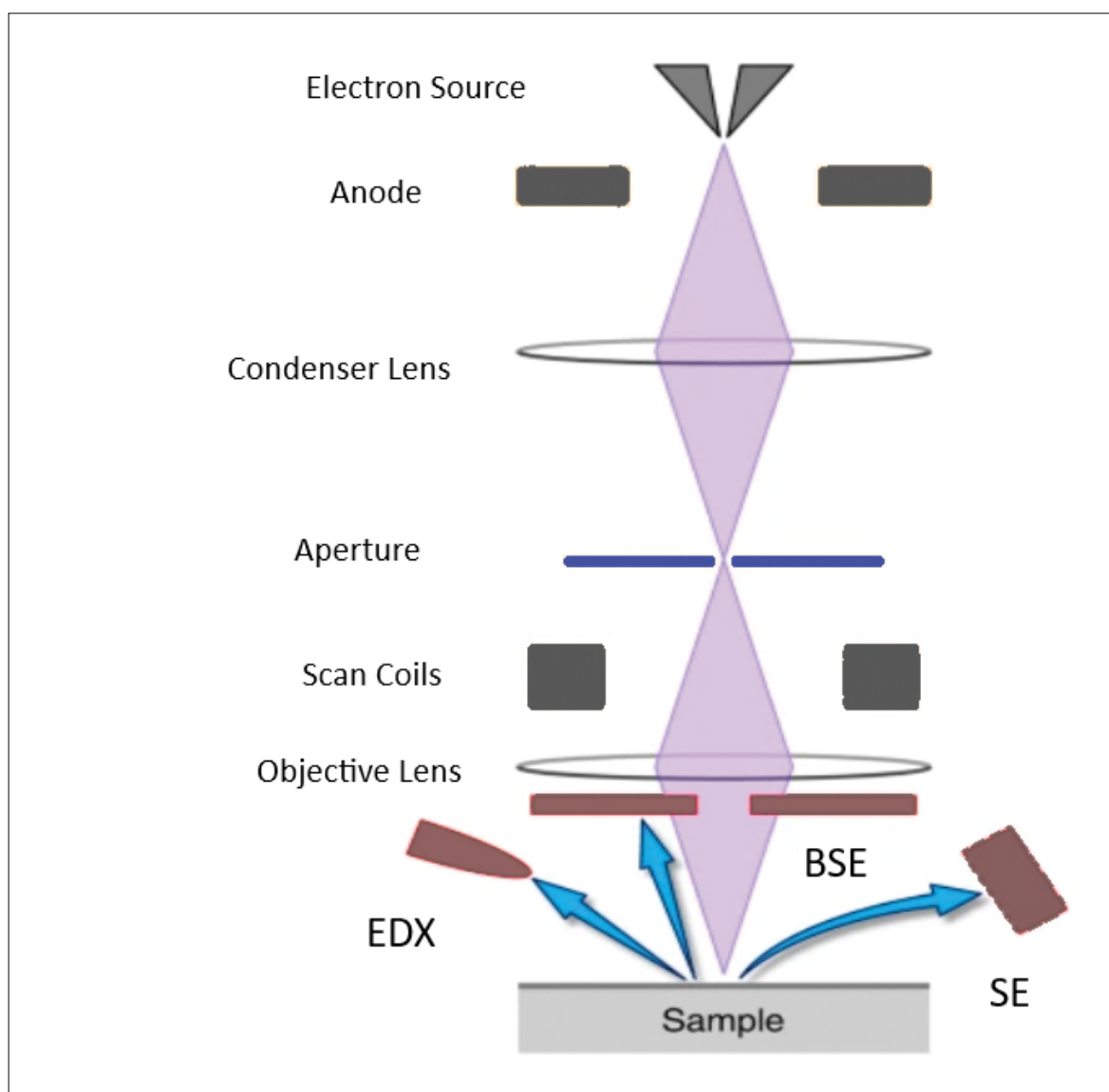


Fig. 4 Schematic presentation of SEM method (made by: S. Rončević)

Scanning electron microscopes (SEM) enable us to see details under much higher magnification, with high resolution. It gives possibility to measure fine details of sample structures. The advantages of microanalysis of archaeological artefacts with a SEM are numerous. It provides a relatively quick and nondestructive means of obtaining qualitative information on the constituents of examined material. However, the procedure of sample preparation can be time-consuming and rather expensive. For example, nonconductive materials must be coated with an ultrathin layer of a conductive material such as gold or graphite, to prevent an electric charge building up on the sample surface.

PLASMA SOURCE METHODS (ICP-OES, ICP-MS)

In numerous studies, it has been shown that excellent sensitivity and good detection limits of applied analytical technique are essential to investigate archaeological and historical materials since in most cases trace elements provide more information than the major ones. Notable advantages of atomic spectrometry methods based on inductively coupled plasma source with optical or mass detection (ICP-AES, ICP-MS) lay in reliable and high dimensional quantitative elemental characterization of various materials.

To generate plasma, an argon gas is supplied to plasma torch, and high frequency electric current is applied to the work coil at the tip of the torch (Fig. 5). Using the electromagnetic field created in the torch by the high frequency current, argon gas is ionized and plasma is generated. Plasma source has high electron density and temperature (10 000 K) and this energy is used in the excitation or ionization of the elements present in the sample. Samples, which are usually decomposed by acid digestion are introduced into the plasma through nebulizer as fine aerosol of solution.

One of the main advantages of optical plasma spectrometry (ICP-OES) for elemental analysis is that it can be used to measure almost all the elements in the periodic table. The technique has a wide dynamic concentration range and can measure elements at trace to high concentrations. Detection limits for most elements are in the range of micrograms per liter to milligrams per liter. Another advantage of ICP-OES is that multielemental quantitative analysis can be carried out in a period as short as 1 min with a small amount of sample solution (usually 0.5–1.0 mL). Those characteristics make ICP-OES a useful method for elemental analysis in various forensic laboratories. The technique combines good quantitative multielement capability, wide linear dynamic ranges, good sensitivity, limited spectral and chemical interferences, low detection limits, and speed and ease of data handling and reporting with widespread instrument availability and reasonable costs (Nölte 2003; Pollard et al. 2007).

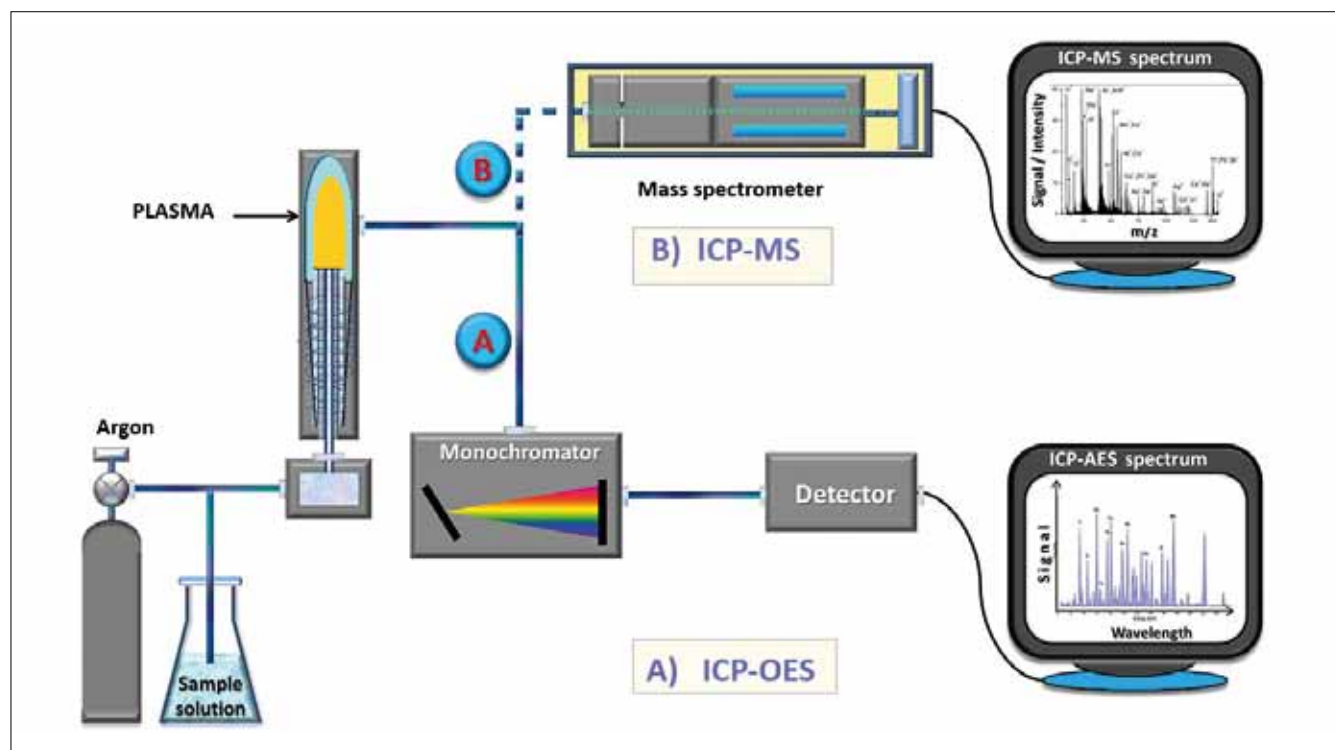


Fig. 5 Schematic presentation of ICP-OES and ICP-MS method (made by: S. Rončević)

Inductively coupled plasma mass spectrometry (ICP-MS), a powerful characterization tool used in the process of finding new materials and in elemental analysis of various kinds of samples, has evolved as the most versatile detection technique. It is capable of identifying and measuring the most of the elements from the periodic table and is deployed in diverse fields such as biophysics, environmental science, forensic science, materials science, speciation analysis, etc. It is an instrumental technique capable of measuring nearly every element at concentrations as low as 1 part in 10^{15} (parts per quadrillion) on noninterfered low-background isotopes. This is achieved by ionizing the sample in plasma and then using a mass spectrometer to separate and quantify generated ions (Fig. 5) Compared to atomic optical plasma spectrometry, ICP-MS has greater sensitivity and a potential to determine isotope ratio in sample material (Desaulty et al. 2008; Blakelock et al. 2009; Font et al. 2012). However, ICP-MS introduces many interfering species such as argon from the plasma, component gases of air, and contamination from glassware or sample solution, which can affect the measured results.

Liquid sampling is a powerful method for bulk compositional characterization but sometimes it present a problem in archaeological artefacts studies. In contrast to bulk chemical analysis techniques, laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a direct solid sampling micro-analytical technique. It is capable of performing spatially resolved multi-elemental analysis of the solid samples and it has a number of advantages for the analysis of crude material, including minimal sample preparation, no loss of volatile elements, reduced contamination from reagents, and high sample throughput. This method can be used to produce chemical information in a wide range of archaeological applications including the analysis of ceramic surface treatments, paste composition, temper composition, and identification of post-burial chemical alteration (Giussani et al. 2009; L'Héritier et al. 2016).

The main disadvantage of LA-ICP-MS is the problem of precision and accuracy, which are worse than those of ICP-MS with conventional pneumatic nebulization of solutions. The preferred method for accurate quantification in LA-ICP-MS is external calibration relying on matrix-matched calibration standards (certified reference materials or in-house prepared standards), which are used to minimize the influence of matrix effects. Due to the lack of multiple matrix-matched certified reference materials, glass reference materials are regularly used as standards in provenance studies (Vannoorenberghe et al. 2020). However, insufficient matrix-matching materials as external calibration standards can lead to systematic measurement errors. Generally, hyphenated technique LA-ICP-MS is particularly valuable when used in conjunction with bulk and mineralogical characterization techniques to elucidate which potential cultural, geological, or environmental effects are responsible for bulk compositional patterning (Giussani et al. 2009).

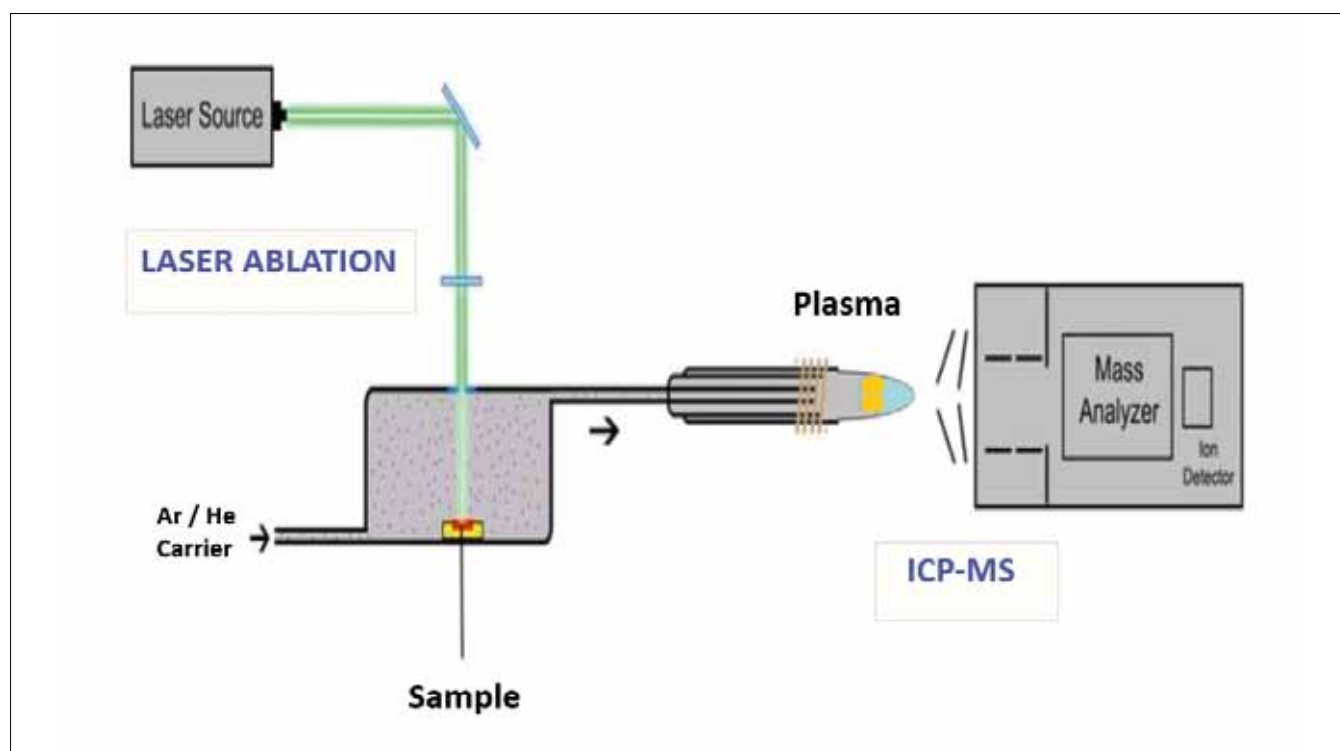


Fig. 6 Schematic presentation of LA- ICP-MS method (made by: S. Rončević)

MULTI-METHOD APPROACH IN ANALYSIS OF ARTEFACTS FROM EARLY-IRON PRODUCTION

Analysis of chemical composition of iron artefacts from ancient bloomery iron production are generally focused on determination of main and trace element contents in raw materials and waste. Elemental profiling and determination of specific elemental signature of artefacts usually denote chemical description of carefully selected sample of final iron-making products as well as to randomly collected samples of slag and pit deposit materials on an excavation site (Coustures et al. 2003; Paynter 2006; Navasaitis et al. 2010; Brenko et al. 2020). Compositional relations between ore, smelting slags, bloom material and iron products, is the most valuable information for provenancing attempts (Eliyahu-Behar et al. 2008)

In reconstructions studies of ancient iron making process, archaeologists have confirmed that different types of slag materials are formed during smelting and smiting processes (Blakelock et al. 2009; Senn et al. 2010). Determination of main and minor element contents in collected materials proves to be helpful for discrimination between the groups of tap slags, bloom slags and ceramic-rich slags that are formed during the smelting process. However, a significant chemical variability derived from furnace, fuel and fluxes in the iron-making process can make the provenancing attempts rather uncertain (Humphris et al. 2009). The serious problem arises from representativeness and proper recognition of samples from iron-making sites, especially when they are collected from large clusters or dissipated piles of slag. Further problem is that a few grams of the starting inhomogeneous material often serve as a basis for the analysis of chemical composition and description of provenance and technology. For this reason, the question of representative analytical sample selection has been pointed out as one of the most challenging issues in archaeometallurgical research (Charlton et al. 2012).

There are several different strategies to minimize the problem of sample representativeness. One example is selection of a large set of samples and construction of larger databases, which would extend from main element content to additional minor and trace elements of material chemical fingerprint. By using the multi-method analytical approach (NAA, PIXE, XRD, SEM, XRF, ICP-MS), the elemental signature of material can be extended from main and minor constituents to trace ones. Combination of different analytical instrumental methods allows collection of an expanded set of compositional data from numerous samples, which is needed for detailed archaeometric descriptions of iron-making sites (Coustures et al. 2003; Nemet et al. 2018). The large set of obtained data often needs additional processing through statistical treatment. Therefore, a multivariate statistical treatments of a large set of spectrometric data is requisite. Thus, chemometric methods based on univariate and multivariate statistics are often applied in archaeometric studies (Charlton et al. 2013). This approach can provide better insight into differences of the similar features of heterogeneous material and allows the classification of a large number of findings. Moreover, the distinctions among objects with quite similar macroscopically characteristics become visible by using chemometric tools. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) are the most often applied statistical treatments in archaeometry, which exploits expanded chemical signature as a reference for the discrimination and classification of a large group of archaeometallurgical objects. Multi-method approach facilitates recognition of different types of materials from early-iron production sites, especially when collected artefacts show very similar macrostructural characteristics.

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MULTI-METHOD ANALYSIS OF ARCHAOMETALLURGICAL IRON SLAGS

Analysis of early-iron production remains by a combination of advanced instrumental methods is presented in this work. Samples were excavated in the Turopolje region, at the Okuje site, under the supervision of the Zagreb City Museum. The sample selection was guided mostly by their visual similarity. Different types of bloomery iron production debris were analysed for an enlarged set of elements including major (Al, Ca, Fe, K, Mg, Mn, P, Si, Ti) to trace constituents (Cr, Cu, Mo, Ni, Pb, V, Zn, Zr, and REE's), by use of a combination of plasma spectrometric methods with X-ray fluorescence (XRF) and scanning electron microscopy (SEM-EDS). The combination of morphological data obtained from SEM-EDS along with elemental signature and performed statistical treatment enables the identification of chemical characteristics of analysed archaeometallurgical remains. Using statistical analysis (PCA and HCA) on an enlarged set of measured data, the similar features of heterogeneous material become clearly discernible. Different types of slag, such as furnace slag, tap slag and ceramic-rich slag, were classified successfully according to their elemental fingerprint. The collected results might be of exceptional benefit for further studies of early-iron production in the Pannonian basin area.

Key words: archaeometry, chemometry, ICP-AES, ICP-MS, SEM

INTRODUCTION

Special properties of metallic iron when compared to other nonferrous metals are known from ancient times. Early attempts of iron production were based on direct reduction, namely the bloomery iron production process. The metal was obtained by the reduction of ores in smelting furnaces, using charcoal as a fuel and a reducing medium (Grdenić 2001). The resulting products contain porous iron with high content of impurities, and this material is called "iron bloom". Easily accessible iron ores, such as bog iron ores, were used in the smelting process (Pleiner 2000: 88; Thelemann et al. 2016; Brenko et al. 2021). Generally, the smelting process resulted in an iron bloom, a conglomerate of iron and trapped slag, and for this reason, the next step was consolidation and refining in order to expel excess slag and gain purified iron (primary smithing). The primary and secondary smithing processes allow removal of adherent slags and, finally, shaping of desired tools (Fig. 1). Accumulation of waste associated with different stages of the iron production process resulted in huge piles of slags, which were dissipated around the production site (Portillo et al. 2018; Stepanov et al. 2020). Archaeological evidence of smelting and smithing slags from iron production are numerous, but, from a mineralogical point of view, they are very often hardly distinguishable (Eliyahu-Behar et al. 2008; Ion et al. 2015). The chemical discrimination of slag material is helpful in discerning types of smelting and smithing slags (Blakelock et al. 2009). Moreover, the sourcing of raw material by chemical correlation of ore and smelting slags has a particular significance for understanding the factors affecting the iron production process (Coustures et al. 2003; Brauns et al. 2020). Analytical tools based on a multi-method approach combined with statistical treatment of a collected set of quantitative results allow elemental profiling of archaeometallurgical slags and discrimination between visually similar materials (Žabinski et al. 2020). With chemical characterization, archaeologists gain valuable information for interpreting the production technology.

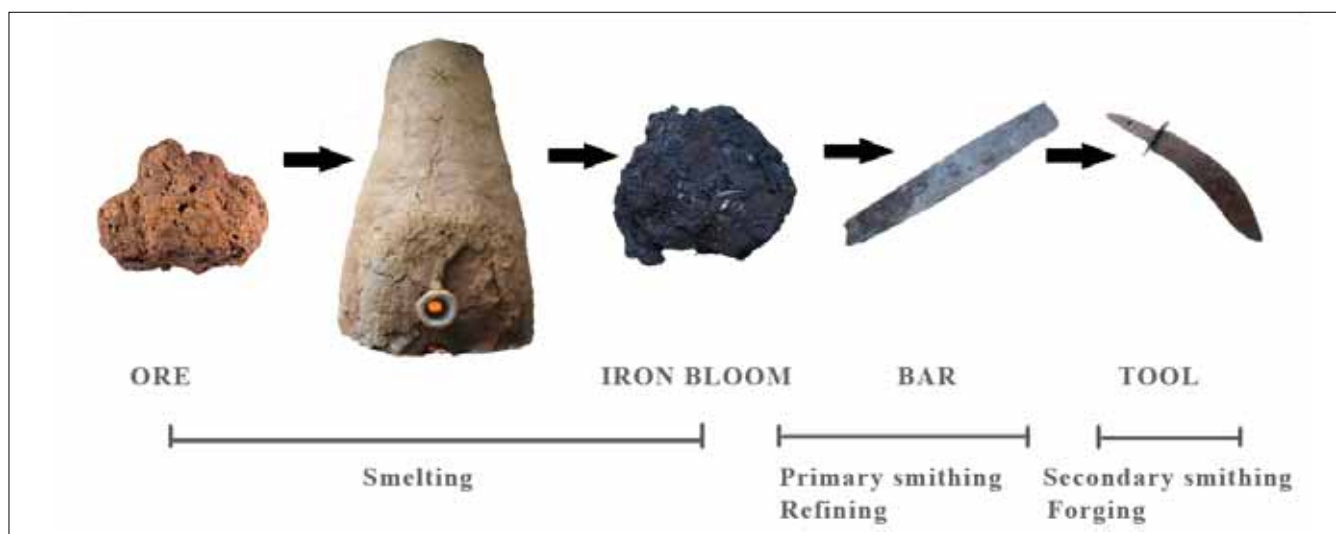


Fig. 1 Schematic presentation of bloomery iron production (made by: I. Nemet, T. Karavidović)

SAMPLE SELECTION AND PREPARATION

Samples of metallurgical waste such as slag, detached pieces of bloom, and technical ceramics were excavated during the archaeological research under the supervision of Zagreb City Museum, at the site near village Okuje in the Turropolje region. Over 500 kilograms of material was collected from dissipated piles of slag at this site. Samples were deposited into the Museum's repository. Randomly chosen samples, from stored remains, were taken for analysis. Typical representatives of collected samples are a) slag adhering to technical ceramics (furnace walls with slagged lining or tuyeres with traces of slag), b) tap slag and c) furnace slag or possibly bloom compacting/primary smithing slag (Fig. 2).

Before analysis, chosen samples were carefully cleaned with a plastic brush and soaked in deionized water. Dried samples were cracked by a diamond tool before grinding. Few cracked samples were selected for XRF and SEM-EDS analysis. Plasma spectrometric analysis was performed on previously powdered samples by use of a wet digestion procedure in a microwave oven. A small amount of each sample powder was digested using a mixture of mineral acids. For the determination of the accuracy of measured results, certificate reference materials of steel and rare-earth ore were prepared and analysed under the same conditions used for sample analysis. Detailed procedures of sample preparation and measurement are described in our previous work (Nemet et al. 2018).

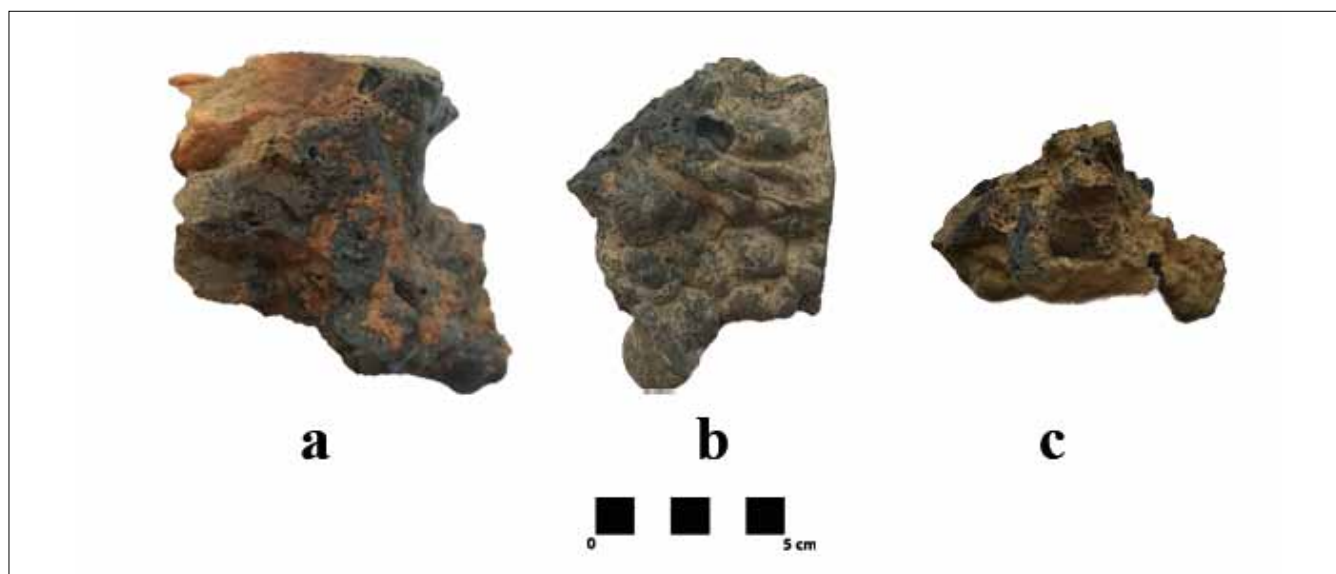


Fig. 2 Typical samples from Okuje site: a) furnace walls with slagged lining; b) tap slag; c) furnace slag (photo and editing: I. Nemet, T. Karavidović)

MORPHOLOGY OF SLAG SAMPLES BY SEM-EDS

The microstructure of samples was examined by SEM-EDS analysis by observation of backscattered electrons (SEM-BSE), which revealed morphological variances between slags and differences in the composition of slag samples. The samples that were described as tap slag, furnace slag or primary smithing slag showed the same textures and assemblages at the microstructure scale. The composition of the examined surface consists of dendritic and skeletal forms. Dendritic forms observed by SEM-BSE mapping matched a reduced form of iron oxide (FeO), i.e., mineral wuestite and aluminosilicate matrix. Earlier, Portillo et al. (2018), described the difference between dendritic and skeletal textures of wuestite and attributed it to variation of iron content. It was found that the lower iron content manifested through more pronounced dendritic forms. They attributed observed matrix effects to incorporated Al_2O_3 and SiO_2 . In our work, we have observed similar discrepancies in iron content between the group of examined iron-bearing slags (Nemet et al. 2018) (Fig. 3).

Another group of samples examined by the SEM method consisted of non-homogeneous material, the furnace wall fragments with adhering slag and ceramic tuyere shards. The porous sample surface examined by SEM-EDS consists of silicates and cavities. Visible wuestite forms and signals of iron obtained after SEM-EDS mapping were established in samples 8C and 8D. We concluded that both samples were linked to the smelting process, even though they do not show similar shape and morphology, as was the case in the first group of samples.

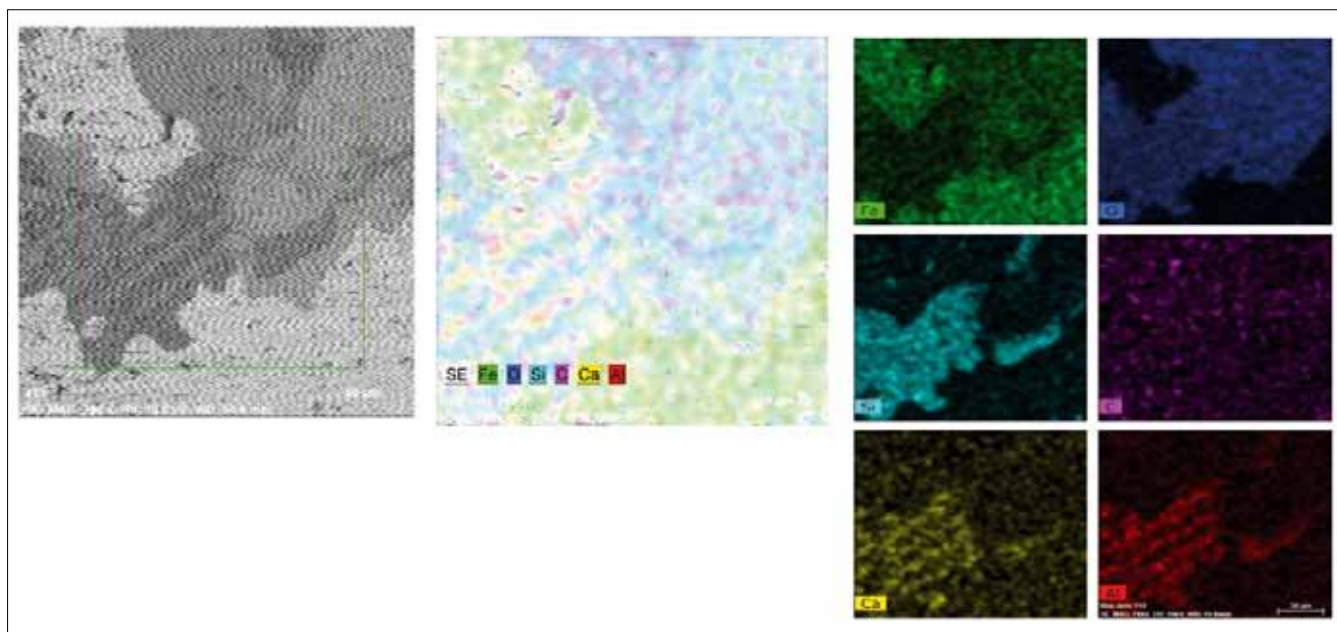


Fig. 3 SEM mapping of a tap slag sample (made by: I. Nemet)

ELEMENTAL ANALYSIS OF SLAGS BY XRF, ICP-OES AND ICP-MS

Main elements content in selected slag samples were determined by the XRF method, while minor and trace constituents were determined by use of ICP-OES and ICP-MS method. The measured iron content calculated as FeO ranges between 10 and 60 % in the whole set of examined samples. Measured SiO_2 content shows the variations in the range from 23 to 62 % within the observed set of samples. The Al_2O_3 and CaO content are between 8-12.5 % and 0.3-1.3 %, respectively. The ranges of main oxide content in samples observed in this work are expected, compared to the published studies on slag composition. It was described earlier that the main oxide ratios are good indicators to explain the compositional differences between the set of examined slag samples (Blakelock et al. 2009; Charlton et al. 2012). In these studies, the classification through oxides ratio refers to different types of slags such as tap slag, bloom slag (slag directly attached to the bloom, removed with a wooden mallet before bloom purification i.e. primary smithing), ceramic-rich slag (influence of molten furnace lining) and smithing slag. Generally, tap slag and bloom slag are compositionally very similar, but they found that the latter mainly has decreased iron oxide content. Ceramic-rich slag is characterized by higher SiO_2 content, while smithing slag included some additional elements (Ca, Mg, P and K) to a greater extent. The authors pointed out some constraints in classification, despite that they reproduced the bloomery process in controlled experiments. Generally, the problems arise from wide variability in the composition of individual samples and improper sampling on primary iron

production sites. The additional problem represents rather limited information on chemical composition.

Following their conclusions, we decided to enlarge the set of examined data from main elements to minor and trace constituents of slags, as much as was possible to analyse from sample solutions. In that way, the examined set of elements includes representatives of transition metals, refractory metals, heavy metals, rare-earth elements, and non-metals like phosphorus and sulphur. The results of trace element analysis obtained by ICP-AES and ICP-MS measurements are collected in a matrix, which consisted of 18 cases and 30 variables that denote samples and elements respectively (Nemet et al. 2018). Multivariate analytical strategies are a very useful tool for revealing the slag compositional groups, and for this reason, the large set of obtained data was subdued to principal component analysis (PCA) and hierarchical cluster analysis (HCA) (Fig. 4).

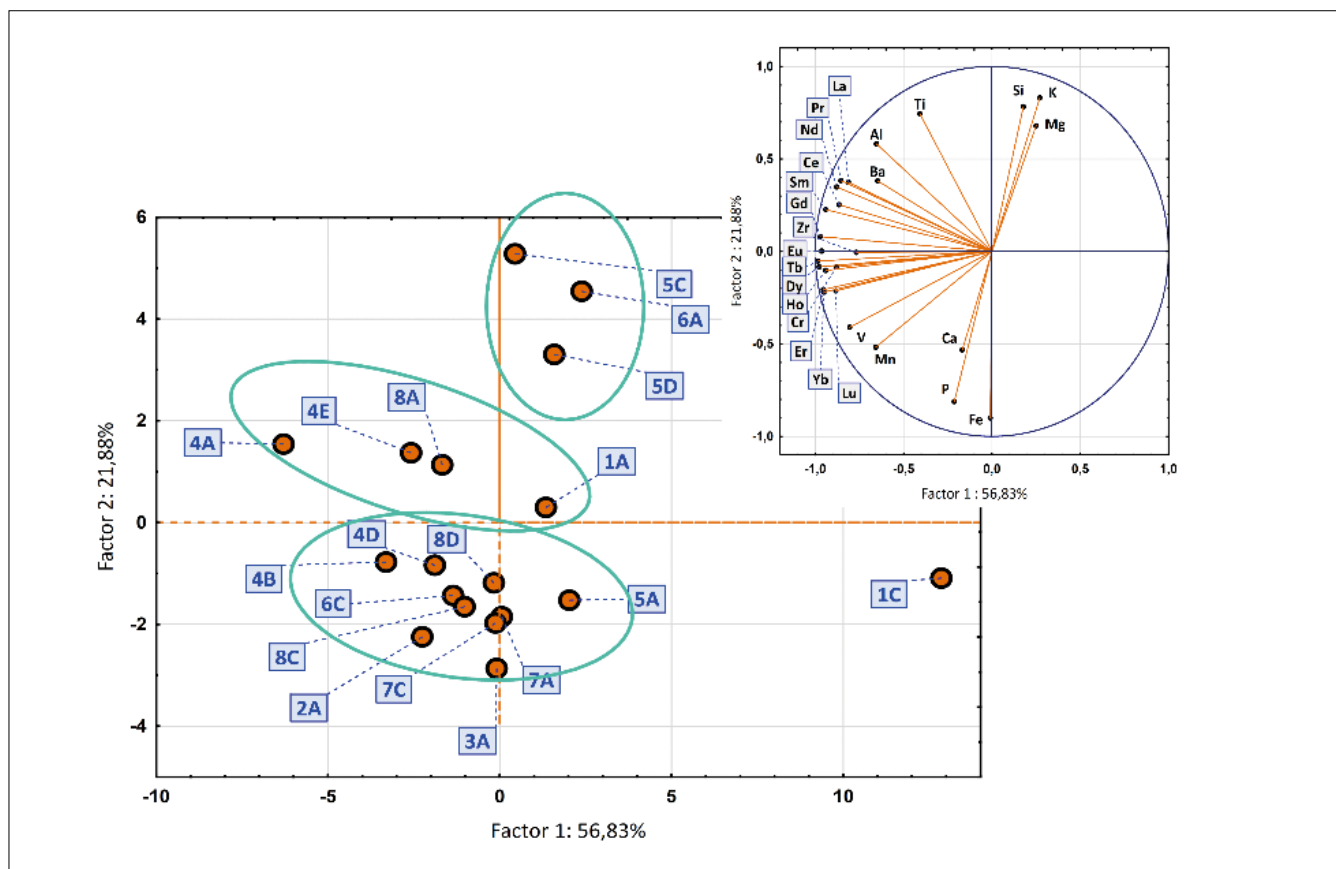


Fig. 4 PCA score plot and loadings of variables (made by: I. Nemet)

Figure 4 displays the first two components, which explained 79 % of the total variance of the dataset, and the graph shows the factor loadings of elements. The Scatter plot of the case scores (Fig. 3) shows a grouping of one set of samples along the negative part of PC2. This group is significantly enriched with elements such as Fe, Mn, P, Ca, V, and the group of heavier lanthanides. Sample 1C is isolated from the rest of the samples within this group. The second group of samples along the positive PC2 axis is characterized with relevant loadings of Si, K, Mg, Al, Ti, Ba, and the group of lighter lanthanides. The sample scores are well separated between different types of materials, e.g. group of tap, furnace or primary smithing slags and ceramic rich slags (slag adhering to technical ceramics). One can notice that sample 1C is isolated from other samples in the PCA statistics. However, several scores do not match to visual inspection of sample morphology. In order to explain the observed ambiguity, the hierarchical cluster analysis that can show the rate of similarity between samples was performed on the same dataset (Fig. 5).

The resulting dendrogram shows the similarity rate between samples, and according to these observations, all examined materials group between two main clusters. The upper group of samples (1A - 4D) comply with bloom iron slags and tap slag, and the lower group of samples (4E - 5D) denotes ceramic-rich slag material. The sub-cluster with samples (1A - 8C) represents material with iron content higher than 45 % of FeO. The second sub-cluster consists of samples with iron content below 45 %, and with a greater contribution of SiO₂ and Al₂O₃. Among ceramic-rich slags that are present in the second cluster, there are samples taken from the tuyeres with traces of slag (6A, 8A) and the slag attached to furnace

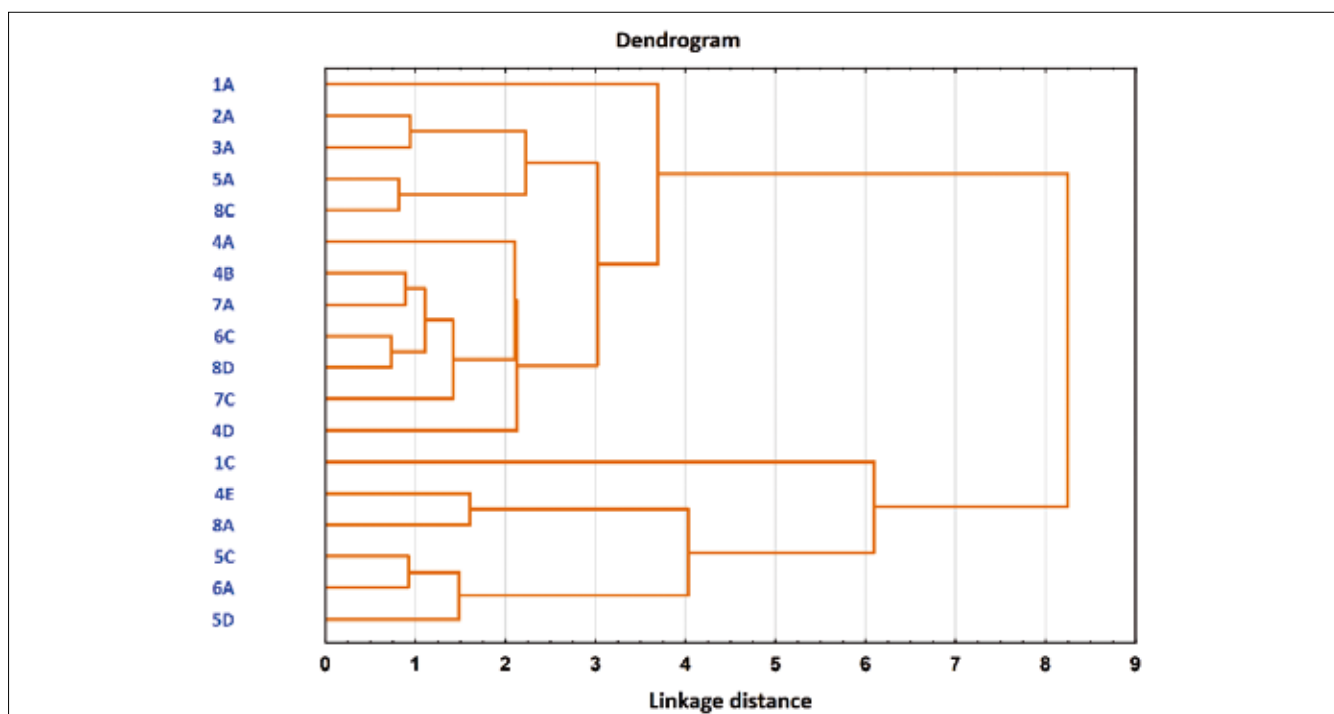


Fig. 5 Classification of samples by HCA (made by: I. Nemet)

walls (4E, 5C, 5D). Among the first sub-cluster of iron-rich samples, there is a distinction between samples of tap slag and bloom compaction/consolidation slag or furnace slag.

Sample 1C shows separation from clusters in the HCA dendrogram. The SEM-EDS spectra of this sample show the absence of wuestite forms. In the microstructure of the sample is prevailing the presence of quartz and goethite minerals that are characteristic of goethite ore (Portillo et al. 2018). The elemental composition of this sample is characterized by increased iron, silicon, and nickel content (Nemet et al. 2018). The quantitative composition of other constituents is comparable to the concentration ranges published in the recent surveys on bog iron ore (Thelemann et al. 2016; Brenko et al. 2021). Therefore, with reasonable certainty, we can consider this sample as a starting material for iron smelting, i.e. bog iron ore.

CONCLUDING REMARKS

Valuable information on chemical constituents and morphology of examined materials was obtained by a multi-method approach (SEM-EDS, XRF, ICP-AES; ICP-MS, and multivariate statistical treatment). The benefit of obtaining an extended elemental signature manifests through the ability to discern sub-groups of visually similar slags.

ACKNOWLEDGEMENTS

Our gratitude goes to Mrs Aleksandra Bugar, a curator of the Zagreb City Museum, for allowing the analysis of the excavated iron production samples.

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ROSEMARY CAPO, MIROSLAV KOČIČ, BARBARA HORN

SEARCHING FOR IRON-SMELTING SITES WITH GEOCHEMICAL TRANSECTS: THE CASE STUDY OF THE EARLY IRON AGE COMPLEX OF CVINGER NEAR DOLENJSKE TOPLICE (SE SLOVENIA)

At the prehistoric site of Cvinger near Dolenjske Toplice, several archaeological excavations, intensive surface survey, analysis of LIDAR imagery, and multi-method geophysical surveys have been carried out in recent decades. This extensive dataset forms the basis for comprehensive knowledge of its individual parts, i.e. the settlement, the iron-smelting area, the burial mound necropolises as well as the transitional zones, characterized by holloways and even an embanked pathway leading to the settlement. This provided a suitable basis to test the possibility of detecting iron-smelting areas by geochemical prospecting alone. The survey was carried out in long transects, with measurements taken at regular intervals. The contents of the elements at the sampling points were measured in the field using a portable XRF instrument and presented as their relative differences along the transects. The main aim of this study was to evaluate the possibility of effective use of such an approach for the discovery of iron-smelting centers around other hillforts of the Dolenjska Early Iron Age group, often located in similarly difficult environmental conditions in the forest.

Keywords: Dolenjska region, Early Iron Age hillfort, iron-smelting area, geochemical prospecting, geochemical transects, HHpXRF

INTRODUCTION

The article presents the results of a geochemical prospecting carried out at the prehistoric archaeological complex of Cvinger near Dolenjske Toplice, which is centred on and around the Cvinger hillfort and comprising an iron-smelting area and three necropolises (Fig. 1).

The main purpose of the survey was to correlate the basic archaeological data already known and obtained by other research methods (ALS, geophysics, surface collection and excavation) with the geochemical signature of the distinct areas. For this purpose, we have measured the values of a series of chemical elements using a portable/handheld XRF instrument along long transects across the entire Cvinger complex including surrounding areas without known archaeological remains (Fig. 5).

One of the objectives of the survey was to identify significant correlations of element distribution with different archaeological areas, as well as with the natural environment. In particular we aimed at finding a possible signature of the iron-smelting area and to work out whether and how significantly it stands out from the surrounding areas. From a broader perspective, we were looking for a way to identify iron-smelting areas in the karstic environments of the Dolenjska region, in order to apply this knowledge to other comparable sites (Fig. 2).

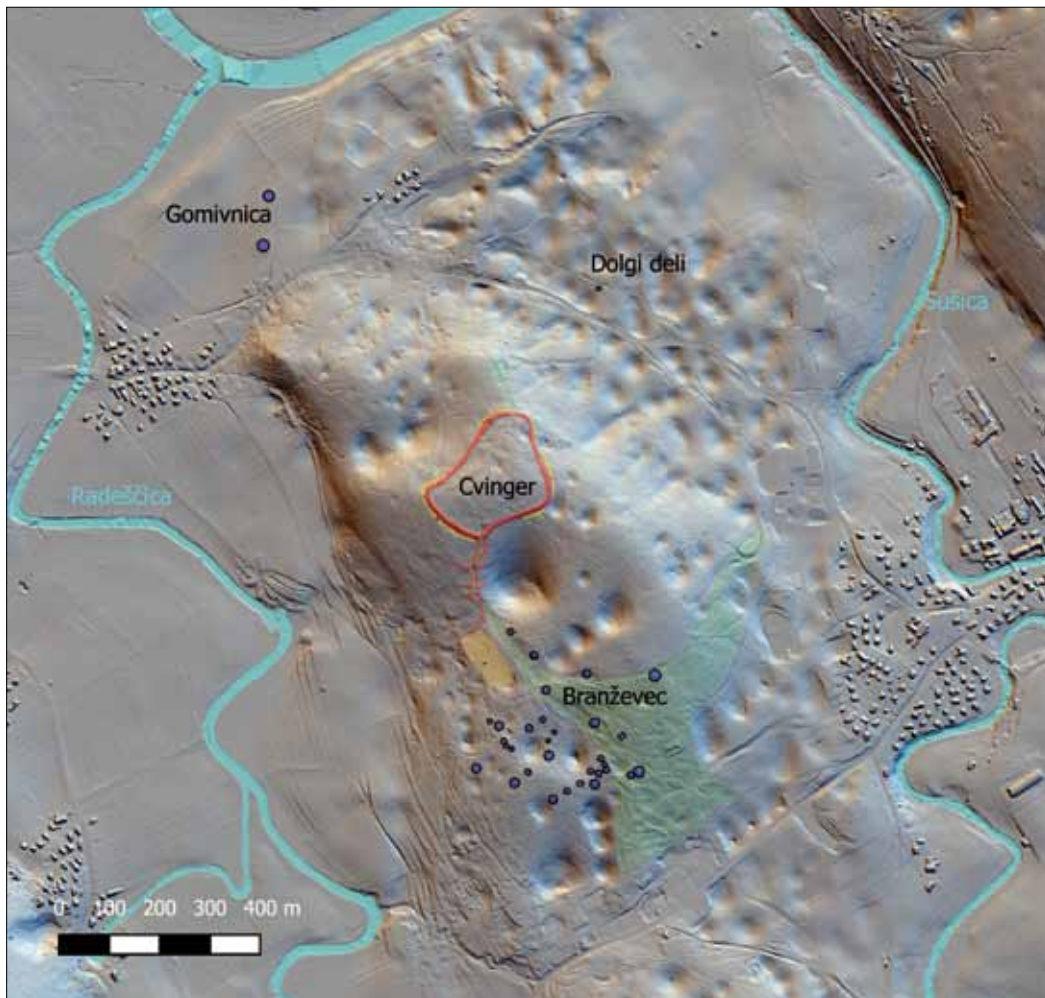


Fig. 1 Cvinger near Dolenjske Toplice complex with all of its currently known archaeological locations (after: Črešnar et al. 2020)

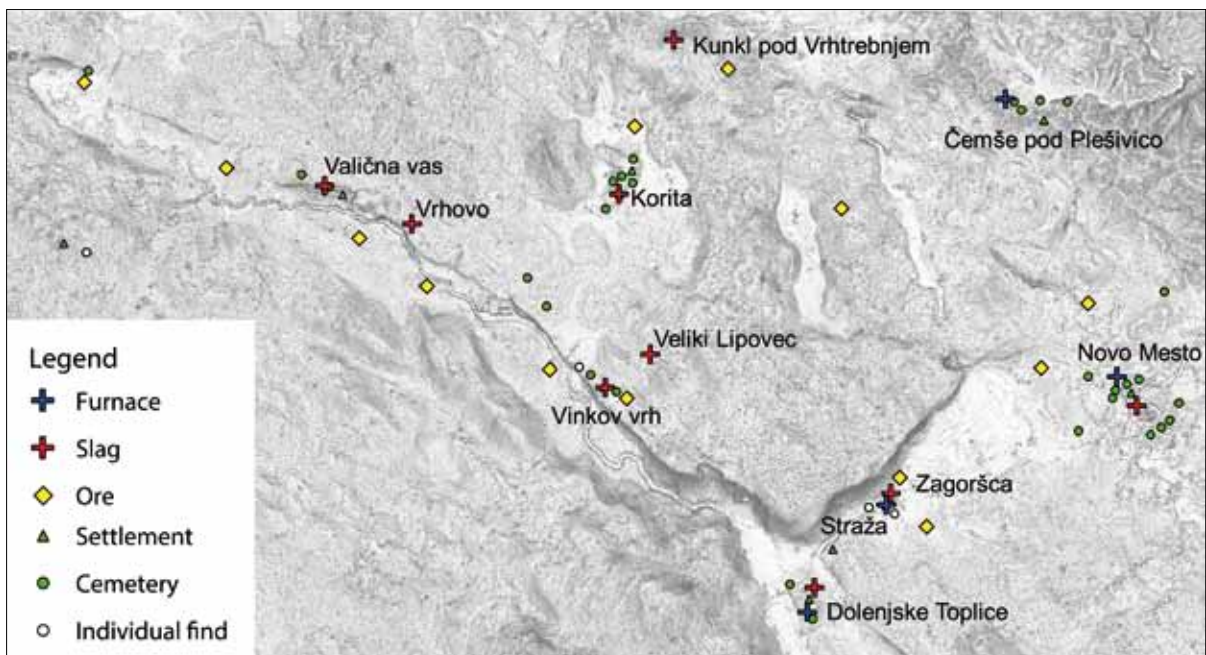


Fig. 2 Cvinger near Dolenjske Toplice and other Early Iron Age sites along the middle part of Krka River with established remains of iron production (after: Črešnar et al. 2017)

CVINGER NEAR DOLENJSKE TOPLICE

The Cvinger archaeological complex is distributed over a limestone hill (max. 265 m a.s.l.), above the Krka River alluvial plain, framed also by the Radeščica and Sušica tributary stream valleys (Fig. 1). The contemporary forested hill is composed of karstified Jurassic limestone (Pleničar, Premru 1977) with the prevailing large karstic features like dolines and caves along the wide band of fault zone within the fractured limestone.

The hillfort was first settled in the Late Bronze Age (10th–9th cent. BC). After its temporary abandonment, it was resettled in the Late Hallstatt period (6th–4th cent. BC), when further areas around the hilltop were occupied by an iron-smelting area and several burial mound necropolises (Fig. 1). Lidar scanning and further fieldwork have identified additional features, such as the embanked pathway leading to the hillfort and the holloways, representing ancient communication directions, all of which could influence the environment, including its chemical fingerprint. Nevertheless, it is the considerable size of the iron-smelting area (approx. 0.6 ha) that places Cvinger among the most important Iron Age centres in the Dolenjska region (Dular, Križ 2004; Črešnar et al. 2020).

Although the research of prehistoric hillforts in the Dolenjska region (including Cvinger) started as early as the late 19th century, it was Janez Dular with his team who systematically mapped and archaeologically investigated most of them at the end of the 20th and the beginning of the 21st century (Dular, Tecco-Hvala 2007; Dular 2021). Therefore, basic data are known about most of the hillforts in the region, such as periods of occupation and their dynamics. However, much less is known about the areas of iron production, which was probably one of the backbones of the so called “flourishing Dolenjska region Hallstatt period”. Similarly little is known about their impact on the surrounding areas and about the types of land use around hillforts and in their broader environment.

The advantages of the investigations presented are that Cvinger was not resettled after the end of the Early Iron Age, so that later interventions have largely spared the archaeological remains, and that it has also already been extensively investigated geophysically and archaeologically (Fig. 3). Consequently, the geochemical results can be very well supported by the already known data (Mušič, Orengo 1998; Dular, Križ 2004; Črešnar et al. 2020). Therefore, we expected that the conclusions obtained would be sufficiently reliable, to lead us to the discovery of similar iron-smelting areas elsewhere in the Dolenjska karst region.

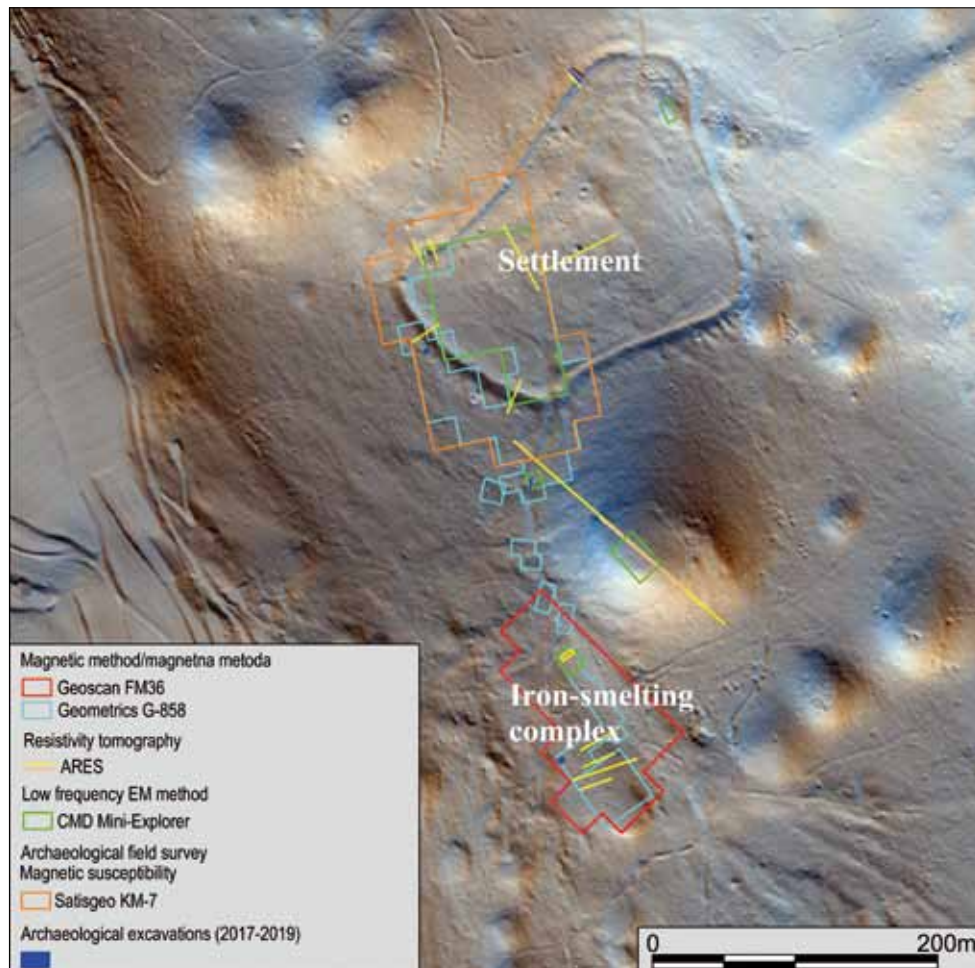


Fig. 3 Cvinger near Dolenjske Toplice with outlined areas of geophysical measurements and recent archaeological excavations

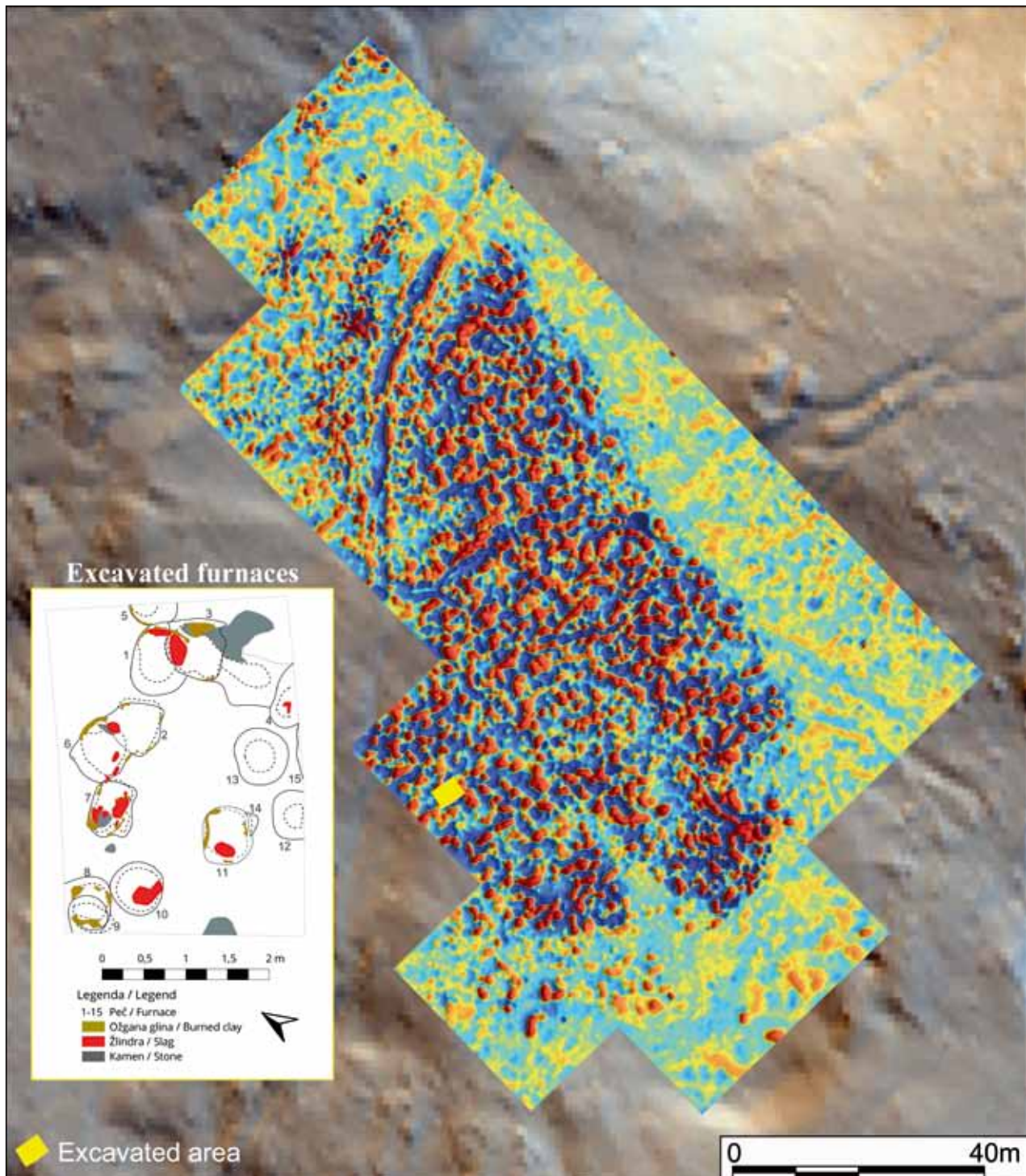


Fig. 4 Results on magnetic prospection obtained by fluxgate gradiometer *Geoscan FM36* (see: Mušič, Orengo 1998) after applying Gaussian filter in colour scale display using Histogram equalisation (Dynamics: $-62.31/+74.48$ nT/m) and ground plan of furnace remains discovered during archaeological excavations in 2017 and 2018 (see: Črešnar et al. 2020)

In order to additionally discuss the connection of the geochemical results with the results of the magnetic method, we have included the magnetic results from two locations, namely the iron-smelting area (Fig. 4) and an area to the NE of the settlement that shows only modest evidence for possible presence of archaeological remains obtained by surface collection (Fig. 5).

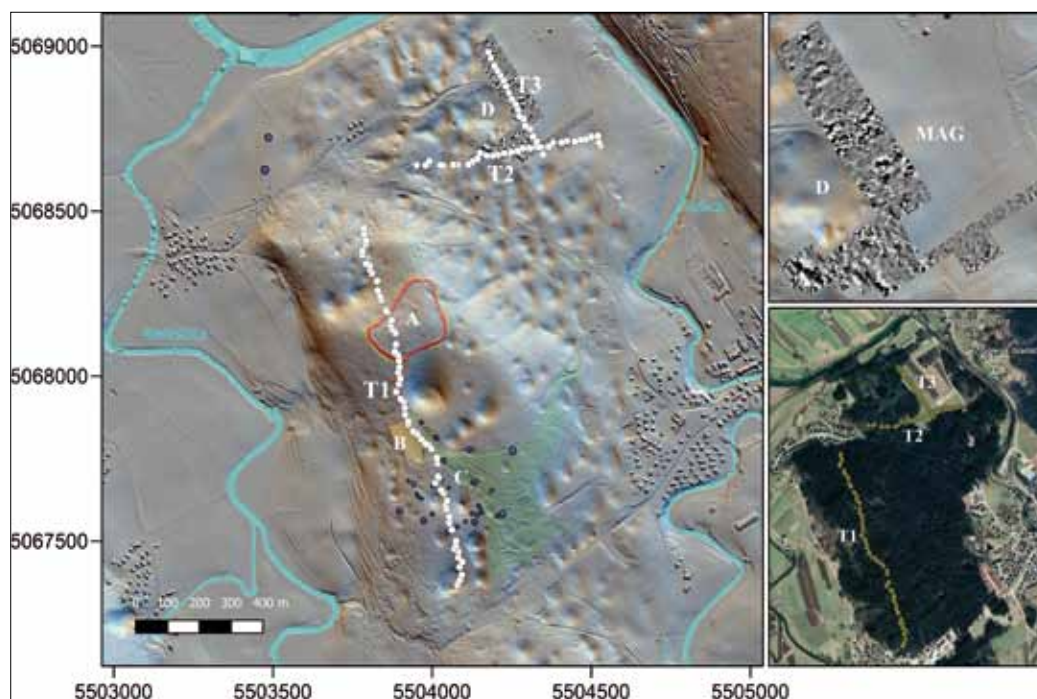


Fig. 5 Sampling points along the geochemical transects T1, T2 and T3 on LIDAR image (left) and aerial photography (bottom right): A – settlement, B – iron-smelting area, C – necropolis with burial mounds, D – archaeologically poorly explored area in the lowland area northeast of the settlement with results of magnetic prospection (MAG) (top right)

METHODOLOGY

ARCHAEOLOGICAL GEOPHYSICS

Magnetic surveys have been repeatedly used successfully to locate individual or clusters of iron-smelting furnaces (see: Abrahamsen et al. 1998; Mušič, Orengo 1998; Crew 2002; Powell et al. 2002; Črešnar et al. 2020). Magnetic mapping has thus proved to be the most appropriate geophysical technique to identify the strong magnetic anomalies generated by remains of iron-smelting furnaces in the form of bottom slag blocks and/or deposits of iron-smelting waste material. The mineral composition with a large proportion of magnetic iron minerals, alongside the sufficiently large volume of *in situ* bottom slag blocks, generates the distinct bipolar magnetic anomalies recorded by all modern magnetometers. Our first magnetometer survey of an iron-smelting area was carried out using a fluxgate gradiometer (*Geoscan FM36*) (Figs. 3 and 4). This instrument is used to measure changes in the gradient of the vertical component of the Earth's magnetic field with respect to the zero reference point (Mušič, Orengo 1998). Sensitivity and working speed are lower than for the modern caesium vapour magnetometer sensors, for instance. Nevertheless, the easily portable design of the magnetometer makes this instrument efficient for the detection of iron-smelting remains also in unfavourable environmental conditions on karstified limestone bedrock in the forest. As the results of this initial geophysical prospection using this magnetometer have already been presented in detail elsewhere (Mušič, Orengo 1998; Mušič 1999; 2001; Črešnar et al. 2020), only a brief overview of the results relevant for planning of geochemical transects, shall be summarized here.

The most prominent geophysical targets at the Dolenjske Toplice iron-smelting area are remains of furnaces in the form of oval pits with bottom slag blocks in a hemispherical shape with variable diameters from 0.5 m to 0.9 m and equally variable depths below the present-day surface (Dular, Križ 2004). The magnetic response of each bottom slag depends on its mineral composition, shape, volume and depth. It has been empirically demonstrated that the three-dimensional magnetic modelling (Mušič, Orengo 1998) provides a fairly reliable quantitative interpretation, as it estimates the volume of magnetic sources, in this case exclusively bottom slag blocks. Due to their thermic history, they have the thermoremanent character of magnetic dipoles with high intensity, variable shape and diameter/dimension in horizontal plane. A low, upright cylinder was used as the most appropriate geometric model for slag blocks (Telford et al. 1990), which is as similar as possible in shape and three-dimensional space to the expected shape of the bottom slag blocks. Thus, we

indirectly confirmed the existence of objects with similar magnetic properties as those excavated by Borut Križ (Križ 1990; 1993; Dular, Križ 2004) within the area delimited based on the distribution of surface finds of metallurgical waste products (Mušič, Orengo 1998). Subsequent prospection using the magnetic method (Mušič, Orengo 1998) led to the discovery of a large smelting activity area, covering about 6000 m². It contains hundreds of strong magnetic anomalies, caused by single or clusters of pits filled with very magnetic bottom slag and other metallurgical waste. The magnetic map presented here brings a re-evaluation of the data using *Histogram equalization adjustment* (e.g.: Acharya, Ray 2005). In this way, magnetic gradient readings can be better distributed on the histogram to provide insight into weaker, discrete magnetic anomalies on previous magnetic surveys using Fluxgate gradiometer *Geoscan FM36* (Mušič, Orengo 1998) (Fig. 4). Archaeological data and recent geomagnetic dating of the remains of one of the furnaces from the smelting area have also confirmed that it was most likely last used in the timeframe between the late 6th and early 4th century BC (Črešnar et al. 2020).

Comparison of the results of the magnetic method obtained with the caesium magnetometer (*Geometrics G-858*), covering a part of the previously investigated area (see: Fig. 3), with the excavated remains of the furnaces in general shows a good spatial correlation between the excavated furnaces and the gradient, bottom and top sensor magnetic anomalies (see: Črešnar et al. 2020). One of the quite unexpected conclusions is that in most cases we cannot identify individual furnaces. In fact, the magnetic anomalies of the furnaces at short distances always overlap. After the recent archaeological excavation, it became obvious, that the situation at the iron-smelting area is even more complex than the results of magnetic method alone would suggest (Fig. 4). The total number of furnaces is even much larger than can be calculated from the magnetic anomalies.

The iron-smelting area could also be delineated by mapping the apparent magnetic susceptibility using hand-held instruments (*Kappameter KT-5*) (Mušič, Orengo 1998), the low frequency electromagnetic method (*CMD Mini-explorer*), the 2D/3D resistivity tomography (Črešnar et al. 2020) and even by mapping self-potentials using a home-made system with digital multi-meter (*Protec 506*) and two flower pots filled with copper sulphate (Mušič 2001). However, as expected at the initial phase of this geophysical investigation in the Dolenjska karst region, the most beneficial results were acquired with the magnetic method, regardless of the magnetometer used.

Therefore, a magnetic survey of an area northeast of the hillfort was also carried out in the area of the geochemical transects T2 and T3 (Fig. 5: D, MAG). Both, the geochemical survey and the magnetic prospection of this area were conducted in cooperation with the University of Pittsburgh in 2017. The *Bartington 601-2* fluxgate gradiometer, used for this purpose is primarily intended for large-scale prospecting in a relatively short period of time. In the present archaeological context of an Early Iron Age site magnetometer resolution is sufficient to detect archaeological remains by thermoremanent magnetization of burnt clay (kilns, furnaces, etc.). In this way, we supplemented the research methodology and expanded the research areas in the wider surroundings of the Early Iron Age centre.

GEOCHEMISTRY

The geochemical prospection was carried out with a Niton XL3t hand held portable X-ray Fluorescence Spectrometry device (HHpXRF). The main advantage of this non-destructive survey is that it allows on-field measurements without prior preparation of the soil sample, rather than taking the samples to the laboratory for analysis. Over the last 25 years (see: Helmig et al. 1989), the use of portable and handheld XRF instruments (HHpXRF) has seen a dramatic increase for a variety of archaeological applications (Scott et al. 2016a). Current HHpXRF spectrometers are often marketed as 'point-and-shoot' instruments, meaning that the user can analyse and quantify the chemical composition of the material using factory settings. Since one of the first applications of HHpXRF was in the mining industry, the use of handheld spectrometers to analyse the composition of metal ores and metal slags is well established (Frahm, Doonan 2013; Scott et al. 2016a). HHpXRF can easily provide qualitative data, but these data are only comparable to other qualitative data, using the same device. Quantitative data collection is possible, but can be more problematic, especially if the material in question is heterogeneous in nature (Scott et al. 2016b). In our study, we were looking for an efficient methodology to detect sites associated with iron production and the qualitative nature of the data is sufficient for this purpose.

As mentioned above, the Cvinger complex was best suited for the comparative geochemical study, that would lead to the introduction of criteria regarding the possible archaeological significance of individual element values measured along geochemical transects (Fig. 5: T1, T2 in T3). The basic purpose of the geochemical measurements in transects was to determine if and how the various archaeological areas, i.e. the settlement, iron-smelting area, necropolises, embanked pathway, as well as the surrounding with no clear archaeological remains, are reflected in the geochemical values.

Each transect consisted of a series of individual sampling locations spaced approximately 25 m apart in average, but with alternation due to the rough terrain. At each of the 118 sampling locations in the transects (T1: 66, T2: 32, T3: 20) we measured values for 12 elements (Rb, Sr, Zn, Th, Pb, Fe, Mn, Ni, Zn, As, Cu and Mo). Analyses were recorded using the instrument's in-built Fundamental Parameters calibration mode, in this case, the 'soils mode'. Three filters were selected (Main, Low and High) to optimise the detection of the range of elements noted above. A total integration time of 25 seconds was selected for sampling.

The longest transect T1 ran roughly in a south-north direction from the southern foothills of the Cvinger hill, across the central burial mound necropolis, the iron-smelting area, over the gently rising ground with the embanked approach pathway, across the settlement, and ended at the northern foothills where no archaeological remains have yet been recorded (Fig. 5). The other two transects (T2, T3) ran through archaeologically poorly known/researched territory north of the settlement and the Dolgi deli necropolis, which yielded only one burial mound. The first recent positive archaeological information from this arable area came from a surface collection, which was supplemented with a magnetic survey as a part of our investigation (Fig. 5: D, MAG).

Several studies that have already looked at the correlation of elevated values of examined chemical elements in different geological environments came to slightly different conclusions. Cu, Pb and Zn are repeatedly recognized as indicators of ancient human activity, such as burning, waste disposal, or industrial activities (Wilson et al. 2009; Dirix et al. 2013). Cu and Mn can be associated with burials and Cu, Pb, Mn with mining, metal smelting and production areas (see: Oonk et al. 2009: Table 1), while Fe, Pb, Zn, Cu, Rb, Sr and Th can also be indicative of farms, houses and hearths (Wilson et al. 2008; Oonk et al. 2009).

To determine the strongest correlations between the element distributions, we performed two statistical analyses. The first was analysis of the correlations for each individual element and the second was a cluster analysis to classify the elements into groups based on their similar abundances within the distribution. For graphical representation, we divided the element quantities (ppm) into equal intervals indicating the relative differences for individual elements along the transects.

RESULTS AND INTERPRETATIONS

STATISTICAL ANALYSIS OF GEOCHEMICAL RESULTS

The correlation analysis between pairs of elements shows a strong correlation between three pairs of elements: Zr-Sr, As-Zn and As-Fe (Fig. 6). A moderate, but still significant correlation is observed between the element pairs Pb-Zn and Fe-Zn. Among the weak correlations, the highest correlation coefficients are observed between the pairs As-Mo, Fe-Cu, Zn-Mo, Fe-Rb, Fe-Th, Th-Rb, Ni-As, Ni-Zn, As-Pb, Pb-Mn, Rb-Sr, Th-Zr, Th-Sr and Mn-Zn.

The cluster analysis divided all studied elements into two main groups (Fig. 7) according to their similarities in distribution. The first group ("Natural background elements") includes Sr, Rb, Th and Zr. The second group ("Anthropogenic elements") is further divided into two subgroups: a) Subgroup 1: Cu, Fe, Pb, Ni and b) Subgroup 2: As, Zn, Mo, Mn.

INTERPRETATION OF GEOCHEMICAL CHARACTERISTICS ALONG THE TRANSECTS

In this part of the analysis we started from the known to the less known/unknown, in order to be able to interpret the data of all transects. Starting with transect T1 and based on the values of individual elements along its course, we first compared the degree of correlation between geochemically anomalous areas and the content of already known archaeological units. Only then we transferred this experience to archaeologically poorly explored areas where only surface collection and magnetic prospection had been carried out prior to the measurements in transects T2 and T3 (Figs. 8 – 10).

THE NATURAL ENVIRONMENT

The elements of the first group (Rb, Sr, Zr, Th) (Fig. 7) show very similar values along the transects at all sample locations (Fig. 8). Their values are relatively stable especially in the areas with no known archaeological remains, while they drop in the most archaeologically influenced areas, i.e., the hillfort and the iron-smelting area. Therefore, we can most probably understand them mainly as the natural background elements without significant archaeological relevance.

Of these elements, particularly the contents of Sr, Th and Zr are lower in the areas between the iron-smelting area and the settlement and are of much higher variability than in the surrounding areas without known archaeological remains. This may be attributed to the altered geochemical image of the natural record in areas of intensive use in the Early Iron Age.

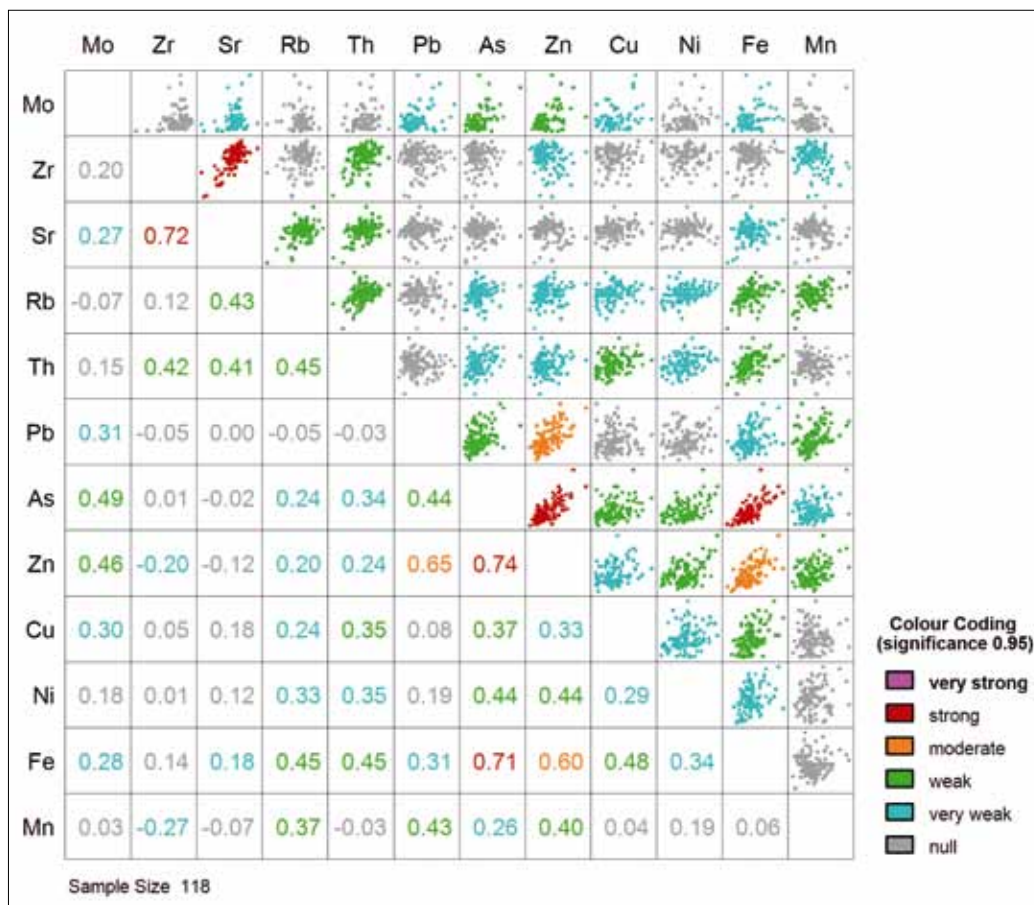


Fig. 6 Element correlation with correlation coefficients

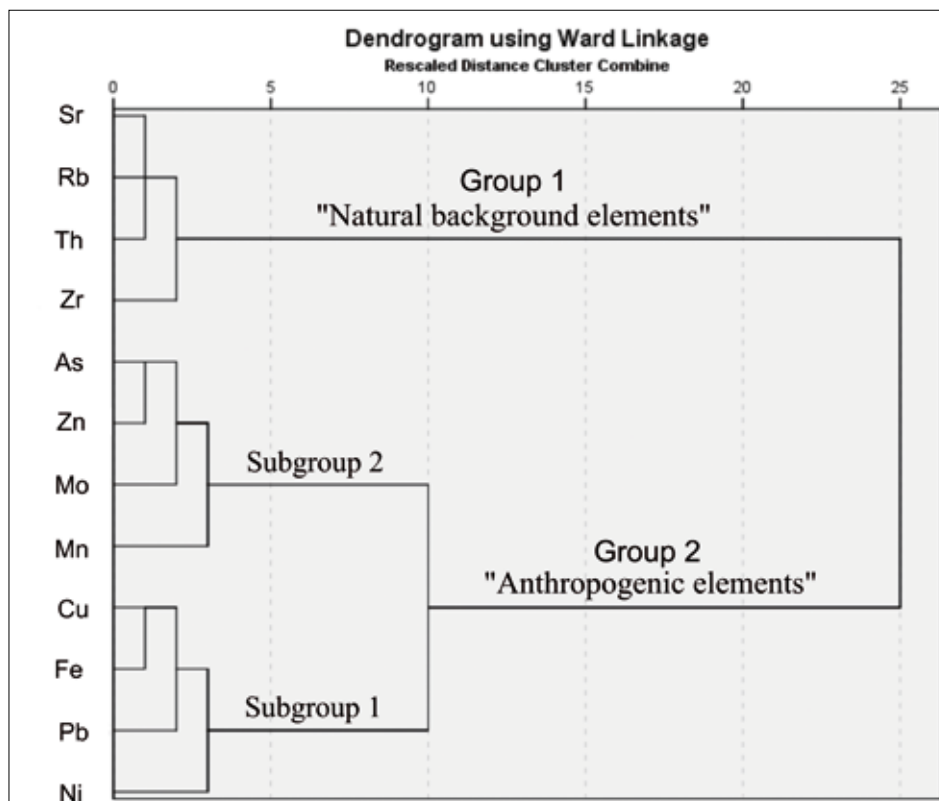


Fig. 7 Dendrogram obtained by cluster analysis, showing the two main groups of elements "Natural background elements" and "Anthropogenic elements", the second being further subdivided into two subgroups

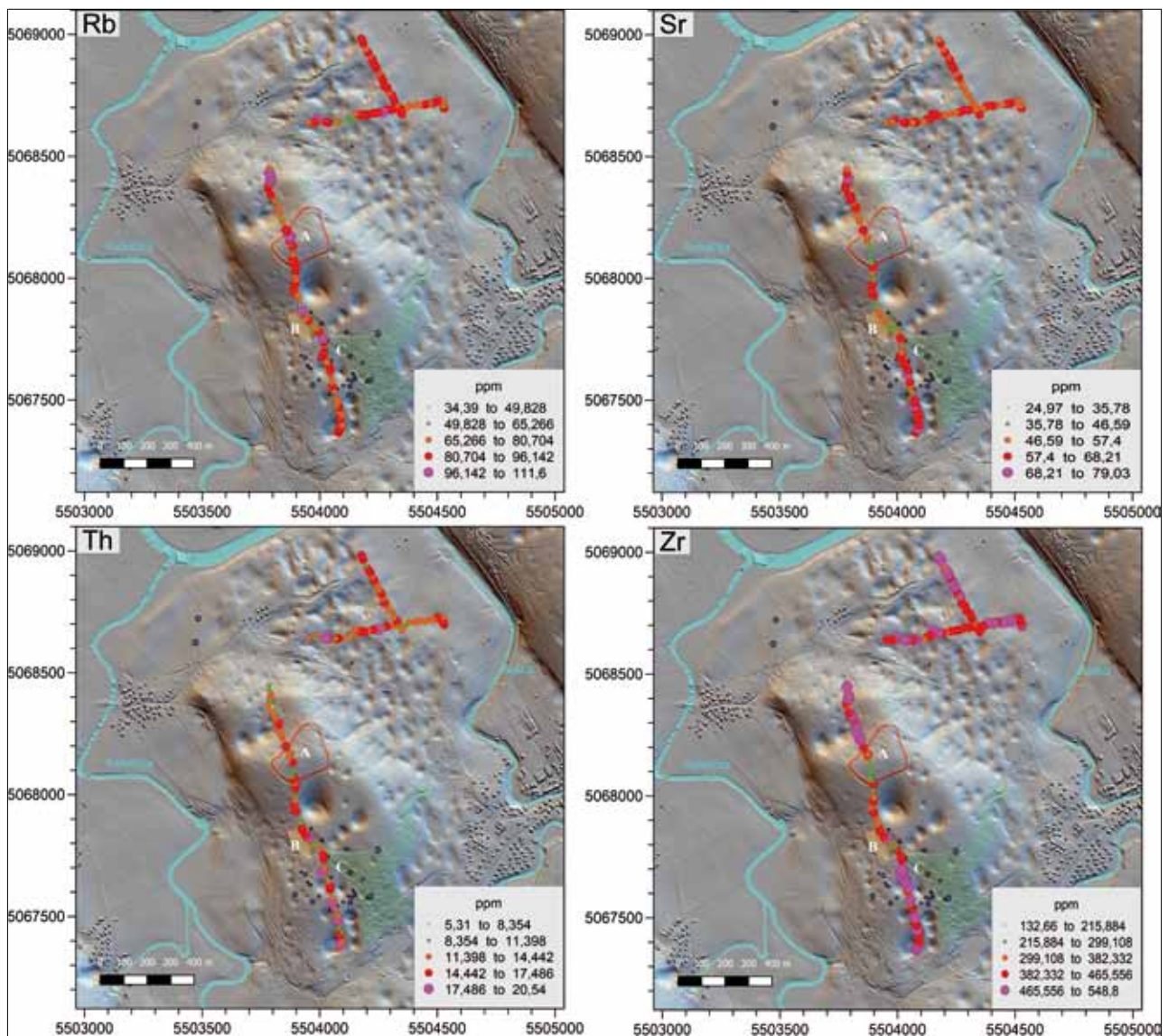


Fig. 8 Relative differences in the content of elements attributed to the “natural background” (Fig 7: group 1) along geochemical transects shown by a linear distribution with equal intervals. Despite the obvious predominant influence of the natural background, differences in the contents of Rb, Sr, Th and Zr, could also be partly a consequence of human impact in the past

In other situations, the content of a particular element, apparently of natural origin, may be much higher than expected. In limestone, for example, the radioactive element thorium is present in accessory minerals, and its content does not usually exceed 3 ppm (Pękala 2017). In our case, the highest measured Th values in the area of the mound necropolis were between 15 and 20 ppm, for which we do not yet have a fully adequate explanation. Among other unknown sources, it is possible that these are local accumulations due to leaching of thorium-bearing accessory minerals from the earthen mantle of the burial mounds. In any case, this should be considered as a possible indicator of areas of destroyed burial mound necropolises in the Dolenjska karst region. The Rb contents are slightly higher than the background on both the iron-smelting area and the settlement. Therefore, we can assume that the possible reason for higher Rb contents is also an anthropogenic influence, although in our case this element generally reflects the natural composition of the soil on limestone. Moreover, Rb is often mentioned in archaeological contexts as an indicator of settlements as well as smaller settlement units (see: Oonk et al. 2009). We can conclude that even with the obvious elements of natural background, we cannot completely exclude differences caused by human activities in the past. We assume that this can be an important indicator of a longer-term occupation with the intensive and diverse land use in the archaeological past with a substantially altered chemical composition.

THE IMPACT OF THE HUMAN ACTIVITIES

Elements with higher contents that are spatially consistent with the distinct archaeological areas (Fig. 7: Group 2) were according to the cluster analyses results divided into two subgroups (Fig 7: Subgroup 1 and 2). In contrast to the elements of the first group discussed above, the elements of the second group, which includes subgroup 1 (Cu, Fe, Pb, Ni) and subgroup 2 (As, Zn, Mo, Mn) show highly variable levels along the transects, most likely reflecting the anthropogenic influence on the studied soil (Figs. 9 and 10).

The first subgroup generally contains elements with continuously elevated contents between the iron-smelting area and the settlement (Fe, Pb, Ni and Cu) (Fig. 9). The second subgroup contains all other “anthropogenic” elements without such continuity and with increased values in partly different, more spatially restricted areas (As, Zn, Mo and Mn) (Fig. 10). The relations are, however, more complicated. As we can see on Figs. 9 and 10, the three elements of subgroup 1 (Ni, Pb, Fe) and two elements of the subgroup 2 (Zn, As) clearly show the highest abundances in the iron-smelting area, and can thus be considered as indicative also of similar complexes elsewhere. The following section discusses the importance of geochemical analyses primarily for the discovery of iron-working areas but also of settlements and other archaeological remains within Early Iron Age complexes.

a) The first subgroup of “anthropogenic” elements

This subgroup includes elements that, due to their good correlation with the archaeologically recognized areas, are

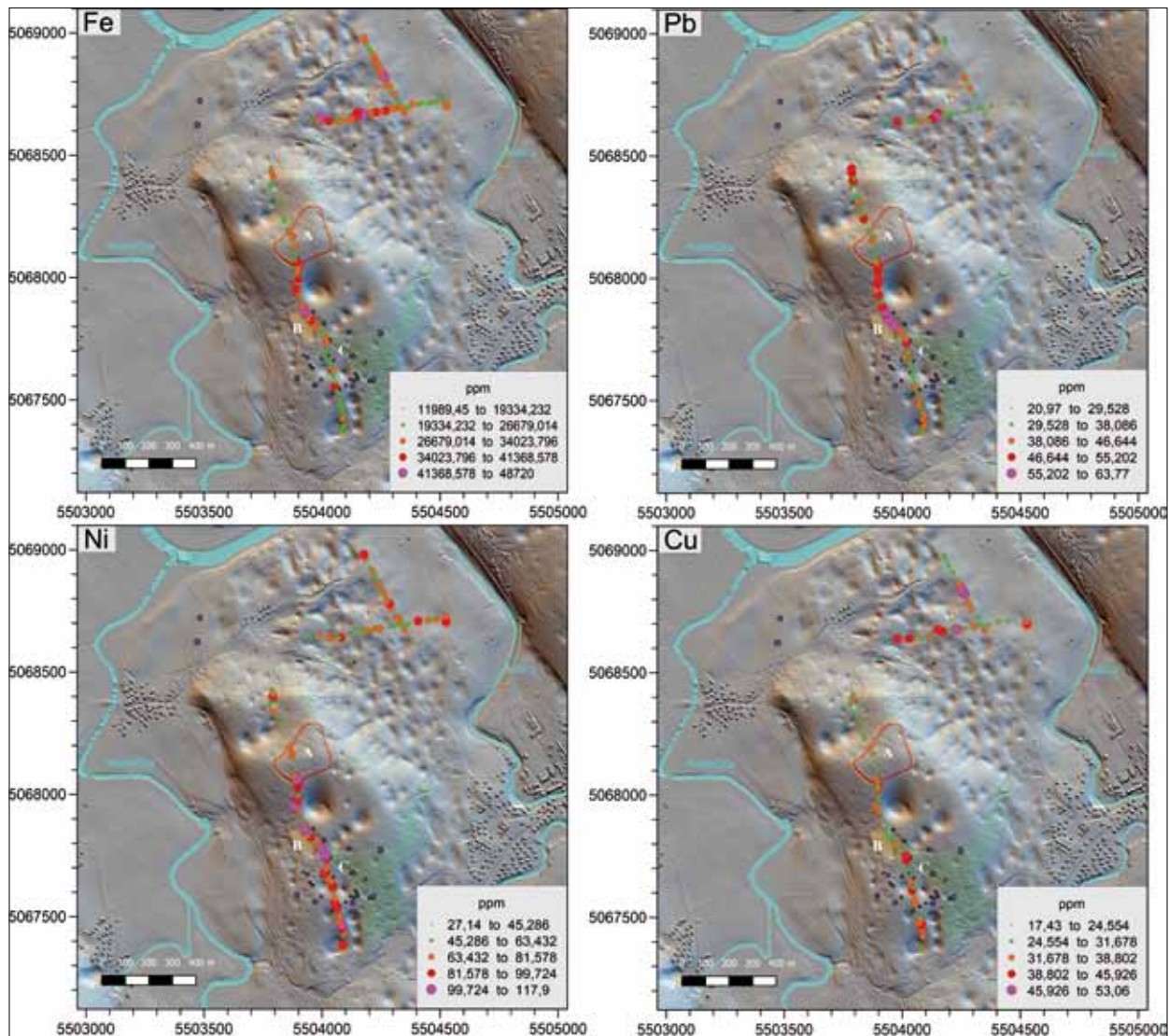


Fig. 9 Relative differences in the contents of elements attributed to the “anthropogenic group” (Fig. 7: subgroup 1) along geochemical transects represented by a linear distribution with equal intervals. The spatial correlation between the highest contents of Fe, Pb, Ni and location of archaeological areas is quite strong, while for Cu it is less pronounced, though still clear enough

of key importance for planning similar geochemical surveys along transects at other Early Iron Age sites in the Dolenjska karst region (Fig. 9).

Fe: Significantly higher Fe contents run continuously from the beginning of the iron-smelting area to the southern edge of the settlement, but with only moderately higher contents in the settlement. From this correlation, it can be inferred that areas with iron-smelting activities can be identified based on the Fe content values. However, elevated Fe contents were also found in the western part of the T2 transect and in the central part of T3 transect. If we were to conclude on the basis of geochemical mapping of the Fe content alone, we might suspect iron-smelting activity in these areas as well. Moreover, these anomalous areas are spatially coincident with the strongest magnetic gradients (see: Fig. 5). However, since no other archaeological data are available for this area, it should be flagged only as high potential for further investigations.

Pb: Significantly higher Pb contents can be once again observed from the beginning of the iron-smelting area to the southern edge of the settlement, but not in its interior. Thus, the distribution of high Pb content, again indicates areas of iron-smelting activity. Patches with slightly elevated levels also occur in the area of the burial mound necropolis, while very high levels also come from the archaeologically unexplored areas in the extreme northern part of the T1 transect and in the western part of the T2 transect. This also correlates in part with elevated Fe values.

Ni: High Ni contents were measured in an even longer part of the T1 transect, as they run continuously from the southern part of the burial mound necropolis to the southern edge of the settlement. However, the highest contents were recorded between the beginning of the iron-smelting area and the settlement, but again not in its interior. The contents

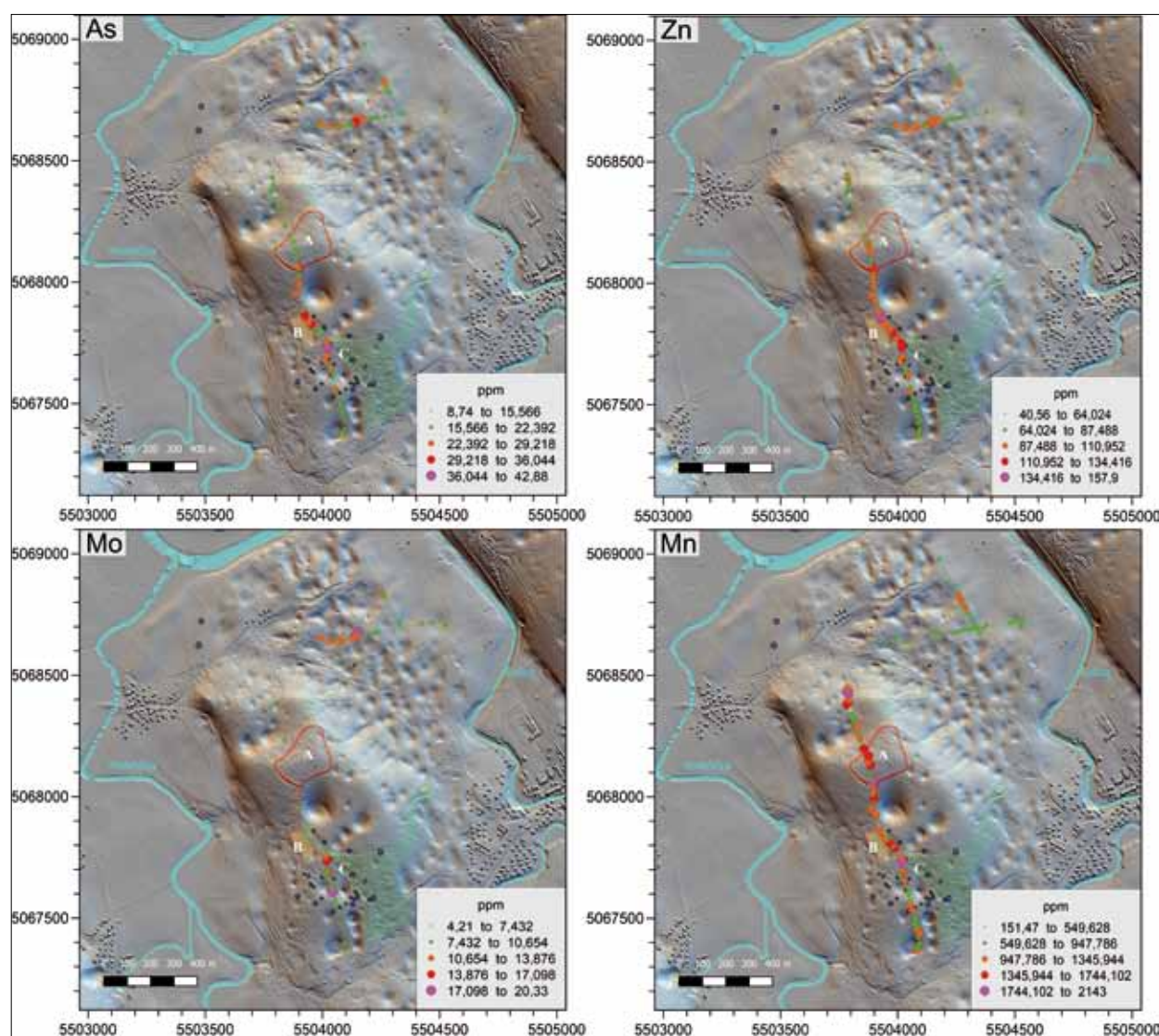


Fig. 10 Relative differences in the contents of elements attributed to the “anthropogenic group” (Fig. 7: subgroup 2) along geochemical transects represented by a linear distribution with equal intervals. The spatial correlation between the highest contents of As, Zn, Mn and the position of archaeological areas is quite strong, while for Mo it is less pronounced

are also slightly higher in the extreme northern part of the T1 transect and in the greater parts of the T2 and T3 transects. The Ni content also allows areas with iron-smelting activity to be identified, although this element clearly shows a broader picture of human impact (necropolis).

Cu: Although this element was expected to be in the first group of “anthropogenic” elements, there were no Cu anomalies at the iron-smelting area. However, moderately elevated contents were found along the entire length of the transect section across the necropolis with burial mounds. Significantly higher contents were found in the transition area from the necropolis to the iron-smelting area as well as in the western part of transect T2 and in the central part of transect T3, where the strongest magnetic anomalies were also measured (see: Fig. 5).

b) The second subgroup of “anthropogenic” elements

This subgroup includes elements that can make an important contribution to the identification of areas with certain activities in the archaeological past, but their relevance in this regard is not yet entirely clear everywhere (Fig. 10), and we provide preliminary explanations below.

As: Significantly higher As contents are found in the northern part of the necropolis, in the iron-smelting area, in the transition area to the southern edge of the settlement, and in the western part of the T2 transect, where the strongest magnetic anomalies were also measured (see: Fig. 5). The As content can be used to identify areas of smelting activities, but it could also be an indicator of other human activities.

Zn: Moderately elevated contents run continuously from the northern part of the necropolis through the iron-smelting area to the southern edge of the settlement, with the highest contents occurring in the iron-smelting area. Slightly elevated Zn values are also present in the settlement and on the western part of T2 transect, where the strongest magnetic anomalies were also measured (see: Fig. 5). Areas of iron-smelting activities can be identified from the Zn contents, although this element clearly shows a broader picture of various human activities (settlement).

Mo: Slightly higher Mo contents were found only on the necropolis with burial mounds and on the western part of the T2 transect, where the strongest magnetic anomalies were also measured (see: Fig. 5).

Mn: Moderately higher Mn contents run continuously from the northern part of the necropolis to the settlement and are even higher within the settlement. Significantly higher values are also found in the archaeologically yet unexplored area in the extreme northern part of the T1 transect. Based on the Mn content, we can identify areas of iron-smelting, although this element clearly shows a broader picture of human impact (necropolis and settlement).

CONCLUSIONS

The positive results of the geochemical prospecting to identify the iron smelting area at Cvinger near Dolenjske Toplice are a meaningful upgrade to the already extensive interdisciplinary investigations. The broad data set provides a crucial basis for reliable interpretation of the pioneer geochemical prospecting in transect, carried out with a hand held portable XRF instrument in the region. This type of instrument is a suitable solution as there is no need for a more scientifically relevant quantitative analysis for the set objectives, but only relative relations in the contents of individual elements along the transects. The measured content of elements is often strongly influenced by the content of moisture and organic matter in the topsoil (see: Scott et al. 2016b). This is a complex problem that we sought to circumvent, at least in part, by testing this approach in the relatively controlled circumstances of the Cvinger Iron Age hillfort. Despite the very good results, we are aware that this is not a unique solution that would allow to transfer this valuable experience to other similar sites in other natural environments. For this reason, we have limited our objectives and expectations to a relatively uniform geological and pedological composition of the Dolenjska Karst region. The importance of this study lies mainly in the fact that it is a rapid and economical geochemical prospecting when a large number of chemical samples are needed along several 100 m long profiles. In this sense, it is also the most appropriate solution and therefore deserves special attention. The focus of this investigation was on iron-smelting areas, but we do not neglect the importance of the results of this method for the discovery of areas with other activities in prehistory, which we have mentioned in this article in places where we considered them useful.

The area with significantly elevated levels of the elements Fe, Pb, Ni, As, Zn and Mn, identified as the geochemical footprint of the iron-smelting processes, extends from the iron-smelting area through the transition area to the settlement (Figs. 5: T1; 9 and 10). For copper, otherwise considered one of the most important indicators for metallurgical activities, there is no similarly clear correlation between elevated values and the iron-smelting area for copper.

The contents of Zn, Ni and Fe are only slightly elevated in the settlement. This is a surprising finding, since surface finds and the results of small-scale archaeological excavations in the past indicate possible forging activity in the settlement. Only elevated contents for Mn were found in the settlement, generally one of the most important indicators of archaeological sites (see: Oonk et al. 2009). Since the prospection was carried out in a single transect, it is possible that we bypassed these areas or that there is some other, as yet unexplained, reason for the different mobility of these elements (Zn, Ni and Fe) in a slightly different environment with a thin soil layer and greater leaching at the top of the limestone hill.

On the other hand, higher contents of these elements were confirmed in the transition zone between the iron-smelting area and the settlement, where the “dense daily traffic” took place. The geochemical footprint of the iron production extends to the south side to the burial mound necropolis and partially into it. This is attributed to large-scale soil contamination from iron smelting, possibly by airborne transmission of dust particles and probably also by leaching to topographically lower areas.

One of the aims of this investigation was also to test the possibility of identifying archaeological contents in yet unexplored areas (Fig. 5: T2 and T3) that were partly also covered by magnetic prospection. In this area we also found a good correlation between the content of the elements Fe, Pb, Cu, As, Zn and Mo (Figs. 5: T2 and T3; 9 and 10) and relatively stronger magnetic gradients. The archaeological significance of these results is not yet debatable, but they are significant and will certainly be taken into account when planning further intensive multi-method geophysical prospections and small-scale excavations in the future. The same applies to the relatively small area in the far northern part of the T1 transect (Figs. 5, 9 and 10), where elevated contents of the elements Fe, Pb, Ni and Mn were measured. This is again a similar geochemical footprint to that on the iron-smelting area.

We must not forget the importance of the group of “natural background elements” (Fig. 8: Rb, Sr, Th and Zr) in identifying the intensive use of the space in prehistory. This is shown by the lower contents of Sr, Th and Zr both on the iron-smelting area and in the transitional zone from its northern part to the settlement.

From the results of the geochemical prospection in the three selected transects we can conclude that they met and even exceeded our expectations. In the given context of archaeological content and natural factors, it is undoubtedly possible to clearly identify iron-smelting areas on the basis of the geochemical footprint obtained with the pXRF device. The most obvious positive spatial correlation is observed between the iron-smelting area and the content of the elements Ni, Pb, Fe, Zn and As.

It is likely that it is also possible to determine the extent of prehistoric sites by identifying areas of more intensive land use in prehistory by lower values of elements otherwise classified in the “natural background elements” group.

ACKNOWLEDGEMENTS

The research on the Cvinger archaeological complex was restarted in the years 2013–2016 in the framework of the *ENTRANS (Encounters and transformations in Iron Age Europe)* project, which was led by Ian Armit (University of Bradford), with Matija Črešnar (University of Ljubljana) and Hrvoje Potrebica (University of Zagreb) as co-PIs. The project has received funding from the European Union’s Seventh Framework Programme for research, technological development and demonstration under grant agreement no 291827. The project is financially supported by the HERA Joint Research Programme (www.heranet.info) which is co-funded by AHRC, AKA, BMBF via PT-DLR, DASTI, ETAG, FCT, FNR, FNRS, FWF, FWO, HAZU, IRC, LMT, MHEST, NWO, NCN, RANNÍS, RCN, VR and The European Community FP7 2007–2013, under the Socio-economic Sciences and Humanities programme. In the following years (2017–2019) the research as well as other activities were conducted in the frameworks of several research and heritage promotion projects. One of them was the *Iron-Age-Danube* project, led by Marko Mele (Universalmuseum Joanneum Graz) and Matija Črešnar as the Slovenian PI, which was co-financed by the Interreg Danube Transnational Programme. The investigations of the “off-site” areas, including geophysical prospections and HHPXRF geochemical transect mapping was conducted in the framework of the bilateral project *ScienceProHeritage* (BI-US/18-19-088), led by Bryan Hanks (University of Pittsburgh) and Matija Črešnar. Additional funding for the 2017 phase of research was provided by the University of Pittsburgh through a Social Science Initiative Grant (Bryan Hanks, PI, Rosemary Capo, Co-PI) and from the Centre for Comparative Archaeology. We also wish to acknowledge the contributions of undergraduate and graduate students from the University of Pittsburgh in 2017, Benjamin Hedin, Patricia Smith and Regina Gee. Further analysis of data and their interpretation continued as a part of the ARRS funded research programme Archaeology (No. P6-0247).

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RESULTS OF MAGNETIC PROSPECTION IN CONNECTION WITH THE ARCHAEOLOGICAL EXCAVATION FINDS OF LATE ANTIQUE AND EARLY MEDIAEVAL IRON PRODUCTION SITES VELIKE HLEBINE AND DEDANOVICE IN THE PODRAVINA REGION, CROATIA

Several sites containing a concentration of surface material with relatively high quantities of waste products from the bloomery iron production collected during archaeological field survey in the Podravina region as part of the TransFER project were subsequently investigated by magnetic prospecting. Among geophysical methods, the magnetic method is the most effective in identifying various archaeological remains of ironworks due to the high magnetic susceptibility of materials in iron production workshops, which was confirmed in the case of magnetic prospecting in relation to the results of archaeological excavations at Velike Hlebine and Dedanovice sites. The high content of strongly magnetic iron minerals in various iron production waste finds occurs during the smelting process. Other reasons for the higher magnetic susceptibility are fragments of burnt clay from the furnace construction and features such as shallow pits with burnt bottom, and all other materials that were exposed to high temperatures (other technical ceramics and the like). The sites of former bloomery iron production were therefore reliably identified on the basis of their magnetic properties and the results evaluated in relation to the excavated features.

Key words: magnetic method, apparent magnetic susceptibility mapping, iron production workshops, early medieval, Velike Hlebine, Dedanovice, Podravina region, Croatia

INTRODUCTION

The surface finds collected during the archaeological field survey in the lowland area along the Drava River (Podravina Region) as a part of the TransFER Project indicated that some activities related to iron production took place at the location Velike Hlebine and Dedanovice in the Hlebine district (Valent et al. 2017: 5–25; 2018: 142–147; 2019: 5–25; Valent 2018: 77–98). The results of the archaeological field surveys to date have contributed to the planning of an effective geophysical research strategy (Valent et al. 2017: 5–25; 2018: 142–147; 2019: 5–25). Surface finds, among which various iron production waste finds, predominately from iron ore smelting activities determined the magnetic method to be the most favorable geophysical method. The *in situ* remains of iron smelting furnaces, reheating furnaces and heaps of iron production waste are all remains with a strong thermoremanent type of magnetization, which can be detected by all types of modern magnetometers (see: Črešnar et al. 2020: 529–554). This type of magnetization is characteristic of certain archaeological materials that have undergone changes in the composition of iron minerals due to the high temperatures during activities such as the iron ore smelting and further processing of the iron bloom. Magnetic prospecting is used to detect such materials due to their strong magnetization (Crew 2002: 163–182). In archaeological contexts associated with intensive iron production activities, significant quantities of specific types of burnt clay are always present, such as pieces of clay furnace structures and other technical ceramics. The main feature of the thermoremanent type of magnetization is the

strong magnetic field and the relatively clear bipolarity of these magnetic anomalies in a direction similar to the direction of the Earth's magnetic field today. It should be emphasized that this is true only for *in situ* remains of iron production, while the direction of the magnetic field of similar type of remains at secondary positions may deviate significantly from this direction.

With the aim of more clearly defining the character of the sites themselves, in order to better assess the archaeological potential for planning small-scale archaeological excavations, a non-invasive, geophysical survey was carried out during the initial phase of the on-site analyses. Archaeological targets of geophysical surveys using the magnetic method and magnetic susceptibility mapping were therefore the remains of Late Antique and/or Medieval iron production workshops.

The strategy of geophysical prospection was prepared according to the findings from the archaeological excavations and geophysical survey at Sušine site near the village Virje (Sekelj Ivančan, Mušič 2014: 177–184) and also taking into account the results of geophysical prospection in similar archaeological contexts in the Podravina region (Mušič et al. 2019: 117–122; 2020: 135–142).

The geophysical prospection included the application of the magnetic method to measure changes in the gradient of the total earth magnetic field density (Geometrics G-858) and the mapping of the magnetic susceptibility of the topsoil with the hand held susceptibility meter (Kappameter KT-5). The main motive for using the magnetic method was to find archaeological remains with strong thermoremanent magnetization characteristic of the furnaces, forges, scatters of larger slag fragments on the surface or beneath the topsoil, and larger deposit areas with various waste material from the bloomery iron smelting process. Using the magnetic method, we focused primarily on relatively stronger magnetic anomalies of the thermoremanent magnetization type, which can be assumed to have arisen from certain remnants of iron production activities. Target objects of magnetometry were remains of smelting/forging/smithing (?) furnaces *in situ* as well as parts of furnace walls at secondary positions, larger slag fragments and other technical ceramics (such as burnt clay house plaster), various waste deposition areas etc.

During a preventive archaeological excavation campaign conducted in the summer of 2016 at the position Velike Hlebine, near the village of Hlebine, in Koprivničko-križevačka County, parts of an iron production workshop were excavated. The position of the 200 m² excavation trench was carefully determined after the geophysical survey of the site, which was carried out on an area of one hectare, in spring 2016 (Fig. 1: Area 1). The purpose of this investigation was to obtain accurate data in order to recognise various parts of the iron production workshop (Sekelj Ivančan 2019a: 5–20). The excavation area for one larger and three smaller trenches (Trench 1 – 4) at the Dedanovice site near Hlebine (total area of 1,010 m²) was carefully selected on the basis of the results of geophysical surveys on the larger area (4,000 m²) (Fig. 1: Area 2). During the archaeological excavations in 2018, two furnaces were investigated, which were used for one of the demanding processes of iron production operating chain, processing of iron bloom (reheating and/or further smithing). Both furnaces had a rectangular clayey construction (furnace walls), opened to one side and a oval shallow pit in front that provided access to the interior of the furnace, the firebed. The furnaces were probably active during the same period; their firebeds were side by side but back to back, with pits facing outward (Sekelj Ivančan 2019b: 129–135).

GEOPHYSICAL SURVEY

BASICS ON MAGNETIC METHOD APPLIED AND RESULTS

Magnetometry is a passive geophysical method, because magnetometers measure local changes in the Earth's magnetic field resulting from changes in the magnetic susceptibility of the material beneath the surface. The task of archaeological geophysics is to detect various magnetic anomalies resulting from the fact that different types of archaeological remains are carriers of different types of magnetization due to differences in the physical properties of the material that they are composed of. In archaeological prospecting, gradient measurements of the Earth's magnetic field in the (pseudo)gradient mode (nT/m) are much more commonly used than total sensor measurements of the field (nT). In general, the gradient mode acts like a low-pass filter, actually enhancing weak magnetic anomalies from small objects at shallow depths and eliminating long-wavelength anomalies that are a consequence of the geological background. The greatest depth at which we can detect iron production remains with a magnetic method depends on the contrast in magnetic susceptibility between the archaeological materials present and the soil in which they are buried, but the size, shape and position of the archaeological features below the surface are equally important.

A Geometrics G858 high-sensitivity, optically pumped caesium vapour magnetometer in pseudo-gradient mode was used for magnetic prospecting. Data was acquired in bidirectional mode along parallel transects spaced 0.5 m apart at 5 readings per second. The distance between the top and bottom sensors fixed on the survey cart was 1 m and the ground sensor was kept at a constant height of 0,3 m above the ground (Fig. 2).

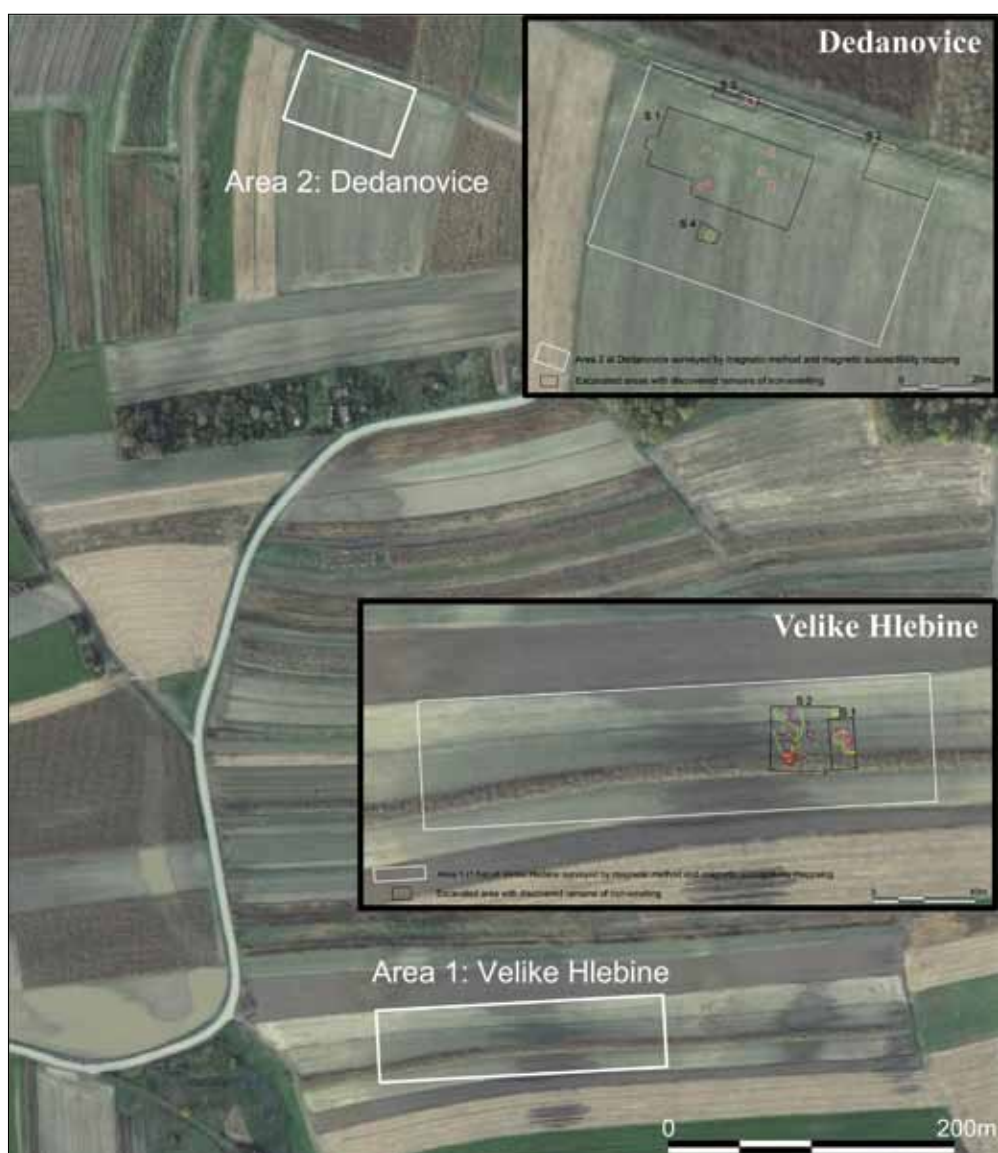


Fig. 1 Location map of the areas investigated by the magnetic method (Geometrics G-858, gradient mode) and mapping of the magnetic susceptibility of the topsoil (Kappameter KT-5) with the outlines of archaeological trenches and discovered remains related to iron production on aerial photographs (Courtesy of Geodetic Administration of the Republic of Croatia) (image prepared by: B. Mušič)



Fig. 2 Magnetometer Geometrics G-858 in gradient mode fixed on survey cart for constant position of sensors above ground during survey at archaeological site of Velike Hlebine (foto by: B. Mušič)

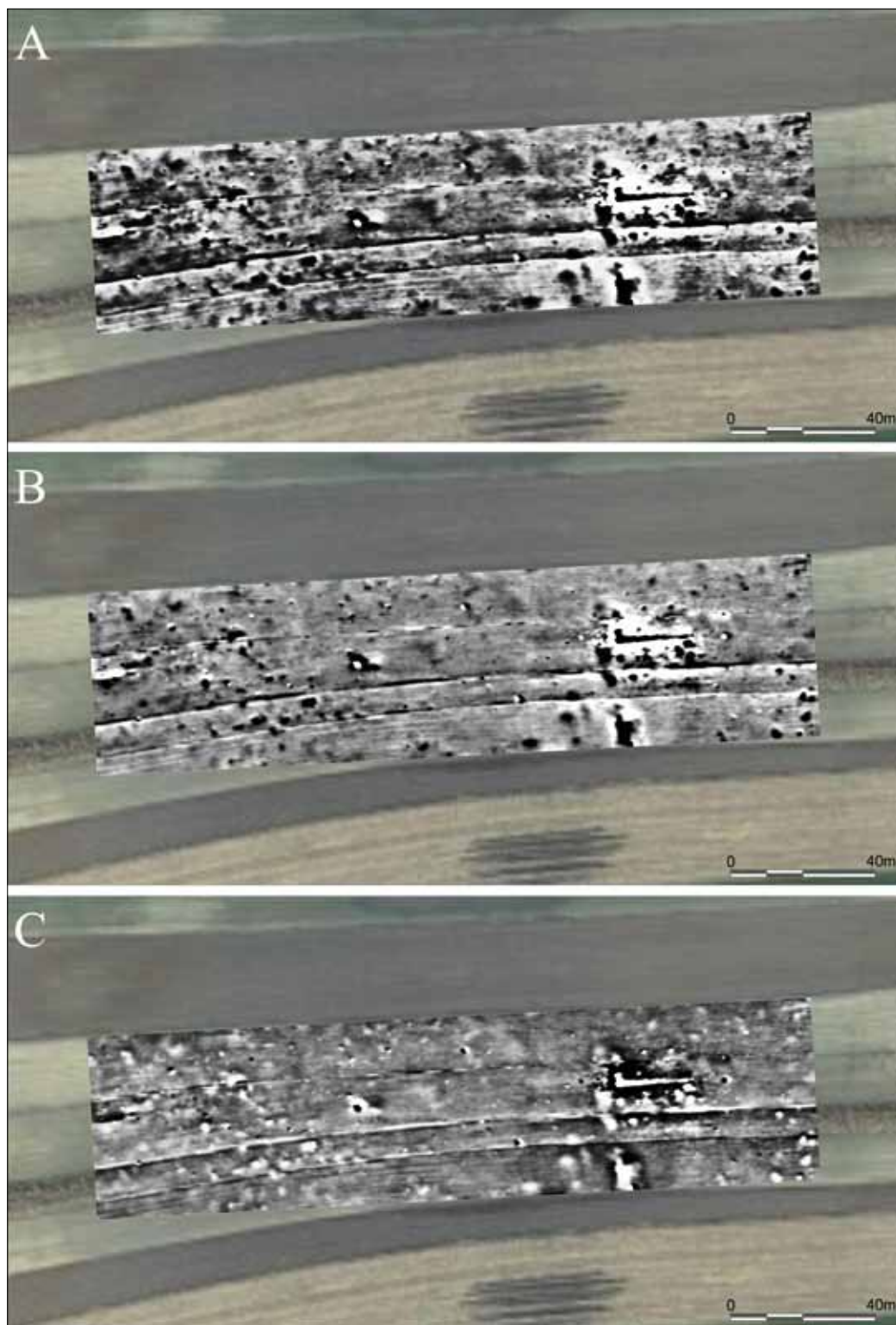


Fig. 3 Velike Hlebine. Results of magnetic prospection: A - histogram equalisation; B - linear grey scale; C - inverted linear grey scale (image prepared by: B. Mušič and B. Horn)

Due to the bipolar nature of the geomagnetic field, magnetic anomalies from well-preserved furnaces/kilns and similar constructions *in situ* at this latitude are clearly asymmetrical, even if the shape of the magnetic source is symmetrical. Therefore, such archaeological objects with thermoremanent magnetization can be recognized by extremely strong anomalies and often pronounced bipolarity. The results of magnetic measurements are presented by the histogram manipulation approach with histogram equalization, linear distribution and semi-logarithmic plots and different ranges of displayed values in accordance with the statistical properties of the measured magnetic gradient distribution.

With histogram equalisation, the total magnetic field readings can be better distributed on the histogram to get insight into weaker, discrete magnetic anomalies. Basically, this histogram manipulation allows areas of a lower contrast to have a high contrast. Histogram equalisation accomplishes this by effectively spreading out the most frequent intensity values (Acharya, Ray 2005). In this way the areas “contaminated” by small fragments of debris from iron production, which were distributed over larger areas by ploughing, can be easily recognized (Figs. 3 and 4: A). With the linear distribution, which is the most common approach, we gain a general insight into the ranges of values to identify the strongest anomalies at the sites with iron production residues with thermoremanent magnetization (Fig. 3: B and C; Fig. 4: B, C and D). The semi-logarithmic scale is used to highlight zones of positive and negative gradients for magnetic anomalies generated by *in situ* features with thermoremanent magnetization. Depending on the measurement range, the scale is chosen to show the *in situ* features as clearly as possible, which is usually achieved with a scale that increases by a factor of two with each step (Crew 2002: 163–182) (Figs. 5–8).

Based on the results of the magnetic prospection, several archaeological trenches were excavated at both sites to gain a better insight into the archaeological remains and were used to evaluate the results of the magnetic prospection. Within the investigated complex of features connected to bloomery iron production at Velike Hlebine site, four smelting furnaces were discovered *in situ* in various states of preservation. The documented situation indicates the existence of one particular pair of furnaces and one pair that was probably superimposed. However, it should be emphasised that this is the second archaeologically researched site, not only in Podravina, but in the whole northern part of Croatia, where

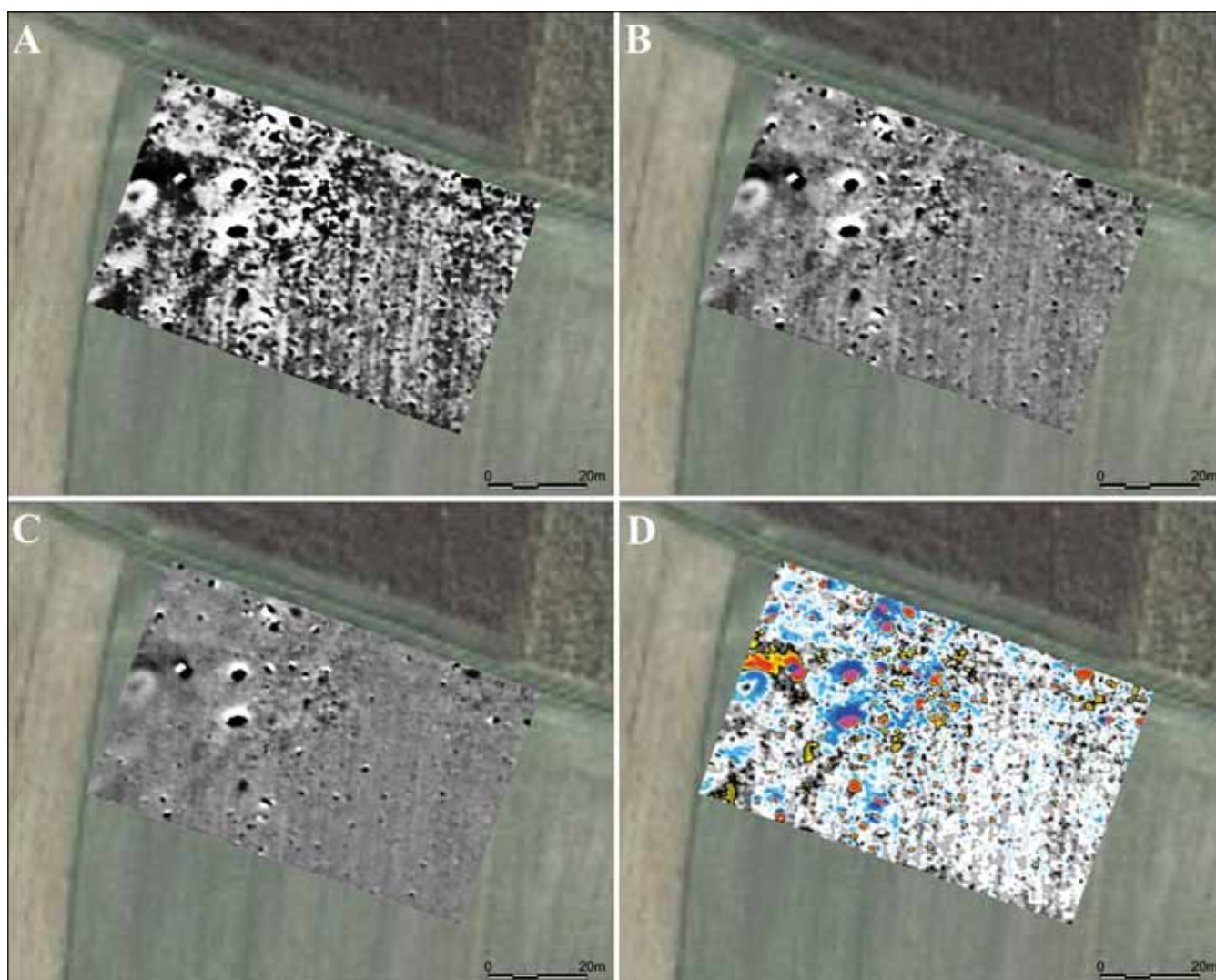


Fig. 4 Dedanovice. Results of magnetic prospection: A - histogram equalisation; B - linear grey scale; C - inverted linear grey scale; D - linear colour scale (image prepared by: B. Mušič and B. Horn)

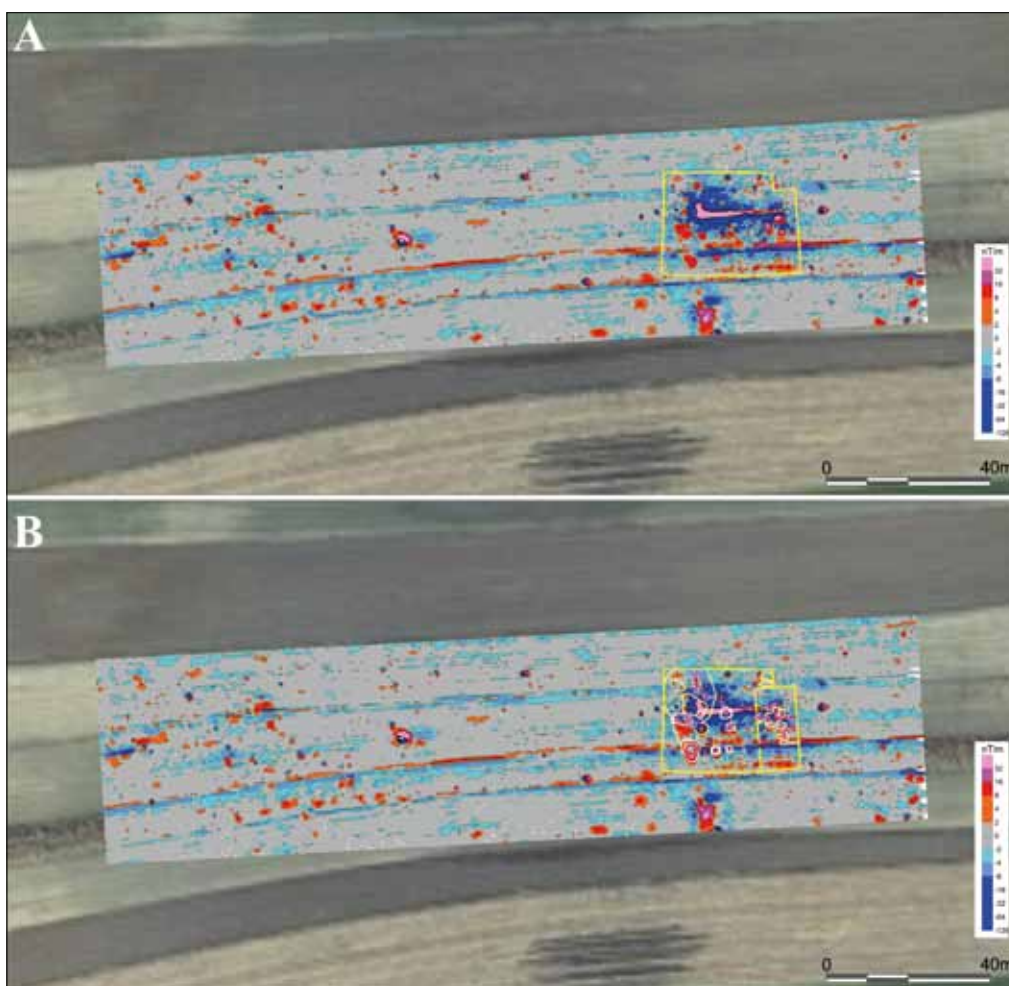


Fig. 5 Velike Hlebine. Results of magnetic prospecting represented by a semilogarithmic scale and the outlined area of archaeological excavation (A) and with the excavated remains of iron production activity (B) (image prepared by: B. Mušič, B. Horn and K. Turkalj)

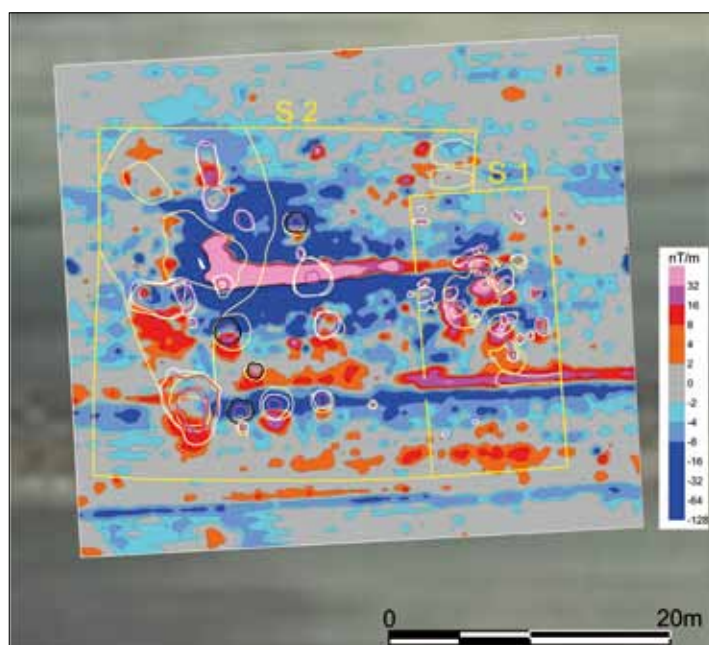


Fig. 6 Velike Hlebine. Detail of the results of magnetic prospecting, represented by a semilogarithmic scale, in the area of the archaeological excavation with the excavated remains of iron production activity (image prepared by: B. Mušič, B. Horn and K. Turkalj)

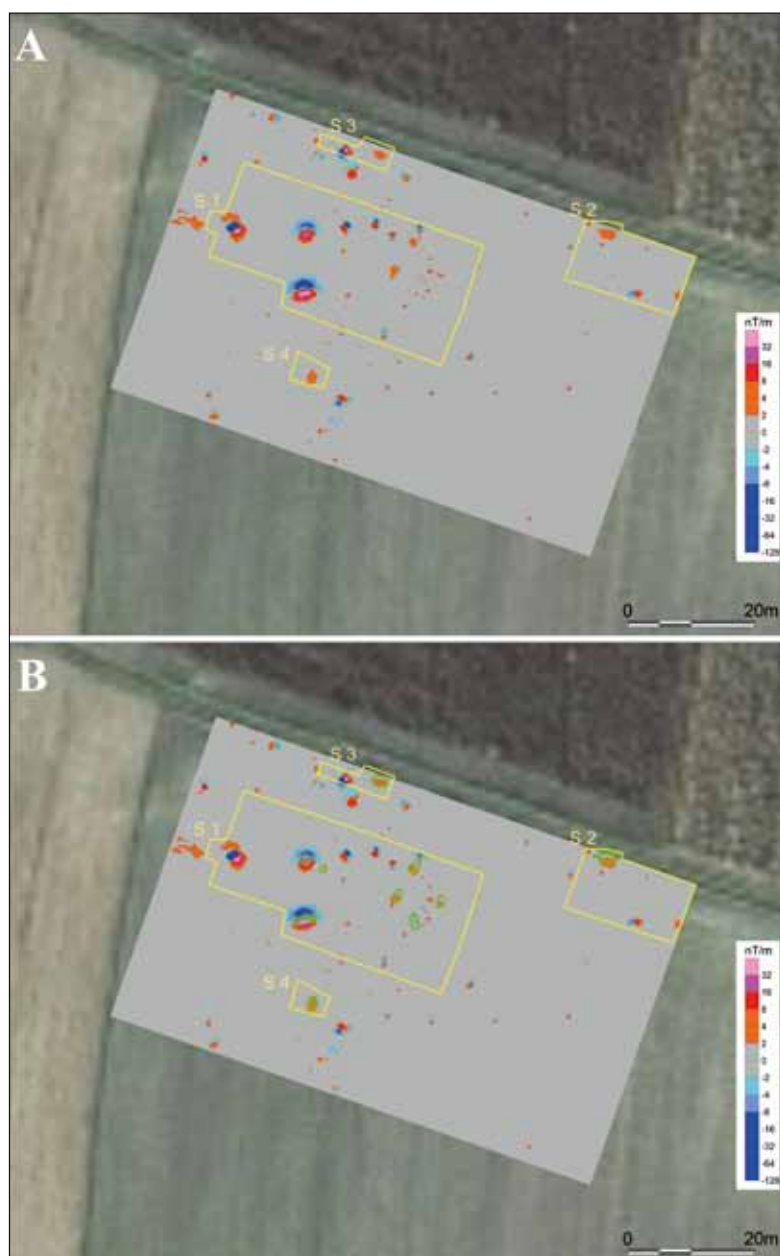


Fig. 7 Dedanovice. Results of magnetic prospection represented by a semilogarithmic scale and the outlined area of archaeological excavation (A) and with the excavated remains of iron production activity (B) (image prepared by: B. Mušič, B. Horn and K. Turkalj)

activities connected with processing of iron ore were recognised. Moreover, considering the fact that the furnaces were discovered *in situ*, they are of utmost importance not only for the regional, but also for the wider European scientific and professional community (after: Sekelj Ivančan, Valent 2017: 104–108). The area of iron production activity outlined on the basis of magnetic method results was indisputably confirmed by archaeological excavations, but it turned out that despite the relatively good correlation between the two results, not all individual objects could be reliably identified from the results of the magnetic method (Fig. 6). The main reason for this is the large quantity of strongly magnetic fragments of iron production waste beneath the plough zone of an agricultural field, which obscured the weaker magnetic anomalies of the poorly preserved *in situ* remains.

At the Dedanovice site, the correlation between the results of the magnetic method and the excavated remains of iron production was very good. The most outstanding finds were the remains of two furnaces, whose magnetic effect was clearly evident from the results of the magnetic method (Figs. 4, 7 and 8). The investigated furnaces were located

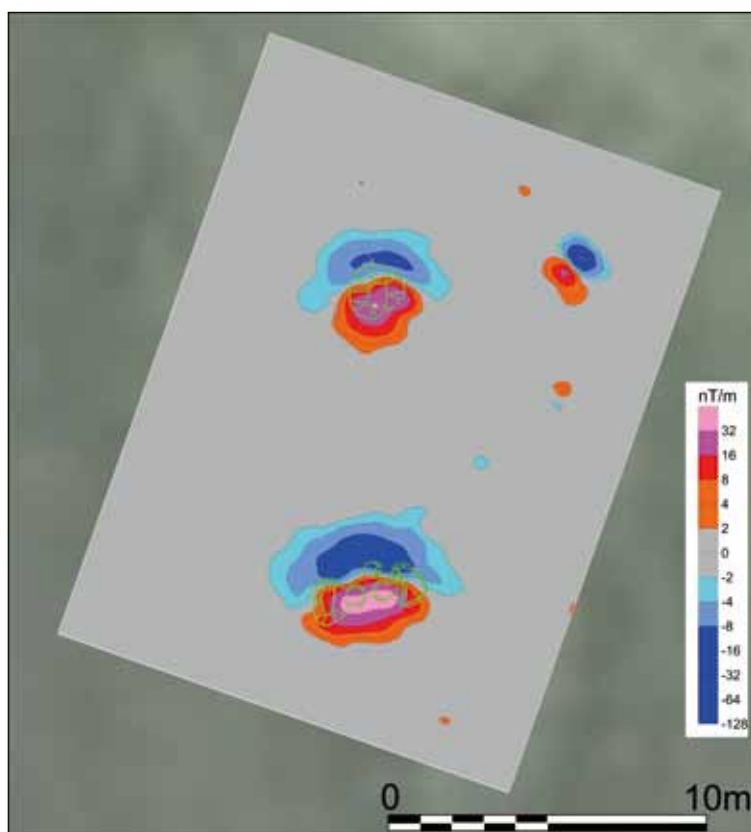


Fig. 8 Dedanovice. Detail of the results of magnetic prospecting, represented by a semilogarithmic scale, in the area of the archaeological excavation with the excavated remains of two furnaces (image prepared by: B. Mušič, B. Horn and K. Turkalj)

near the contemporaneous features, where pieces of roasted iron ore were found in addition to pottery. Both furnaces had a rectangular firebed with a pit in front of it, or a place from which the inside of the firebed could be accessed. They were probably in use at the same time, and it should be emphasized that furnaces/hearths were set side by side, but with the 'back' so that the pits were on the outer side. The circumstances of the find suggest that the tuyeres for air supply to the furnace firebeds were built into the walls of both furnaces on the north side. The furnaces at Dedanovice differ significantly in their basic characteristics from those found at the nearby site Velike Hlebine, but the furnaces at the two investigated sites are close temporally (end of the 6th – mid 7th century), almost contemporaneous, as shown by the results of radiocarbon analysis, so it seems that at these two sites different procedures related to the iron production took place but represent interrelated actions of the same social community, which ultimately obtained the desired product (Sekelj Ivančan 2019b: 129–135).

BASICS ON APPLIED MAGNETIC SUSCEPTIBILITY MAPPING AND RESULTS

In addition to magnetometry, measurements were made to map the magnetic susceptibility of the topsoil to a depth of only 5 cm using a hand-held Kappameter KT -5 in regular grids. The aim of measuring magnetic susceptibility was to identify areas of topsoil contamination with iron minerals as a result of iron production. The basic assumption for the magnetic susceptibility mapping in this case is that the destruction of archeological layers at shallow depths during plowing significantly alters the magnetic image of the upper soil horizon due to abundant contamination with small fragments of various magnetic materials associated with iron production. In fact, the magnetic properties of the topsoil change significantly due to metallurgical wastes in the form of tiny fragments that come to the surface during plowing. The crushing of various fragments of iron production waste in the topsoil continues during intensive plowing, so that most of this material is ground into very small fractions, so that slag residues are no longer visible at the surface. Their presence in the topsoil is often only clearly indicated by the results of magnetic susceptibility mapping (see for instance: Mušič, Orengo 1998: 157–186; Mušič 1999: 349–405). This also applies to the situation in Velike Hlebine and Dedanovice, where archaeological layers with the remains of iron production debris occurs at a shallow depth below the surface. The

greatest changes in the magnetic susceptibility of the topsoil are always caused by the high content of strongly magnetic iron minerals in various waste finds created during the iron production process. Other reasons for the higher magnetic susceptibility of the topsoil are fragments of furnace walls together with shallow pits with burnt bottom bowl-shaped in cross section, places where iron ore was roasted or charcoal was being produced, and all other finds and features from the workshops exposed to high temperatures (other technical ceramics and the like). The sites of former iron production activity can thus be reliably identified on the basis of changes in the magnetic susceptibility of the soil.

It should be emphasized that these anomalies are generally much larger in spatial distribution than those detected by magnetometers, due to a wide dispersion of the material by plowing mechanisms (Figs. 9 and 10). This is otherwise known from the analysis of the distribution of surface finds from archaeological field survey. In this sense, the results of the magnetic susceptibility mapping are equivalent in terms of the magnetic properties of the soil (see: Mušič et al. 2020: 132–146). Therefore, by mapping the magnetic susceptibility on the ground under favorable conditions, we can determine the position and estimate the dimensions of the workshop based only on the “contamination” of the topsoil with slag and burnt clay fragments, although the depth range of susceptibility measurements is only 5 cm.

CONCLUSIONS

The geophysical investigations with the magnetic method and the magnetic susceptibility mapping confirmed beyond doubt the existence of features and finds related to iron production at both sites as well as settlement remains, which was generally already expected based on the archaeological surface survey results. The strongest magnetic anomalies and the highest values of magnetic susceptibility are located precisely at the locations with larger quantities of slag, pottery and technical ceramics, indicating the site character associated with iron production, and with the settlement remains.

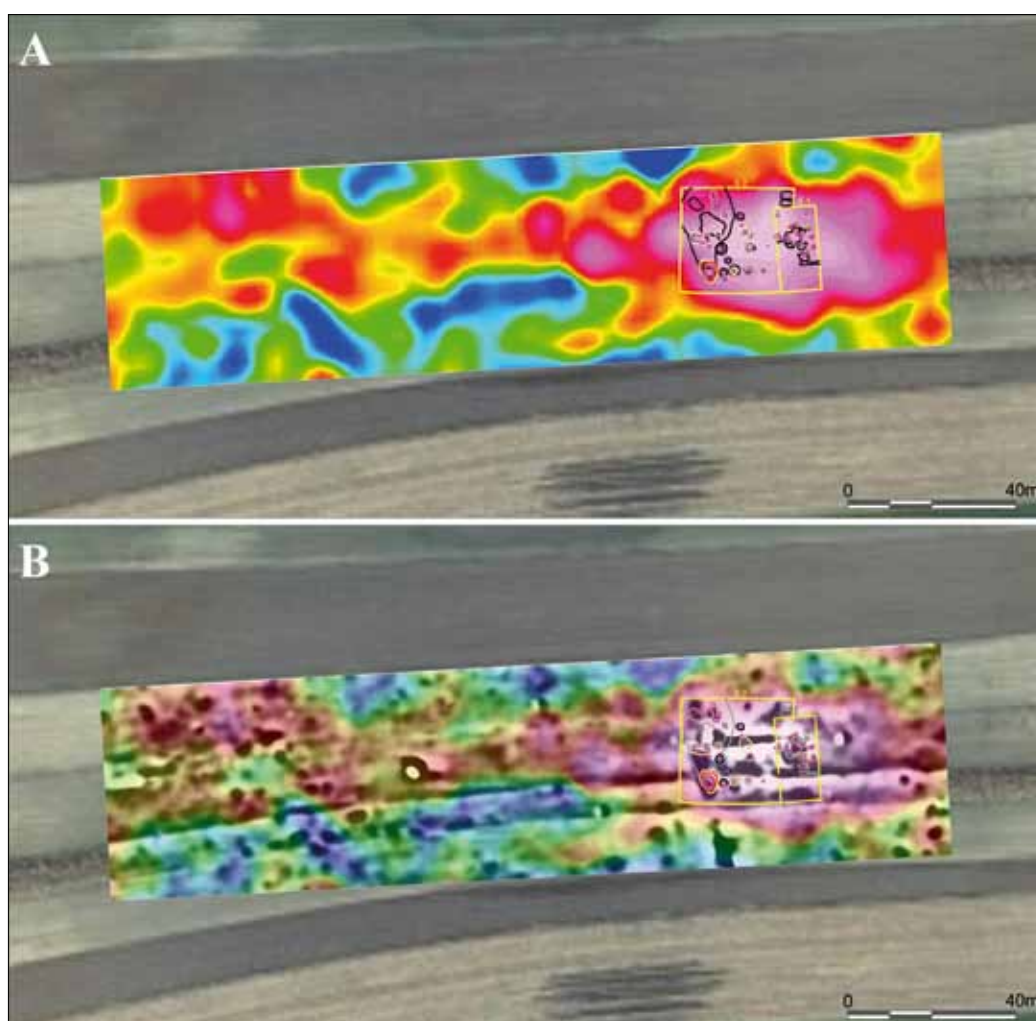


Fig. 9 Velike Hlebne. Results of magnetic susceptibility mapping with susceptibility range 0.4-1.7 SI (A) and semi-transparent susceptibility map on top of magnetic map (B). See also Figs. 3, 5 and 6 (image prepared by: B. Mušič, B. Horn and K. Turkalj)

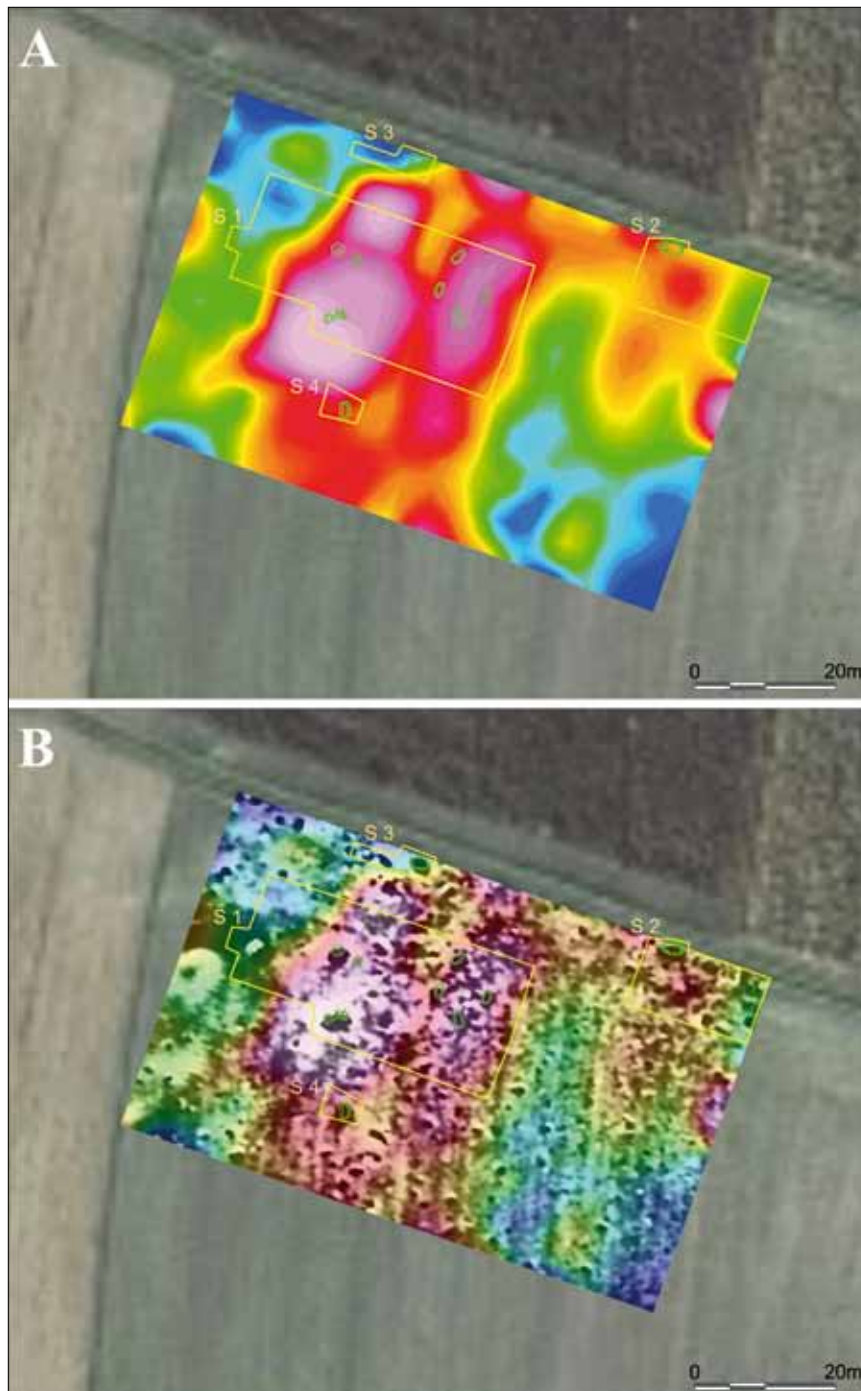


Fig. 10 Dedanovice. Results of magnetic susceptibility mapping with susceptibility range 0.3-1.3 SI (A) and semi-transparent susceptibility map on top of magnetic map (B). See also figs 4, 7 and 8 (image prepared by: B. Mušič, B. Horn and K. Turkalj)

The areas of iron production determined on the basis of the results of the magnetic method were confirmed beyond doubt with the archaeological excavations, but it turned out that, despite the relatively good correlation between the two results, not all individual objects could be reliably identified on the basis of the results of the magnetic method. The main reason for this, especially at the site Velike Hlebine, is the large amount of strongly magnetic fragments of iron production waste beneath the plough zone of the agricultural field, which masked the weaker magnetic anomalies of the poorly preserved *in situ* remains.

Based on the mapping of magnetic susceptibility, we came to important conclusions regarding the identification of sites with iron production remains in the Podravina region that have been subjected to intensive agricultural land

usage. Anomalous areas of magnetic susceptibility are always located in places with strong magnetic anomalies, but areas with higher values of susceptibility are distributed over a much larger area than magnetic anomalies. This is due to the contamination of the soil with high amounts of iron minerals at the site of the workshops and especially at the iron production waste dumping areas/layers with high concentration of iron production waste finds.

Among all geophysical methods, magnetometry contributes most to the recognition and separation of individual objects related to iron production, such as various furnace remains, hearths, other features with traces of burning (for instance iron ore roasting and/or charcoal production remains), and, moreover, all kinds of depositional surfaces containing waste material from iron production. All these objects are certainly visible on magnetograms, but it is not always possible to provide a completely accurate and unambiguous interpretation with the exact type of archaeological sources of magnetic anomalies.

ACKNOWLEDGEMENTS

The geophysical surveys on the archaeological sites Velike Hlebine and Dedanovice were a part of the archaeometallurgical research within the project TransFER (Iron production along the Drava river in the Roman period and the Middle ages: creation and transfer of knowledge, technologies and goods) in the period 2017–2021 (Hrzz: IP-06-2016-5047), led by Tajana Sekelj Ivančan (Institute of Archaeology, Zagreb). Further analysis of geophysical data and their interpretation continued as a part of the ARRS funded research programme Archaeology (No. P6-0247).

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FOLLOW-UP PEDOLOGICAL AND GEOLOGICAL STUDY OF TWO GLEYSOLS PROFILES IN PODRAVINA REGION LOCATING POSSIBLE BOG IRON ORE FORMATION ZONES

This paper brings new evidence for possible bog iron ore (neo)formation in the soils of the Podravina region, NE Croatia. Archaeological field surveys led to discoveries of numerous archaeological sites where signs of possible iron production and processing was occurring. Previous geological and pedological studies discovered iron anomalies in the Gleysols and Fluvisols pointing to possible bog iron ore formation in the study area. Two new soil profiles were analysed for their physico-chemical characteristics and mineral composition. Based on soil colour the two profiles show distinct differences between them, with Peteranec–Ciglène profile showing several decimetres thick yellowish and orange interlayer in the bottom part of the profile. Soil analyses revealed that Novigrad Podravski profile is characterised by slight acidic to neutral pH, while Peteranec profile is moderately to slightly acidic. The mineralogical analysis confirmed the presence of typical soil minerals including quartz, plagioclase, feldspar and variable amounts of clay minerals and dolomite. Significant amount of goethite is noted in Peteranec profile, correlating with orange interlayer, while in Novigrad Podravski profile goethite was recorded only in one interval. The results of this paper bring new data on soil characteristics of the area and point to possible currently forming bog iron ore deposit in Podravina region.

Key words: bog iron ore, pedology, pH, CEC, mineralogy

INTRODUCTION

Throughout the Podravina region, surface finds indicating iron production and iron smithing were recognized on well over 150 locations (Valent et al. 2021). Recent pedological and geological field surveys in the Podravina region, NE Croatia revealed signs of bog iron ore occurrences (Brenko et al. 2020; Brenko et al. 2021). Based on previous excavation (Sekelj Ivančan, Marković 2017; Brenko et al. 2020), it is believed that the locally occurring bog iron ores were the main ore used in iron ore production in the study area. Bog iron ore is sedimentary type of iron deposits (Ramanaidou, Wells 2014), that is typically occurring in the lowland area such as river valleys, bogs, swamps or any type of micro-depression where the groundwater table is close to the surface (Kaczorek, Zagórski 2007). These terrestrial accumulations of Fe are mostly composed of goethite and ferrihydrite (Banning 2008), and are mostly developed in hydromorphic, loamy, sandy and clayey alluvium and soil (De Geyter et al. 1985; Landuydt 1990), such as the Gleysols. They are formed due to seasonal oscillations of groundwater that produces an oxidising zone in the upper part of the soil profile and a reductive zone in the lower part of the profile (Stoops 1983; Kaczorek, Sommer 2003). According to Kaczorek et al. (2004) and Thelemann et al. (2017) as has been confirmed in previous geological studies in the area (Brenko et al. 2021), bog iron ores are distinguished in three different types based on their macromorphological characteristics and development stage: (i) a soft, unstable form, often referred to as “soft” bog iron, (ii) randomly distributed concretions, block or nodules in soil and (iii) well-cemented, massive horizons, continuous or discontinuous, often referred as “hard” bog iron.

Following previous pedological investigations in the study area of the Podravina region (Brenko et al. 2020), two additional soil profiles were chosen for additional pedological and mineralogical analyses. However, the chosen profiles are located in parts of the region where very little, or no archaeological evidence for bog iron ore and iron production was previously detected. Therefore, it is possible that the two selected soil profiles can give insight into new zones where the formation of bog iron ore is currently or was previously occurring.

This paper deals with the following research questions: (i) defining mineralogical and physico-chemical characteristics of the selected two soil profiles from the Novigrad Podravski–Milakov Berek and Peteranec–Ciglene locations and (ii) opening the possibility for the discovery of potential new bog iron ore accumulations in the study region. In order to answer these questions, two profiles were analysed in the study area based on their visible Fe accumulations. Their mineralogical composition and detailed physico-chemical characteristics were determined in order to identify potentially bog iron ore formations.

STUDY AREA

Podravina region is located in the north-eastern part of Croatia, belonging to the Croatian part of the Pannonian Basin. It is elongated in the northwest-southeast direction and bounded by the Bilogora hills in the southwest and by the Croatian-Hungary border in the northeast. The region geomorphological characteristics were developed in the previous 50 thousand years, during the Holocene and Pleistocene geological periods (Head 2019). Torrential floods caused by melting of snow in the Alps transported large quantities of loose sediments and deposited them in the Podravina region. Deposits of sands, silts, gravels and clays have shaped the present-day morphology of the region (Feletar, Feletar 2008). Most prominent geomorphological feature in the study area is the large, meandering Drava River, surrounded by its many tributaries (Fig. 1). Large alluvial plain, consisting of three river terraces surrounds the river. The oldest, third terrace,

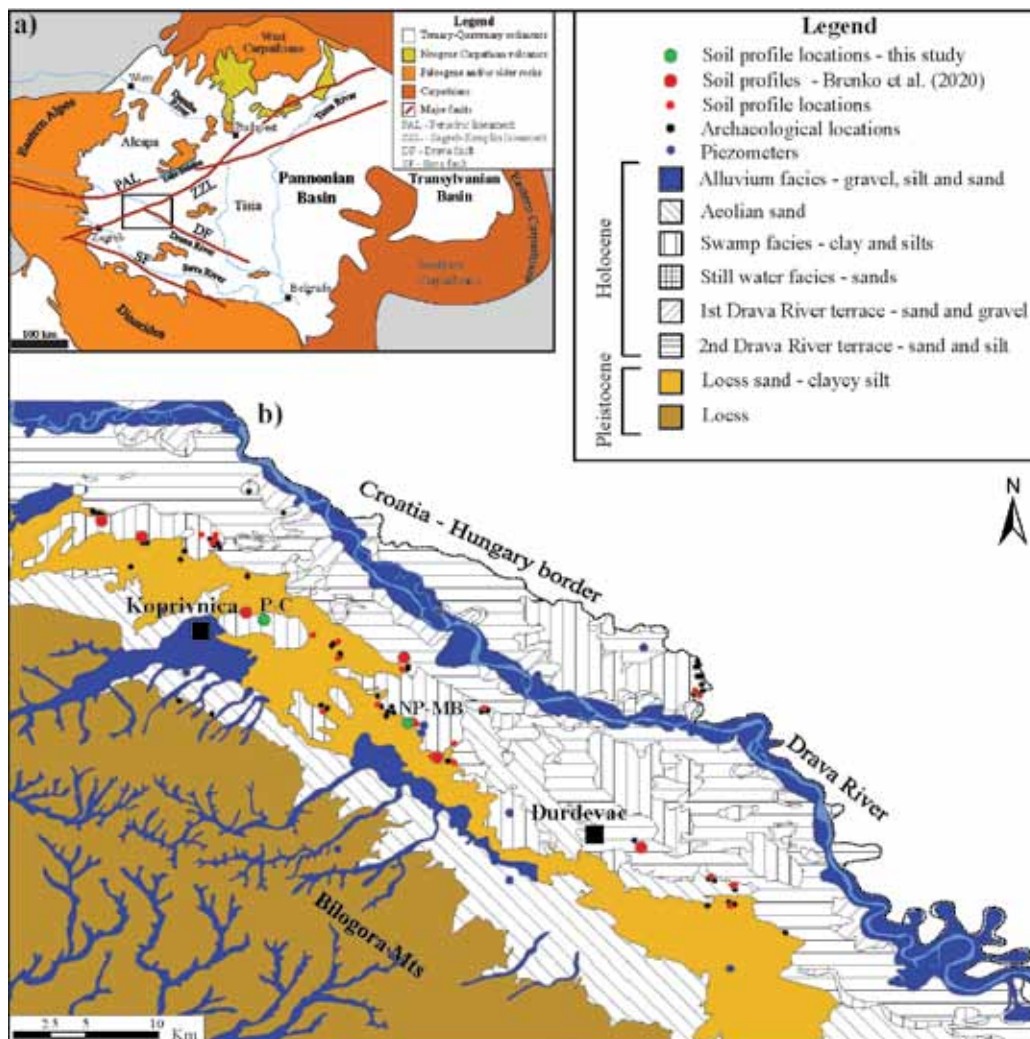


Fig. 1 Geological map of the Podravina region with the location of two analysed soil profiles (modified according to Brenko et al. 2020 and the references therein)

was formed during Late Pleistocene. During the formation of this terrace, alternation between dry and cold weather was a common thing, with a formation and accumulation of aeolian material, sands and loess, formed from the river material. Occasional floods during warmer period led to the formation of fluvial accumulations. The second river terrace formed during second Würm interglacial period. This terrace is characterized by an erosion-accumulation (Prelogović, Velić 1988). It is overlying the sediments on the third terrace. This terrace went through all stages of formation, from coarse grained gravelly sand at its base to the fine-grained silts at the top. Based on the mineral composition (Mutić 1975), it can be assumed that this material originated in the Eastern Alps. The first river terrace is the youngest and is located between the second river terrace and the Drava River channel. It was formed during the third Würm interglacial period. Due to the river flow and floods, this river terrace is highly altered. The terrace itself is not fully formed, as it only went through several phases of floodplain formation, leaving the surface uneven. Therefore, during high waters in spring and autumn, it is often flooded. Main lithological units found on this terrace include sands, gravelly sands and sandy gravels (Šimunić et al. 1990).

Due to the meandering nature of the river, there are several abandoned riverbeds, some of them still containing water, forming still waters and ponds. Abandoned riverbeds are formed as a result of the river finding new flow paths, and simultaneously cutting off previously existing riverbeds. These abandoned riverbeds can often be found on first and second river terrace with fluvial deposition of fine-grained material such as silty sand and silt. Swamp, marsh and bog sediments are very often associated with this sort of abandoned riverbeds. They consist of silty clays, clayey-sandy silts and clay with organic components. Peat deposits are sometimes found below clays (Bognar 2008).

Another important lithological unit found in Podravina region is aeolian sand, covering the third river terrace. These materials were previously a part of the river fluvial sediments, but they were transported in southwest direction due to the strong winds, where they can be found today. The thickness of this lithological unit is quite variable, reaching up to 2 m on hilly relief, and up to 10 m in flat areas (Galović 2016; Pavelić et al. 2016).

The most common soil types in the study area are Fluvisols and Gleysols located on the Pleistocene and Holocene sediments, with Stagnosols and Regosols sporadically appearing in some parts of the region (Bašić 2013) (Fig. 2). Gleyed (waterlogged) soils are generally characterised by highly localised patterns of redoximorphic features, mainly Fe oxyhydroxides, as a result of concentration and depletion due to complex and variable redox conditions (Husnjak 2014).

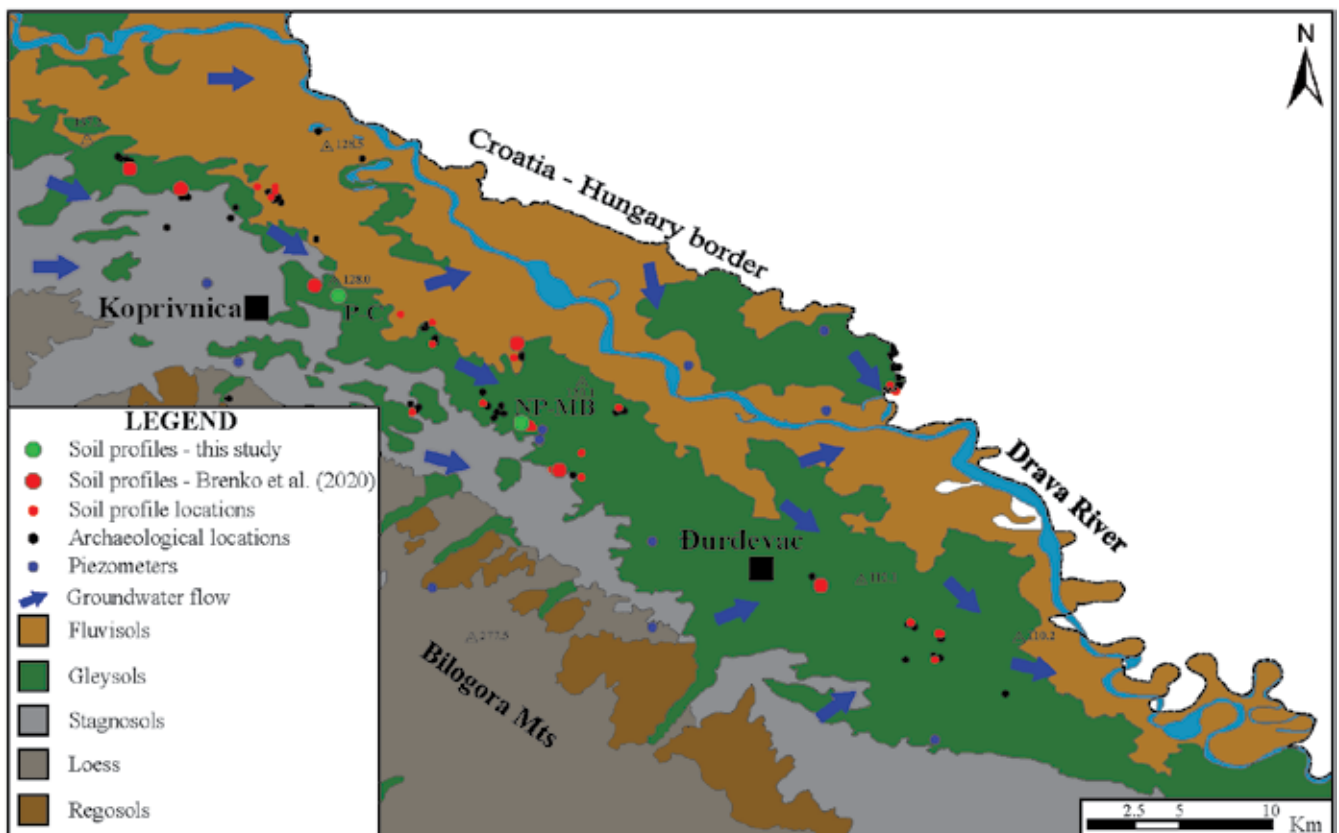


Fig. 2 Pedological map of the study area with locations of the analysed soil profiles (modified according to Brenko et al. 2020 and the references therein)

These soil types mainly occur on older, fluvial accumulations with good horizontal and vertical permeability. Deeper parts of such soil profiles are mostly under constant influence of groundwater (Brenko et al. 2020). Due to that, the lower parts of the soil profile are usually greyish or bluish in colour, indicating an anaerobic and reducing environment. Fluvisols are often formed on alluvial floodplains that are periodically flooded (IUSS WRB 2015). This type of soils does not have well developed horizons, with only the shallowest, hummus horizon being developed. Frequent flooding and transport of suspended particles aggravates pedogenetic processes and the formation of soil horizons. Therefore, Fluvisols are characterized by the flooded material in their soil column. Similarly to Gleysols, Fluvisols are also under the influence of groundwater, often in the first meter of the soil profile. There, the stagnation of groundwater can form a gleyed horizon (G) (Husnjak 2014).

Based on several hydrological and hydrogeological surveys (Brkić et al. 2010; Brkić, Briški 2018), the groundwater table is established at shallow depths, especially during winter periods where it almost reaches surface. Several authors established that groundwater is enriched with various elements, most notably iron (Fe), manganese (Mn) and arsenic (As) (Kopić et al. 2016; Brenko et al. 2020). Central parts of the region tend to have the highest concentrations.

MATERIALS AND METHODOLOGY

SAMPLING METHODOLOGY

During the summer and autumn of 2017 and spring of 2018, several field campaigns were conducted, and over 50 soil profiles were collected using Eijkelkamp auger set for soils. Six profiles were previously selected for detailed geochemical and mineralogical analyses (Brenko et al. 2020). Additionally, two new soil profiles were selected for analysis of pedological and mineralogical characteristics. All soil profile locations were selected as a result of previous archaeological excavations and are usually located in vicinities of discovered archaeological workshops or near location where signs of iron production were found (Sekelj Ivančan, Marković 2017; Valent et al. 2021). Two soil profiles were field classified according to the IUSS Working Group WRB (2015). Following the classification, both profiles were further divided into intervals, based on the field observations of soil texture, mineralogical changes or other visible macro features of discolorations. Each interval was stored in separate plastic bag and transported to Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb. There, part of each sample was air-dried for several days and sieved through a 2 mm sieve and their mineralogical, geochemical and pedological characteristics were analysed.

LABORATORY ANALYSES

The determination of soil colour was conducted using Munsell colour chart (Munsell 1994) on original, non-sieved samples. Munsell colour chart consists of three values, basic colour (hue), lightness (value) and colour intensity (chroma). Soil pH was measured in two different solutions, H₂O and KCl where 5 grams of each soil sample was immersed in a plastic container with 25 ml of distilled water or 1 mol/L KCl suspension. Electric conductivity was measured in 1:5 soil volume to H₂O using WTW cond 3110 conductometer. Carbonate contents were determined using Scheibler volumetric method (ISO 10693 1995) where 1 gram of soil sample was immersed in 15 ml of 10 % HCl. Cation exchange capacity (CEC) is the ability in soil to adsorb and exchange cations expressed as meq/100 g or mmol/100 g. It is usually connected with clay minerals. Solution for CEC measurement was prepared using silver-thiourea method (Ag-TU). 40 ml of 0.01 M Ag-TU complex was added to 0.8 grams of sample, which is then placed on shaker for two hours and then placed in centrifuge for 5 minutes at 3000 RPMs. CEC was measured using atomic absorption spectrometry (AAS).

The mineralogical composition of 13 soil samples was determined using powder X-ray diffraction (XRD) using a Phillips vertical X-ray goniometer (type X'Pert) equipped with Cu tube and graphite crystal monochromator. Scan settings were 3–70° 2 θ , 0.02° step size, 1 second count time per step while generator settings were 40 kV and 20 mA. Minerals were identified using PANalytical X'Pert HighScore software with standardised Powder Diffraction Files (PDF) of the International Centre for Diffraction Data (ICDD) (Newton Square, PA, USA).

RESULTS

PHYSICO-CHEMICAL CHARACTERISTICS OF THE TWO SOIL PROFILES

Two selected soil profiles (Novigrad Podravski–Milakov Berek and Peteranec–Ciglène) are presented in Figure 3. Both profiles are classified as Gleysols. Based on field observations, they both mainly consist of silt material. Novigrad Podravski profile is slightly darker with regards to colour, as seen in the Table 1. Upper part of the profile is yellowish-brown, while the first major difference can be noted in the 80–150 cm interval, when the colour changes to dark greyish. Occurrence of yellowish tonnes is present in following interval (150–180 cm), while deeper parts of the profile consist of black organic interlayer and dark grey tonnes. Brown colours prevail in the upper part of the Peteranec–Ciglène profile, while starting from the 65 cm depth, and especially from 120 to 175 cm depth, yellowish tonnes prevail.

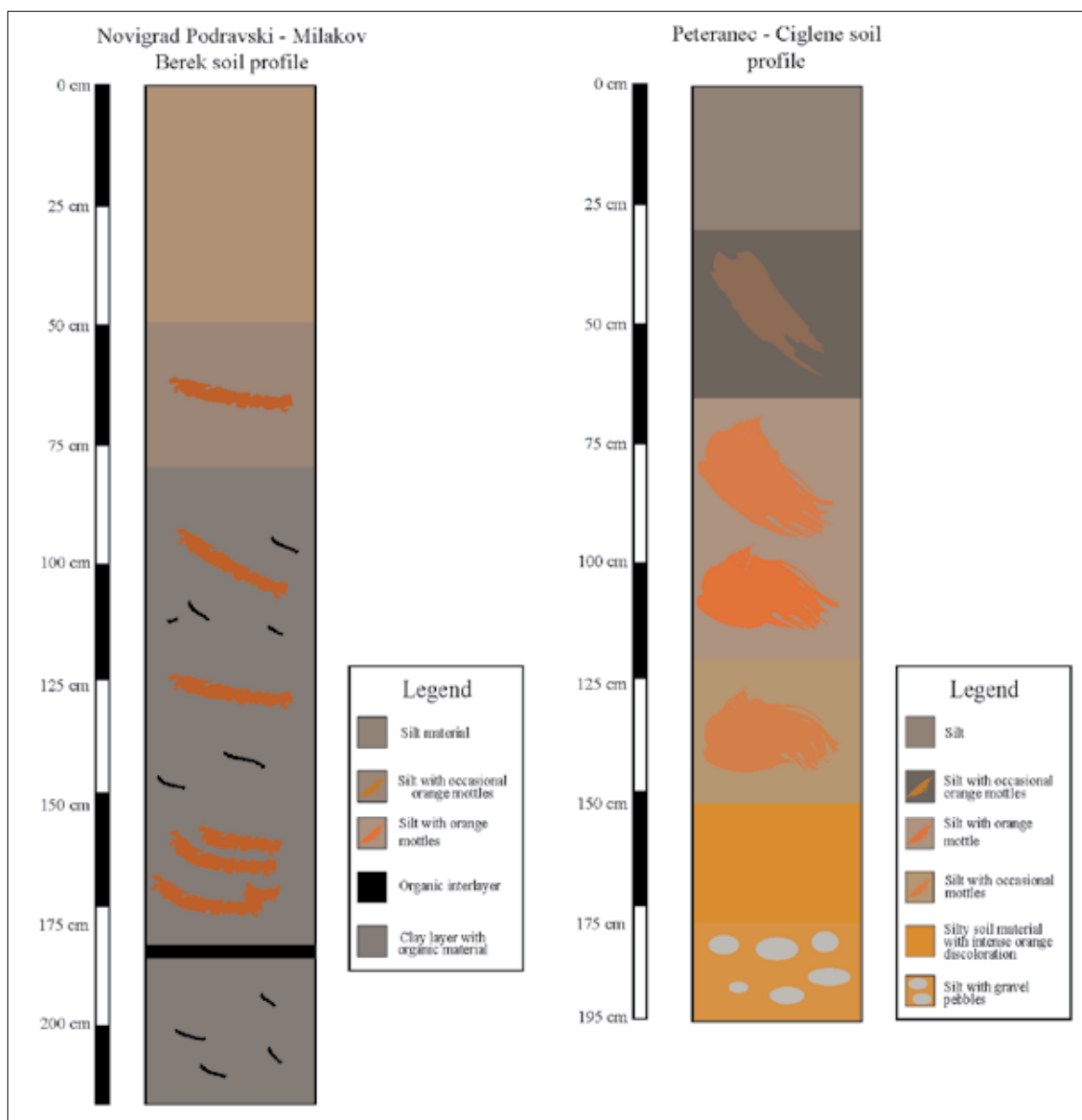


Fig. 3 Schematic drawings of two selected soil profiles from Novigrad Podravski–Milakov Berek and Peteranec–Ciglene locations (made by: T. Brenko)

Soil pH measured in H_2O for Novigrad Podravski profile shows neutral pH, with values slightly above 7.0 and increasing with depth. pH measured in KCl changes drastically with regards to depth (Tab. 1). Upper parts of profile are slight acidic to acidic, while from the 150–180 cm interval the pH changes to neutral with deepest interval reaching values over 7.0. Similar behaviour with regards to pH changes can be seen in the Peteranec–Ciglene profile. pH measured in H_2O ranges in the interval between 5.79 and 6.34 with only the topmost interval having value below 6.0. On the other hand, pH measured in KCl varies with depth, having the lowest value (4.28) in the topmost interval, and growing with depth to 5.85 in the topmost interval. Electrical conductivity (EC) differs between both profiles. In Novigrad Podravski profile, no significant changes can be seen between 0 and 150 cm, where values range between 52.96 and 71.7 $\mu S/cm$, while in the deeper parts EC ranges from 243.56 up to 302.33 $\mu S/cm$. On the other hand, significantly lower variability is noticed in the Peteranec–Ciglene profile, with values ranging from 26.3 in the 65–90 cm interval up to 52.3 in the topmost interval. Carbonate contents in the Novigrad Podravski–Milakov Berek soil profile seem to increase with depth of the profile with the first part of the profile having values below 0.5 mass. %, middle of the profile values around 1 mass. %, and 6.59 mass. % in the deepest part of the profile (Tab. 1). Negligible carbonate contents were detected in the Peteranec–Ciglene soil profile, with only the top and bottom interval having values around 0.4 mass. % (Tab. 1). CEC values in Novigrad Podravski range in a small interval (11.86 – 24.36 mmol/100 g). Highest values are noted in the medium part of the profile, in the 150–180 cm interval, while Peteranec–Ciglene profile has low CEC values (Tab. 1).

Tab. 1 Physico-chemical characteristics of two selected soil profiles in the Podravina region (made by: T. Brenko)

Location	Sample ID	Depth, cm	Munsell value	Colour	pH (H ₂ O)	pH (KCl)	EC, μ S/cm	Carbonate content, %	CEC, mmol/100 g
Novigrad Podravski - Milakov Berek	NP-MB 1	0 - 50	10 YR 4/4	Dark yellowish brown	7.12	5.10	52.96	0.42	11.86
	NP-MB 2	50 - 80	10 YR 3/2	Very dark grayish brown	7.21	5.33	71.70	0.42	20.18
	NP-MB 3	80 - 150	10 YR 4/1	Dark grey	7.21	5.44	58.20	0.69	16.82
	NP-MB 4	150 - 180	10 YR 3/4	Dark yellowish brown	7.31	6.64	302.33	1.12	24.36
	NP-MB 5	180 - 185	10 YR 2/1	Black	7.42	6.79	255.33	1.54	20.30
	NP-MB 6	185 - 220	10 YR 4/1	Dark grey	7.48	7.04	243.56	6.59	14.99
Peteranec - Ciglène	P-C 1	0 - 30	10 YR 5/3	Brown	5.79	4.28	52.30	0.42	13.42
	P-C 2	30 - 65	10 YR 4/3	Brown	6.25	4.57	28.50	0.00	12.48
	P-C 3	65 - 90	10 YR 5/6	Yellowish brown	6.34	4.80	26.30	0.00	7.33
	P-C 4	90 - 120	2.5 Y 5/6	Light olivegreen	6.25	4.81	30.30	0.00	5.76
	P-C 5	120 - 150	2.5 Y 6/6	Oliveyellow	6.21	4.75	31.30	0.00	3.35
	P-C 6	150 - 175	10 YR 6/8	Brownish yellow	6.15	4.95	24.30	0.00	3.61
	P-C 7	175 - 195	10 YR 6/8	Brownish yellow	6.17	5.85	44.90	0.42	5.15

MINERALOGY

According to the XRD analysis, quartz is the dominant mineral phase in both analysed soil profiles. Generally, the mineral assemblage in both cases is relatively similar. Other than quartz, most common minerals are feldspars, plagioclase and mica minerals (probably muscovite). Clay minerals are more abundant at Novigrad Podravski, where they consist of both 10 and 14 Å minerals such as illite, smectite and chlorite. Peteranec–Ciglène differs from the Novigrad Podravski profile due to higher occurrence of goethite, an iron oxyhydroxide mineral (α -FeOOH). Although goethite is detected inside one soil interval (150–180 cm) in the Novigrad Podravski, its contents are much lower than in the Peteranec profile where goethite is detected from the 90–120 cm interval, all the way to the bottom of the interval, with the highest contents in the 150–175 cm interval (Tab. 2).

DISCUSSION

PEDOLOGICAL CHARACTERISTICS OF SOIL PROFILES

Colour through both soil profiles is variable, changing from brown to brownish yellow and in some cases dark brown and black. The changes in colour are mostly influenced by pigments in the soil, such as Fe minerals or organic matter (Schwertmann, Fitzpatrick 1992). Gradual colour change present in the Peteranec–Ciglène soil profile could indicate gradual change in the majorly represented mineral and soil phases in the profile. Upper part of profile is brown, while from the 65–90 cm interval occurrence of yellowish tones is starting. Further down the profile these yellow tones are starting to be the dominant colour. Changes in the soil profile colour indicate increase of goethite contents in the middle part of the profile.

Tab. 2 Mineral composition of two soil profiles. Mineral abbreviations: Chl – chlorite; Fld – feldspar; Gt – goethite; Ms – muscovite; Pl – plagioclase; Qtz – quartz; Sme – smectite (made by: T. Brenko)

Location	Sample ID	Depth, cm	Qtz	Gt	Ms	Sme	Chl	Pl	Fld
Novigrad Podravski - Milakov Berek	NP-MB 1	0 - 50	+++	-	++	+	+	+	+
	NP-MB 2	50 - 80	+++	-	+	+	+	-	-
	NP-MB 3	80 - 150	+++	-	+	+	+	+	-
	NP-MB 4	150 - 180	++	+	+	++	?	+	-
	NP-MB 5	180 - 185	+++	-	+	+	+	?	-
	NP-MB 6	185 - end	+++	-	++	-	+	+	-
Peteranec - Ciglène	P-C 1	0 - 30	+++	-	+	-	+	+	-
	P-C 2	30 - 65	+++	-	+	-	+	+	-
	P-C 3	65 - 90	+++	-	+	-	+	+	+
	P-C 4	90 - 120	+++	-	+	-	+	+	-
	P-C 5	120 - 150	+++	?	+	-	+	+	-
	P-C 6	150 - 175	+++	++	+	-	+	+	-
	P-C 7	175 - 195	+++	+	+	-	+	+	-

Both soil profiles are subjected to different influence of groundwater, as suggested by the hydrological map of Podravina (Brkić, Briški 2018). This different influence is the result of different depths of groundwater table and different duration of saturation. As previously determined by Brenko et al. (2020), different duration of saturation and groundwater table depth is reflected in the occurrence of iron enriched layer in the soil. Based on the relatively subtle iron occurrences in the Novigrad Podravski profile, it can be proposed that the groundwater table is too deep and does not reach higher parts and that the saturation period is therefore too short. When the groundwater table is below 180 cm, it is in the highly reductive zone, as seen by the black organic interlayer. This means that the iron remained in the form of Fe^{2+} , which is the mobile form of Fe. When groundwater occasionally reaches shallower parts where more oxygen is available, oxidation of divalent to trivalent iron is occurring and the precipitation of Fe^{3+} in the forms of iron mottles is seen through the profile. On the other hand, Peteranec–Ciglène profile exhibits continuous yellowish orange layer from, especially from 150–180 cm interval. This indicates that groundwater mostly fluctuates somewhere below this level and that there is enough free oxygen available that precipitation of Fe^{3+} is occurring at more significant rate. This profile differs to a close-by profile Peteranec–Gorice, as observed by Brenko et al. (2020). In the Peteranec–Gorice profile, based on calculations using hydrological map provided by Brkić and Briški (2018), it was established that the groundwater level was below the maximum depth of the profile, and therefore, it was lacking any significant flux of Fe-enriched groundwater and accumulation of Fe minerals.

Values of electrical conductivity are unusually low for this type of soil profiles (Walker et al. 1973). Both soil profiles exhibit different behaviour when comparing the EC. Novigrad Podravski profile starts with low values of EC (52.96–71.70 $\mu S/cm$), but going to 150–180 cm interval, the values are several times higher, indicating significant change in the profile itself. On the other hand, Peteranec–Ciglène profile topmost soil interval has similar EC values to Novigrad Podravski profile (52.30 $\mu S/cm$), while values decline to 20–30 $\mu S/cm$ in the lower parts of the profile. Similar behaviour is noted in the Peterance–Gorice profile, where the topmost values are the highest (139.60 $\mu S/cm$), while deeper intervals are several times lower, implying some regional pattern in EC behaviour (Brenko et al. 2020). It is possible that higher content of clay minerals, such as the 150–180 cm interval in Novigrad Podravski profile, is responsible for elevated values of EC in soil. Besides clay minerals, other minerals, including Fe minerals, such as goethite can contribute to higher EC values (Regber et al. 2011). According to Grisso (2009), electrical conductivity is in direct correlation with the cation exchange capacity. However, in this case, CEC is not the main influence on the electrical conductivity as the correlation factor for Novigrad Podravski ($r=0.56$) and Peteranec–Ciglène ($r=0.44$) indicate low or no correlation.

Cation exchange capacity (CEC) gives insight into the nutrient retention capacity of the soil (Mukhopadhyay et al. 2019). Certain minerals found in soil, such as clay minerals, especially when combined with organic matter, pose as a number of electrically charged sites that can attract and hold oppositely charged ions. The CEC of soils generally increases with soil

pH due to the greater negative charge that forms on different soil phases, such as kaolinite mineral and organic matter due to deprotonation of functional groups as pH increases (Sparks 2003). Based on macroscopic field determination and laboratory analyses, there are some noticeable similarities, and some noticeable differences between the two Gleysols profiles. Soil acidity (pH) differs quite a bit, especially when measured in H₂O. There are several main reasons for soils to become acidic: rainfall and leaching, acidic parent material, organic matter decay, harvest of high yielding crops and nitrification of ammonium (Thomas, Hargrove 1984). Based on field observations, both soil profiles are under same climatic influence with regards to rainfall and similar type of cultures that are sown on both localities. Variable carbonate contents can be noted on two profiles. Difference in carbonate contents plays a key role in pH differences. The effect of carbonates on soil pH and heavy metal migration has been intensively studied (Deromea, Saarsalmi 1999; Bolan et al. 2003; Tang et al. 2003). Soil reaction (soil acidity) in general plays an important role on physical, chemical and biological soil characteristics. This is mostly evident in the dissolution of minerals, formation of secondary soil minerals, humification process, availability and mobility of nutrients (Neina 2019; Penn, Camberato 2019). Therefore, it can be said that the Novigrad Podravski soil profile can be characterized as neutral to slightly acidic based on pH, while Peteranec–Ciglène soil profile can be characterized as slightly acidic to acidic (USDA 2017). Another important parameter that can have influence on CEC values is soil texture (Tomašić et al. 2013). Low CEC values were recognized by Tomašić et al. (2013) for soil at Molve location (distance of several hundred meters from Novigrad Podravski–Milakov Berek location). The authors concluded that unfavourable soil texture with higher sand particle contents and low clay particles contents as well as low pH had an impact on lower CEC values.

According to mineralogical analyses, both soils consist of similar soil minerals, including quartz, muscovite, chlorite, plagioclase and occasionally, feldspar. Similar mineral paragenesis was recognized as in the previous soil study in the area (Brenko et al. 2020). Recognized clay minerals represent typical soil and floodplain minerals (Sokolova et al. 2013; Długosz et al. 2018). Previous study (Brenko et al. 2020) determined that majority of Fe is bound to goethite mineral phase, therefore, the same is assumed here. Two analysed soil profiles greatly differ when it comes to the occurrence of goethite. Novigrad Podravski contains very low Fe contents, as goethite was only recognized in one soil interval (Tab. 2). Considering that there is no significant accumulation of goethite recognized in this soil profile, first assumption would be that the groundwater table is too low throughout the profile, and that the soil at this location is mostly under anoxic conditions. Black interlayer in 180–185 cm interval with accumulation of organic matter confirms the proposition of anoxic conditions. Due to that, Fe most likely remains in its mobile form (Fe²⁺) in the soil profile, leaching out of it, or accumulating in insignificant quantities. However, previous field explorations discovered several bog iron ore fragments from the Novigrad Podravski–Milakov Berek location, in close vicinity to the analysed soil profile (Brenko et al. 2021). Based on the soil profile characteristics with regards to Fe accumulation and mineralogy, it can be proposed that no bog iron ore is currently forming under present conditions. The discovered bog iron fragments are probably remains from the previous periods when soil and climate conditions were more favourable for bog iron ore formation. The reason why the fragments were found at surface could be connected to the agricultural activity, where deep ploughing could have disintegrated a layer into smaller fragments and brought them to surface.

Peteranec–Ciglène profile resembles Kalinovac–Hrastova Greda profile due to the fact that intensively yellowish-orange interlayer was detected throughout the profile. The two profiles have other similar characteristics, namely, both profiles are mainly composed of silt and sand, while the clay content is fairly low. As goethite mineral phase was firstly detected in intervals deeper than 120 cm, with major occurrence at 150–175 cm interval, this could imply that the boundary between oxidising and reductive conditions is located somewhere around this depth. That would also mean that the average groundwater level is also around this depth as at this depth the transformation of Fe²⁺ to Fe³⁺ is occurring. Continuous accumulation of iron at the Peteranec–Ciglène profile could lead to formation of bog iron ore. Bog iron ores are sedimentary type of iron deposit that are mostly occurring in low-land areas, such as the Drava River valley, where the groundwater table is close to the surface (Stanton 1972; Stoops 1983; Ramanaidou, Wells 2014) with the main mineral in bog iron ore being goethite (Kaczorek, Sommer 2003). Previous investigations in the study area confirmed bog iron ore occurrences (Brenko et al. 2020; 2021). The middle and bottom part of the Peteranec–Ciglène soil profile between 120 and 195 cm depth stand out from the rest of the profile due to its colour, indicating high enrichment of Fe oxides. It is proposed that similar formation process as in the Kalinovac–Hrastova Greda soil profile is occurring at Peteranec–Ciglène site. Fe originates from the groundwater and is subject to seasonal fluctuations of the water table, with interchanges of wetting and drying periods, thus producing an overlying oxidized zone with a high Fe content and yellowish-orange colour in a lower part of the profile, and upper zone with no Fe enrichment (De Geyter et al. 1985). If the profile was sampled to a

greater depth, the occurrence of an underlying reduced zone with noticeable darker colour would probably be discovered. All of this points to similar conclusion as with Kalinovac–Hrastova Greda profile, that bog iron ore was probably forming an/or is still forming at this site. However, continuous agricultural activities and melioration of the region in present time significantly hinders the possibility for accumulation of iron needed for the formation of full bog iron ore deposit.

PETERANEC–CIGLENE – HISTORIC OR CURRENT BOG IRON ORE DEPOSIT?

Previous pedological exploration in the study area were conducted based on previous archaeological excavation campaigns around discoveries of iron smelting workshops dating back to Late Antiquity and the Middle Ages in the Podravina region (Sekelj Ivančan, Karavidović 2021) and on surface iron slag findings (Valent et al. 2017). Based on that field surveys, only Kalinovac–Hrastova Greda stood out as the location with current occurring bog iron ore (neo)formation. New pedological analysis suggests that there may be additional current bog iron ore formation deposits.

Two analysed soil profile (Novigrad Podravski–Milakov Berek and Peteranec–Ciglène) both show some signs of iron accumulation, as mentioned in the previous chapter. Soil profile from Novigrad Podravski location shows very little signs of any significant Fe accumulation in the area, as evident by the low amount of goethite throughout the profile and no significant colour changes that could indicate Fe minerals. On the other hand, Peteranec–Ciglène profile exhibits significant accumulation of Fe and possibly other redox-sensitive elements. As only the Peteranec–Ciglène profile exhibits any potential for current bog iron ore formation and development, it will solely be considered in the further discussion.

Current archaeological surveys found no evidence of iron production in the immediate vicinity of Peteranec–Ciglène location. Archaeological evidence for iron production and processing was discovered on surrounding localities, such as Peteranec–Gorica, Novi krči, Petrovci, Podgorica, Pod Siget and Vratnec, where discoveries of smelting and smithing slags, as well as furnace walls and indications of workshops were found (Valent 2018; Valent et al. 2018). The majority of discovered materials were dated between early and late Middle Ages, as suggested by other indicative archaeological surface finds. Other locations where signs of iron production and/or processing were detected are more than five kilometres away. Majority of historic bog iron ore deposits are closely linked with some form of iron workshops or human settlements, as indicated by the occurrence of bog iron ores at Kalinovac–Hrastova Greda and smelting slags at the same location (Valent et al. 2017; Brenko et al. 2020; Sekelj Ivančan 2020). Likewise, bog iron ores were also found in closed archaeological context with other signs of iron production and processing. Therefore, it is possible that local residents from surrounding settlements exploited from Ciglène location and transported the ore to their few hundred meters or one- or two-kilometres distant workshops. It is also possible that the occurrence of bog iron ore at Ciglène location presents neof ormation in the term that it started forming in the last several hundred years. That would also explain initial stage of Fe accumulation at the site and lack of any archaeological evidence. Recent study (Brenko et al. 2021) discovered presence of second phase in bog iron ore development (bog iron nodules) in the fields of Ciglène area. Nodules were discovered in the up most soil horizon after agricultural activity. Relatively low Fe_2O_3 (22.99 mass. %) suggests initial stages of bog iron ore development. Based on that it is most likely that Peteranec–Ciglène location is currently forming bog iron ore deposit, and therefore is not connected with surrounding archaeological sites. However, it is also worth mentioning that bog iron ore was possibly formed at the site during Late Antique or Middle Ages, but the deposit as such was fully exploited, leaving no trace of historical mining activity.

CONCLUSIONS

Previous archaeological surveys indicated the position of possible bog iron ore formations. This resulted in sampling over 50 soil profiles and detailed analysed on six profiles. Additionally, two new Gleysols soil profiles were analysed. The selected soil profiles are located on the second Drava River terrace, where the dominant lithological units are sands and silts, both noticed throughout the profiles. Follow-up pedological analyses of two soil profiles from Novigrad Podravski–Milakov Berek and Peteranec–Ciglène revealed opposite situations. Based on field observations, profile Peteranec–Ciglène show higher contents of silt and sand, while the clay contents seem low. Profile Novigrad Podravski–Milakov Berek shows high contents of silt, with higher clay contents than Peteranec profile, while sand is sporadically occurring. Pedologically, both soil profiles exhibit characteristics typical for river valley regions, with slightly acidic pH and low CEC values due to lower clay contents. Visually, Peteranec–Ciglène profile stands out due to intensive yellowish orange interlayer in the bottom part of the profile. This interlayer is connected with accumulation of significant amounts of goethite in the lower parts of the profile, similar to the occurrence of the goethite in Kalinovac–Hrastova Greda from previous studies. Novigrad Podravski–Milakov Berek exhibits smaller concentration of orange mottles, which is in direct correlation with

lower goethite contents. Previous study implies bog iron ore occurrence at Novigrad Podravski location, however, soil profile implies insignificant occurrence of Fe. Therefore, it can be proposed that bog iron ore was forming at the Novigrad Podravski area, however, due to changes in the climate and the environment, currently there are no favourable conditions occurring in the area that could enable bog iron ore formation. On the other hand, it seems that Peteranec–Ciglène site currently exhibits favourable conditions, based on the amount of goethite forming. Previous archaeological surveys did not discover any signs of iron production or processing in the near vicinity, implying that this bog iron ore deposit is most likely forming for the past several hundred years. However, agricultural activities inhibit formation of fully developed deposit.

ACKNOWLEDGMENTS

This work has been fully supported by the Croatian Science Foundation under the project TransFER (Grant No. 5047) and by the Virtulab project (KK.01.1.1.02.0022), co-funded by the European Regional Development Fund.

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ORE SOURCES OF MEDIEVAL IRONWORKING CENTERS OF THE RYAZAN PRINCIPALITY

Medieval metallurgical complexes in Ancient Rus' that have been studied are far from numerous. Three ore occurrences which exploited in medieval times have been discovered on the territory of the former Principality of Ryazan (now Ryazan region of the Russian Federation). The ore lays closed to the surface and they were easily accessible to medieval miners. All ore occurrences discovered on the territory of Ryazan principality were situated near major craft centers. Ryazan ironmakers employed relatively rich siderite ores. The X-ray fluorescence and optical metallography were used. The ores are characterized by a low content of phosphorus, sulfur, nickel and others elements. Several experiments on the smelting were carried out. We have traced the full metallurgical cycle – from the exploitation of the ore occurrence to the manufacturing of the finished product – at the Istye 2 settlement. Over the course of archaeological and archaeometallurgical study, we localized a rural metallurgical complexes that supported the handicraft production of a large towns with its products.

Key words: Ryazan Principality, metallurgical complex, ore occurrence, archaeometallurgy, technological schemes

INTRODUCTION

Issues related to the identification and characterization of raw materials are among the most complex issues in the history of ancient iron metallurgy. Solving these problems is part of the tasks of the project “Raw materials sources of ancient Russian craft centers”. The search and survey of ore occurrences that could be operated by medieval metallurgists was carried out in the Ryazan region during the project. To obtain additional characteristics, ore samples were used in experimental modeling of the bloomery process. The obtained materials were studied using archaeometallography in the Laboratory of Natural Science Methods of the Institute of Archaeology of the Russian Academy of Sciences. Ryazan principality (12th – beginning 16th c.) was one of the biggest Ancient Russian states. It was situated on the east of Russian lands. The choice of the Ryazan region for field surveys was not accidental. Iron slags were found on most medieval sites on the territory under study, which indicates a wide distribution of iron production in the Ryazan principality (Zavyalov, Terekhova 2013: 41). Ryazan land is rich in raw materials for the development of ferrous metallurgy. The encyclopedic dictionary of F. A. Brockhaus and I. A. Efron notes the Ryazan province among the territories with deposits of brown ironstone. An occurrence at settlement Istye was actively exploited in the 18th and 19th centuries. A partially preserved blast furnace – a unique example of 18th century industrial architecture – remains standing (at a height of up to 6 m) in the settlement today. It is the only remaining blast furnace of that time in Eastern Europe. “The hearth of Ryazan metallurgy”, by the words of historians, was situated in Istye (Vagner, Chugunov 1974: 117). Geological data indicates that the origins of the Istya ore can be traced to the mineralization of limestones of the Carboniferous and Devonian Periods. The average ore bed thickness here is 0.36 m, in some places more than 2 m (Dvorov 1965: 191).

FIELD WORKS

To date, during our researches in the Ryazan region, three iron ore occurrences have been identified that could be operated by medieval metallurgists (Fig. 1). First, this is ore occurrence at the medieval settlement of Istye 2. The site was discovered by V. M. Bulankin in 2008 during archaeological exploration (Bulankin et al. 2012). Istye 2 settlement is located on the right (eastern) slope of the river Istya (right tributary of the Oka River), on a relatively flat, completely plowed area (Fig. 2). It was examined more than 100 sq. m during archaeological excavation of the site. The site in terms of ceramic material and artifacts dates back to the 12th-13th centuries. The ore occurrence, on the outskirts of which the settlement was located, as noted above, was exploited until the beginning of the 19th century. The ore is represented by brown iron ore and sphero-siderite, passed from the outside into brown ironstone. Traces of metallurgical production were discovered at Istye 2 – remains of bloomery furnaces, numerous fragments of iron-slag conglomerate, bloomery iron and fragments of ceramic nozzles (Bulankin et al. 2012). It is important to emphasize that all of the metallurgical artifacts were concentrated in the southwestern edge of the settlement, where metallurgical complexes were likely located. The large scale of these finds indicates that production volumes were significant. The remains of the bloomery furnaces practically did not survive as a result of many years of plowing of the site's area. Only in one case it was possible to fix the base of the furnace (Fig. 3). It consisted of limestone laying of a basement shape measuring about 1.6 x 1.0 m. The base of the furnace had a concave profile, at the bottom of which a thin layer of charcoal with a thickness of 1-2 cm was traced over the entire area. The filling of the structure is represented by numerous pieces of slag-iron conglomerate, total weight of about 60 kg and fragments

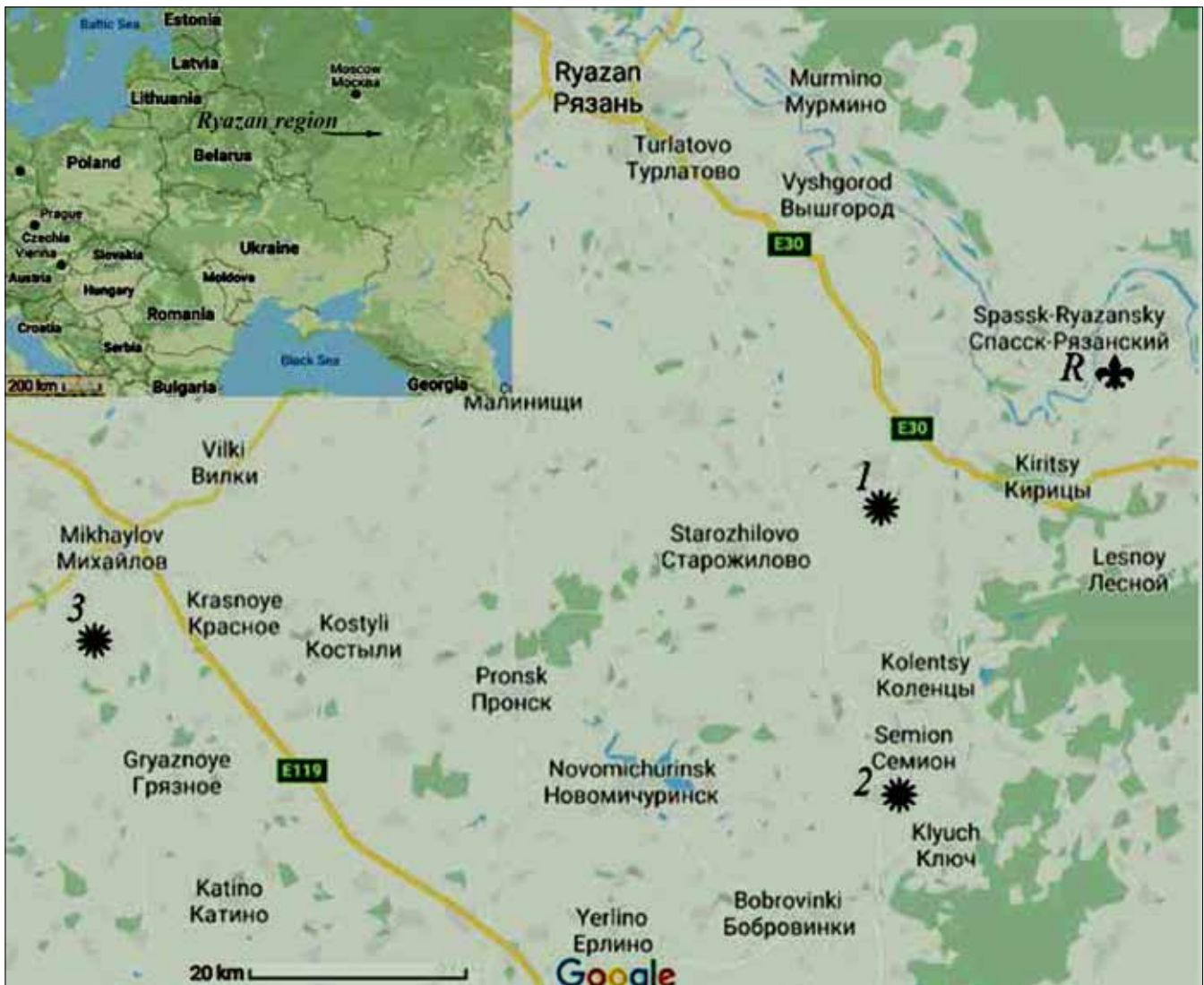


Fig. 1 Map of ore occurrences in Ryazan region: 1 – Istye; 2 – Pronya (near hill-fortress Tolpino); 3 – Loknya; R – the capital of Ryazan principality (Staraya Ryazan) (map by: V. I. Zavyalov)



Fig. 2 Istye ore occurrence (photo by: V. I. Zavyalov)



Fig. 3 Istye 2 settlement. Remains of bloomery furnace (photo by: V. I. Zavyalov)

of clay nozzles (425 fragments). Rare pieces of clay coatings, calcined limestone, iron ore and animal bones were also found during the excavation.

The hillfort Tolpino on the Pronya River was another site where the ore occurrence was examined. Numerous pieces of iron slag were found during the archaeological examination of the settlement, which suggests the presence of local metallurgical production (Ivanov et al. 2005: 343; Chelyapov 2012). Outcrops of ocher-colored ferruginous rock were found during a survey of the territory in the immediate vicinity of the settlement on the slope of the first terrace above the floodplain (Fig. 4). Quite large pieces of iron ore were found in the bedrock. Layers of iron ore were found in the ocher layer during the clearing of the slope.



Fig. 4 Tolpino ore occurrence (photo by: V. I. Zavyalov)



Fig. 5 Loknya ore occurrence (photo by: V. I. Zavyalov)

The third ore occurrence was examined on the river Loknya not far from its confluence with the Pronya river. The deposit is located on the first terrace above the floodplain (Fig. 5). The territory of the ore occurrence is covered with "craters" (covered by ground mining pits), which stretch along the river bank for a distance of about 200 m. The geomorphological situation is very similar to the ore occurrence on the river Istya. The ore occurs in the sandstone shallow from the surface. The ore is similar in appearance to samples from Istye and Tolpino. It should be noted that there are three relatively large ancient Russian hillforts - Mikhailov, Zhokino and Izheslavl (Rusakov 2005) in the immediate vicinity of the ore occurrence on the river Loknya. Craft activities of these towns undoubtedly required a large amount of iron. Thus, three relatively large ore occurrences have been identified in the territory of the Ryazan principality at the present time. All of them are located in close proximity to ancient Russian craft centers. One of them (Istye) was undoubtedly exploited by ancient Russian metallurgists. The location of the other two (Tolpino, Loknya) makes them very likely to be used as ore sources of the Middle Ages.

METHODS

The X-ray fluorescence analyzer NITON XL3t GOLDD+ was used to determine the chemical composition of ore and slag-iron conglomerate from excavation and slag-iron conglomerate, obtained during experiments. The analyses were performed in the Restoration laboratory of the Institute of Archaeology Academy of Sciences Czech Republic (Prague). The specimens for metallographic analyzes were prepared using standard techniques. The examined samples were cut out from functional parts of the objects. Then the samples were mounted into Wood' alloy (Sn-12.5%, Pb-25%, Cd-12.5%, Bi-50%), grinded and then polished with chromium oxide. The microstructures of iron objects were determined with an MMR-2R optical microscope, after etching a polished sample with nital reagent (3 % solution of HNO₃ in ethyl alcohol) at magnifications of 150x and 490x. The size of the grains was evaluated after the Russian state standard (GOST 5639-82). Microhardness was measured on a microhardness machine PMT-3 with a diamond pyramidal indenter with 100 g load.

ANALYTICAL INVESTIGATIONS.

Nine samples of ore from Istye ore occurrence and five each samples from Tolpino and Loknya ore occurrences were selected for characterization of ore (Tab. 1). And also 14 samples of slag-iron conglomerate were selected from finds found during excavation Istye 2 settlement (Tab. 2). Slag-iron conglomerate obtained during experimental smelting of Istye and Tolpino ore were also investigated. It is known, that two processes occur simultaneously during the ironmaking in

Tab. 1 The chemical composition of iron ore from Ryazan ore occurrences

Ore occurrence	FeO	P ₂ O ₅	SiO ₂	Al ₂ O ₃	K ₂ O	CaO	MnO
Istye	56,74	1,81	27,64	7,64	1,43	2,98	1,74
Istye	52,24	0,79	30,79	8,22	3,23	2,53	2,14
Istye	53,12	0,94	31,29	8,89	1,54	2,52	1,32
Istye	53,82	1,33	32,47	7,55	1,71	2,43	0,57
Istye	51,48	1,80	31,34	8,06	1,89	3,88	1,44
Istye	57,08	0,94	23,13	7,99	3,34	3,93	2,54
Istye	55,62	0,91	31,44	7,32	1,18	1,77	1,54
Istye	52,13	1,07	33,33	7,91	1,60	2,33	0,91
Istye	59,61	1,62	25,98	9,23	0,87	2,02	0,49
Tolpino	59,52	2,7	25,39	8,02	0,97	1,34	1,92
Tolpino	62,54	1,18	23,33	7,36	1,18	2,14	2,16
Tolpino	59,38	0	26,41	7,91	1	1,05	3,92
Tolpino	52,18	0,29	34,6	8,88	0,87	1,12	1,64
Tolpino	68,26	0	21,8	7,8	0,98	0,77	0
Loknya	53,78	0	32,41	9,9	0,8	1,85	0,88
Loknya	37,51	0	49,94	8,7	0,98	1,32	1,21
Loknya	36,45	1,06	47,15	7,8	0,84	4,92	1,62
Loknya	36,89	0	51,21	9,7	0,53	0,59	0,96
Loknya	38,62	0	49,84	8,43	0,85	0,78	1,00

Tab. 2 The chemical composition of slag-iron conglomerate from the settlement of Istye 2

Nº	FeO	SiO ₂	Al ₂ O ₃	P ₂ O ₅	K ₂ O	CaO	MnO	MgO
Istye-1	64,69	17,96	7,31	1,05	2,49	5,36	1,05	0
Istye-2	71,34	15,16	7,11	1,13	0,92	0,64	0,81	2,84
Istye-3	71,89	13,74	6,76	1,49	1,09	1,63	2,17	0,96
Istye-4	68,96	14,97	5,71	4,17	0,5	4,98	0,57	0
Istye-5	84,55	7,09	3,55	0,42	0,27	0,4	0	3,64
Istye-6	75,03	16,7	4,95	0,93	0,31	0,51	0,1	0
Istye-7	83,2	11,2	4,44	0,37	0,15	0,38	0,09	0
Istye-8	83,93	10,61	4,34	0,41	0,17	0,39	0	0
Istye-9	66,77	18,77	7,33	0,89	2,07	3,18	0,86	0
Istye-10	69,47	17,66	6,01	1,04	2,26	2,57	0,83	0
Istye-11	70,49	16,87	6,52	2,67	0,53	1,85	0,92	0
Istye-12	70,77	15,85	7,93	1,88	0,59	1,87	0,91	0
Istye-13	69,93	15,94	7,91	2,38	0,79	1,98	0,86	0
Istye-14	69,24	15,46	6,37	0,55	1,8	4,72	1,26	0

bloomery furnace. These are iron recovery from iron oxide (FeO) and slagging of gangue, consisting of silica (SiO₂) and alumina (Al₂O₃) (Kolchin, Krug 1965: 207). At the same time iron is restored in a solid, as a result of what no impurity elements (except carbon, phosphorus, nitrogen) could penetrate into iron (Piaskowski 1969). All impurities detected during x-ray fluorescence analyzes are contained in slags, which are numerous in bloomery iron. First of all let's consider iron content in the ores (Tab. 1). As the tests showed ore from Istye ore occurrence was the richest – from 40 wt% Fe to 59.34 wt% Fe (51.48–59.61 wt% FeO). Iron content in Tolpino ore was high too: it had maximum 53.08 wt% Fe (68.26 wt% FeO). Iron content in Loknya ore was not high – about 20.98–29.76 wt% Fe (36.45–53.78 wt% FeO). But probably it is explained that ore was taken from upper layers which were the poorest in iron content. Note that x-ray fluorescence analyses did not detect either in the ore or slag-iron conglomerate such elements as nickel, cuprum, magnesium, which include in iron ore very often. The results reduced in Table 1 indicate that chemical composition is similar for all three ores. Silicon, aluminum, phosphorus, manganese and sulfur are most interesting among common in ore elements. It is known that main component of bloomery process is slagging of gangue (SiO₂ and Al₂O₃). Silica content in the ores varies from 23.13 wt% SiO₂ to 33.33 wt% SiO₂ in Istye ore occurrence and from 32.41 wt% SiO₂ to 51.21 wt% SiO₂ in Loknya ore occurrence. Alumina content amounted 7.32–9.23 wt% Al₂O₃ in Istye ore and from 7.36 wt% Al₂O₃ to 8.88 wt% Al₂O₃ in Tolpino ore. Phosphorus, which is greatly affected the properties of iron, presents in small quantities in Ryazan's ores (no more than 1.8 wt% P₂O₅), and not detected at all in several samples. This conclusion correlates with the results of mass archeometallographic analyses of iron artifacts from medieval sites on the territory of the Ryazan Principality: phosphorous (high-hard iron) is fixed on single and, as a rule, imported items (Zavyalov, Terekhova 2013: 147). It is interesting to note that both in ore and iron-slag conglomerate the arithmetic mean content of phosphorus oxide is the same 1.23 wt% P₂O₅ in ore and 1.39 wt% P₂O₅ in conglomerate. In this case, the range of phosphorus content is different. In the ore it amounts to 0.8%–1.8% wt% P₂O₅, while in conglomerate it is much bigger – from 0.4 to 4.2 wt% P₂O₅. In all probability, this is due to the fact that analyzed specimens of conglomerate have formed at the different stages of bloomery process. One of the main elements for characterizing ore and slag is calcium. As one can see from the tables, all samples show a relatively high content of lime 0.58–4.92 wt% CaO in ore. The presence of calcium is probably due to the occurrence of ore in limestone rocks.

EXPERIMENTAL WORKS

We have carried out several experiments on the smelting of Istye, Tolpino and Loknya ore (Zavyalov, Ratkin 2009). The most successful experiments were with ore from Istye. The used ore was a solid concretion of irregular shape, with the color of ochre. The preliminary operation of the bloomery process was to enrich the ore by the roasting process. A layer

of ore was placed on the row of wooden piles, which in turn was covered by piles. The roasting of the ore lasted 1-1.5 hours, until all the wood was burned off. Finally, the ore lost 7-10 wt% of its original weight. Our investigations have shown that the separation of gangue (silica and alumina) occurs at this stage. The chemical composition of the ore varied: if the raw ore contained about 30 wt% SiO_2 , then the burnt ore contained less than 25 wt% SiO_2 . The alumina (Al_2O_3) content shows a similar picture. This observation confirms the necessity of conducting such a preliminary operation as roasting ore (Kolchin, Krug 1965: 202), during which not only organic impurities were burned out and moisture was removed, but also a partial purification of the ore from silica and alumina took place. Guided by the type of Ancient Rus furnace known from archaeological and ethnographic data (Kolchin 1953: 26–31; Naumov 2008), we built up an experimental model¹ on which we conducted several smelting processes. An electronic motor with the speed of 260 l/min was used as blower support. The ore/charcoal proportion was 1:1. The smelting processes lasted 2-2.5 hours and for the process 10-12 kg of ore were used. Unfortunately, no more than 1 kg of bloomery iron could be produced during the most successful experimental smelting processes. The metallographic analysis of metal detected a structure of ferrite with disproportionate (big and medium) grains and a large amount of big slag inclusions. The measured microhardness of ferrite is 170-181 HV0,1. Metallographic analysis of the slag-iron conglomerate obtained during the experiments showed similarities with the composition of the archaeological artifact. They contain wustite dendrites in large fayalite crystals. Seven exemplars of slag-iron conglomerate, obtained during experiments were analyzed. The chemical composition of experimental and archaeological slag-iron conglomerate was similar. As mentioned above, Ryazan's ores contain relatively high calcium content. Experimental slag obtained by smelting Istye and Tolpino ore consisted high calcium content too (up to 5 wt% CaO) (Tab. 3). One can note the sample № 1 which demonstrated very high content of calcium oxide (more than 25 wt% CaO) and phosphorus oxide (more than 3 wt% P_2O_5). Most likely, this is due to the fact that the sample consisted part of the inner wall of the furnace. Manganese oxide content in experimental conglomerate was not more than 1.9 wt% MnO (only one specimen demonstrated higher content – 3.22 wt% MnO).

Tab. 3 The chemical composition of slag-iron conglomerate from experimental smelting

SAMPLE	FeO	P2O5	SiO2	Al2O3	MnO	CaO	K2O
konglomerat-1	49,84	3,23	9,83	6,9	3,22	25,82	1,02
konglomerat-2	57,77	2,74	6,49	25,03	1,73	5,02	1,03
konglomerat-3	71,58	0,89	18,35	5,09	1,92	1,02	0,53
konglomerat-4	72,6	1,01	19,64	4,27	1,65	1,07	0,5
konglomerat-5	69,89	0,81	23,58	4,25	0,1	0,52	0,44
konglomerat-6	63,01	0,55	31,32	3,14	0,08	1,19	0,71
konglomerat-7	31,68	0	56,91	6,84	0,52	3,36	0,26

CONCLUSIONS

The results of the research allow us to draw the following conclusions.

All ore occurrences discovered on the territory of Ryazan principality were situated near major craft centers (Istye 2 – Staraya Ryazan, Tolpino hillfort, Loknya – hillforts Mikhailov, Zhokino, Izheslavl).

The ore lays closed to the surface and it was easily accessible to medieval miners.

Ryazan ironmakers employed relatively rich siderite ores. These ores are characterized by a low content of phosphorus, sulfur, nickel and others elements. At present results of chemical composition analyses do not allow to distinguish diagnostic elements for ore occurrences examined.

The important conclusion is that gangue (silicon and alumina) was separated from the ore already at the firing stage.

1 The experimental furnace was composed of firebricks and had a height of 0.8 m and a diameter of 1.05 m, a shaft height of 0.65 m, lower diameter of 0.3 m and upper diameter of 0.2 m.

ACKNOWLEDGEMENTS

Article was prepared with the financial support of the Russian Science Foundation, project 19-18-00144.

The authors would like to express their gratitude to dr. J. Hošek (the restoration laboratory of the Institute of Archaeology of the Academy of Sciences of the Czech Republic, Prague) for providing the opportunity to conduct analytical research using the X-ray fluorescence analyzer, and also express their sincere appreciation to experimental blacksmith M. A. Ratkin for his help and direct involvement in carrying out experiments to model the bloomery process.

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MINING AND METALLURGY IN THE MOUNT TRGOVI AND NORTHWESTERN BOSNIA IN THE ANCIENT PERIOD WITH SPECIAL EMPHASIS ON THE IRON PRODUCTION

The paper describes the geological features of the Mount Trgovi (Trgovska gora), as part of the Banovina region, and Northwestern Bosnia, i.e. the areas located between the towns of Bosanski Novi, Prijedor and Sanski Most. This is actually a geologically unique area of the Upper Paleozoic age and belongs to the Hercynian metallogenic epoch, where the largest deposits and occurrences of metals are located both in the Republic of Croatia and in Bosnia. Iron ore deposits and metallurgical plants in these areas in ancient times are listed, but the findings of mining and metallurgical activities in pre-ancient times are also given. The importance of iron production for the Roman Empire can be determined by the accelerated development of mining and metallurgy of iron from the 1st century BC, which was accompanied by changes in the Roman administration and the construction of the mainland and river routes passed through the mining areas. Also, the goal is to shed light on the then-existing technologies of iron production.

Key words: antiquity, mining, iron metallurgy, Mount Trgovi, Northwestern Bosnia

INTRODUCTION

The area of Mount Zrin (Zrinska gora) is built of sedimentary, igneous, ultramafic and metamorphic rocks, with a chronostratigraphic range from the Paleozoic to the Quaternary. The main deposits and occurrences of metals are related to the border area of the Mt. Zrin and the Mt. Trgovi (Trgovska gora) on the stretch Gvozdansko - Trgovi on both sides of the stream Žirovac (Pikija et al. 2010: 33).

The prevailing opinion is that the iron, copper, lead and barite deposits and phenomena of the Mt. Trgovi are of the Upper Paleozoic age and that they belong to the Hercynian metallogenic epoch. They were formed in the marine environment, and the mineralization was related to submarine volcanism (Jurković 1988: 369–393). Based on the analysis of galena samples, it follows that the mineralization process occurred later in relation to the original rocks, i.e. by epigenetic mechanism, magmatic activities in the Triassic (early Mesozoic) that began in the Permian (late Paleozoic) (Palinkaš 1985: 175). The Paleozoic of the Mt. Trgovi is a northwestern continuation of the much larger and metallogenetically more important Una-Sana Paleozoic, an area located between the towns of Bosanski Novi, Prijedor and Sanski Most. In the Paleozoic of this area, south and east of the town of Prijedor, there are the largest deposits of iron ore - Ljubija and Tomašica (Jurković 1988: 373). Figure 1 shows the position of the Mt. Trgovi and Northwestern Bosnia in relation to the city of Sisak.

Geologically speaking, the unique area consisting of the Mt. Trgovi and Northwestern Bosnia, as well as significant deposits of iron ore and intensive iron production in this area in ancient times, were the motive for writing this paper. Mining and metallurgical activities in this area are described, which were related to the wars of conquest that were fought in these areas, but also to changes in the Roman administration, and to the construction of roads and settlements.



Fig. 1 Position of the Mt. Trgovi and Northwestern Bosnia (according to: Jurković 1989: 348; map modified by: L. Lazić)

MOUNT TRGOVI

Mineral phenomena in Banovina are of hydrothermal origin. The basic ore mineral is siderite (iron ore, FeCO_3) which represents the largest part of ore reserve. Other minerals are chalcopryrite (copper ore, CuFeS_2), galena (lead ore, PbS), pyrite (otherwise not a good raw material for obtaining iron, but has another application, FeS_2), sphalerite (zinc ore, ZnS), and there is also the appearance of barite (barium ore, $\text{Ba}[\text{SO}_4]$). Quartz (SiO_2) occurs mainly as tailings. Later processes in this area lead to the oxidation of carbides and sulfides to iron hydroxides which are the main constituents of limonite. Although limonite is formed in all places where iron minerals come into contact with water and oxygen, it most often occurs in the surface layers, i.e. in the oxidation zone of iron ore deposits. This is also the reason why of all the iron ores in this area, the largest deposits of limonite were found and why it was mined the most (Marković 2002: 56–58).

Certainly the largest and most famous deposits of iron, copper, lead and barite ores are on Mt. Trgovi. In Figure 2 (Šebečić 2000: 100–101) the iron deposits are particularly characterized. During the second half of the 19th century and in the first half of the 20th century, a dozen districts and almost a hundred mines were active in this area. In general, it can be said that these metal ore deposits are of Upper Paleozoic age, that they belong to the Hercynian metallogenic epoch, that they are of igneous origin, and formed in the marine environment, partly in the supply channels (Jurković 1988: 369). The main iron ore deposits on the Mt. Trgovi were in the areas of Resanović Kosa, Gvozdansko, Bešlinac, Jokin Potok and Vidorija. Mining was carried out in the oxidation zones of siderite deposits, and locally also on limonites formed by oxidation of ankerite deposits and ankeriteized limestones and dolomites (Jurković 1993: 42). These are deposits that have been mostly depleted, and had reserves of 1000 t to several tens of thousands of tons of ore (Marković 2002: 44–46).

There are very little informations about mining in Illyrian and ancient times. I. Jurković states that in Illyrian and Roman times iron (limonite) and silver-bearing lead ores were mined in the Mt. Trgovi (Jurković 1988: 369), and in the area of Gradski Potok solid limonite ore was mined from the oxidation zone of siderite deposits (Jurković 1989: 347). Among the oldest iron ore mines, those in Komarska Glavica near Gvozdansko stand out, which were exploited already in the time of the Romans and Illyrians. They were excavated by surface mines and underground mines up to 190 m long. The older

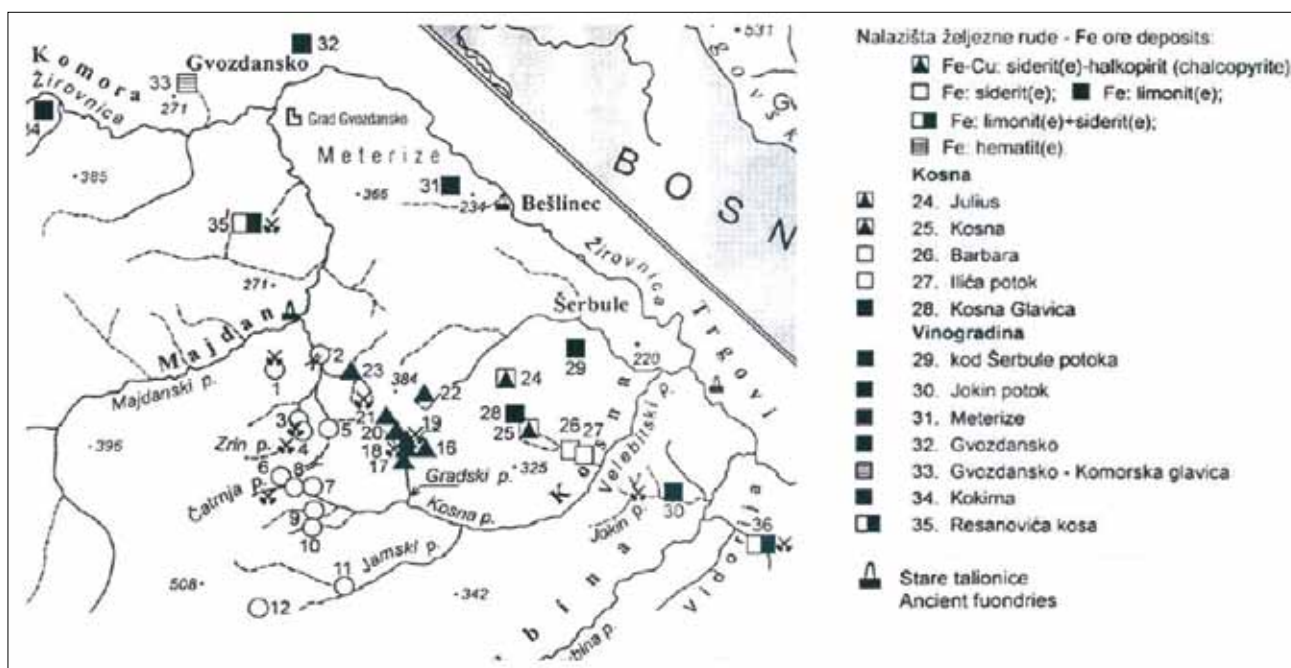


Fig. 2 Iron ore deposits on the Mt. Trgovi, (according to: Šebečić 2000: 100–101; map modified by: L. Lazić)

limonite deposits were in the positions Kosna and Vinogradi, and the older siderite deposits were the ore fields in Ilića Potok and Barbara (Šebečić 2000: 103).

A more detailed historical overview of mining and metallurgy in the area of the Mt. Zrin and the Mt. Trgovi is presented in the paper (Lazić et al. 2010: 56–71). Mining and metallurgical activities in this area date back to the end of the Vučedol culture (Vučedol, an archeological site near Vukovar in the period from 3,000 to 2,200 BC) which spread to the area of today's Banovina in search of copper ores. However, this paper emphasizes the production of iron in this area, which from the beginning was associated with settlements in the area of today's Banovina and the city of Sisak.

Banovina was intensively inhabited in the late Bronze Age (from the 12th century BC), both south and north from the Mt. Zrin to the river Kupa (Durman 1991: 91). Probably at that time, the northern road across the Mt. Zrin was opened, because since the time of the Vučedol culture, there has been communication along the river Una. The whole area was under the dominant control of the Osječenica fortress, located nearby the village of Gorička (south side of Mt. Zrin). This fortress had a long continuity of settlement from the early Bronze Age to the end of ancient times.

The Iron Age in Central Europe was divided into two periods: the early Iron Age: Hallstatt culture (800–450 BC, Wikipedia 2021a) and the late Iron Age: La Tène culture (from about 450 BC to the Roman conquest in the 1st century BC, Wikipedia 2021b). At that time, as well as in the territory of today's Sisak, the development of iron metallurgy was due first to the tribes of the *Western Illyrians*, and then to the *Celts*.

The first settlement in the territory of today's Sisak was built in the 8th century BC due to its important communication position on the Sava, and its existence was ensured primarily by the production of iron from ore coming from Mt. Trgovi. On the right bank of the river Kupa (Pogorelec), i.e. in the riverbed, just downstream from the new bridge in Sisak, there are the remains of the settlement on wooden foundation piles from the end of the 6th to the beginning of the 4th century BC. Pilotage is densely pierced by firm logs (about 20 cm in diameter) and horizontally laid planks and split logs (Durman 1992: 120). This settlement from the Early Iron Age (Hallstatt period) and its connection with iron is most likely the reason that the *Celts*, coming to the Pannonian Plain in the later Iron Age, right here found their most important settlement Segestica.

In the Osječenica fortress two Noric tetradrachms (Celtic silver coins) and one Roman republican denar from 84 BC were found as accidental finds confirming the Celtic and Roman connection with that area. According to the findings of Celtic money in Osječenica, the *Celts* in Segestica focused their iron production entirely on the exploitation of iron ore from Mt. Trgovi. Neither *Celts* nor their predecessors *Illyrians*, had access to large reserves of iron ore from Northwestern Bosnia where another significant metallurgical population, the Illyrian tribe *Mazaei* (*Maezaei*) exists.

Segestica was very important for the *Romans* and they repeatedly tried to conquer it from 156 BC. Finally, in 35 BC, Octavian Augustus conquered and destroyed Segestica, and then founded a new settlement Siscia on the other, left bank of the river Kupa (Durman 2002: 24). The *Romans* took over the already well-established production of iron products in this territory. In their time, special attention was paid to metallurgy due to the need for weapons.

When the *Romans* defeated both the *Celts* and *Mazaei*, they took control of this entire area with significant ore-bearing potential. Only then, the important *officinae ferrariae* along the rivers Japra and Sana are supplemented with iron ores and non-ferrous metal ores (copper, lead and silver) in the area of the Mt. Trgovi.

In Roman times, due to the increased need for iron, communication with the rivers Kupa, Sava, Una, Sana and Japra opened, and the majority of goods traffic turned along this route. At that time, the entire route along the Una, from the Sana and Japra, to the confluence with the Sava, joined the economy of Siscia. The entire system of metallurgical workshops along the Una worked for the Siscia market. This is supported by a group find, downstream from Hrvatska Dubica and not far from an ancient building, of 97 wrought iron pieces as a semi-finished product with an average weight of 4.40 kg (Fig. 3). Iron semi-finished and finished products were delivered to Siscia by rivers, but bricks from Siscia, together with other products, reached the opposite direction as far as Japra (Durman 2002: 28). Most of the manufactured iron products were sent from Siscia to the most important Roman border, the Danube.

For the entire duration of Roman supremacy in Pannonia, in Siscia on the banks of the Kupa operated large workshops for the production of weapons. On the right bank of the Kupa of today's Sisak (in the position of Celtic Segestica), over 200 wooden piles driven into the riverbed can be seen during the low water level (Fig. 4, 5). This position is otherwise called



Fig. 3 Photograph of the wrought iron pieces found in the area of Hrvatska Dubica, Archaeological Museum in Zagreb, inv. No. AMZ A-19811 (photo by: A. Durman 2002)



Fig. 4 Photograph of the position of "Mint" on the right bank of the river Kupa (photo by: A. Durman 2013)

"Mint". It can be considered that in Roman times it served as a port for transshipment of goods, or possibly there were also smithies in which large bellows powered by water were used (Durman 2002: 29). The excavation at that position in 1985, as well as the dendrochronological analyses of wooden samples, confirmed that the wooden piles were driven into the riverbed every eight years in order to support the right bank of the Kupa river, across the center of Siscia, where the port and the mint might have been located (Fig. 6).

Since several wrought iron pieces were found near the "Mint" position (Fig. 7), which in shape and weight correspond to those found near Hrvatska Dubica, it can be used as evidence that these iron semi-finished products were delivered by rivers from the Sana and Japra valleys to Siscia (Durman 2002: 30). The metallurgical plant in the "Mint" position operated from 263 to 423 AD, i.e. from the time of Emperor Gallienus until the death of Theodosius II, which corresponds to the time of the most intensive iron production in the valleys of the Sana and Japra.

Considering the fact that in the sixties for the needs of MK Željezara Sisak (Sisak Ironworks) about 3 million tons of slag was exploited from the area of Northwestern Bosnia, which was created in the period from the 2nd to the 4th century BC, it can be concluded that 750,000 t of iron were produced at that time, which is equivalent to the number of 150 to 200 thousand pieces of the mentioned iron semi-finished products (Durman 2002: 32). If most of this production ended in Siscia, it can be concluded that the daily production of finished iron products was at the level of 10 t.

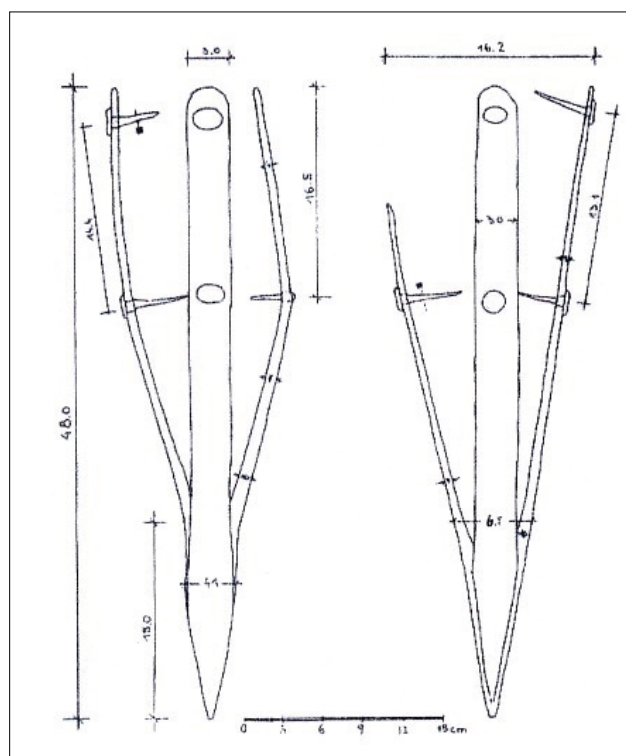


Fig. 5 Find from the "Mint": iron shoes for the wooden piles (drawn by: A. Durman 2002)



Fig. 6 The excavation at "Mint" position in 1985 (photo by: A. Durman 1985)

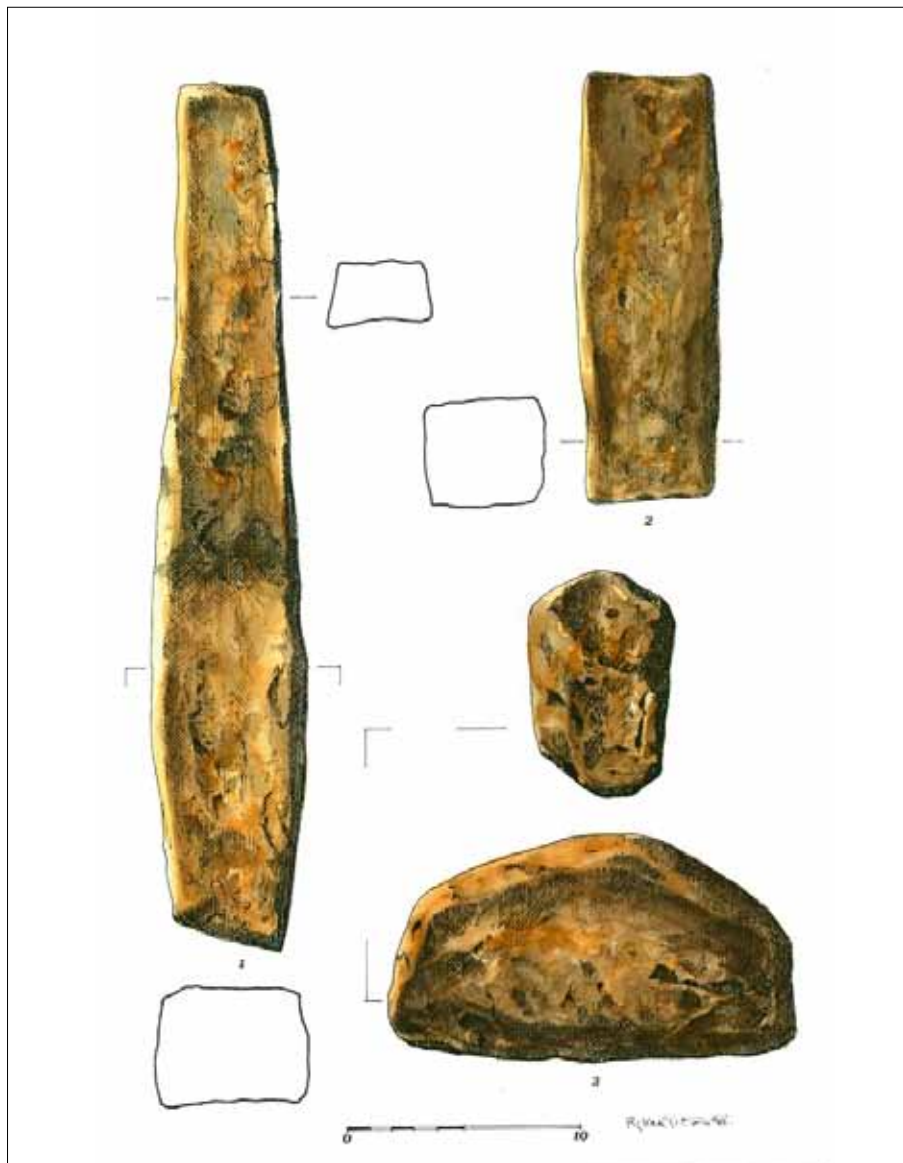


Fig. 7 Wrought iron pieces found near the "Mint" position, City Museum in Sisak, inv. No. GMS 510: SIK 27530-27535 (modified by: A. Durman)

NORTHWESTERN BOSNIA

In some areas of the Roman provinces of Dalmatia and Pannonia, there were ores rich in gold, silver, iron, zinc and lead that were exploited by the *Romans*. In exploitation, at the beginning, the most interesting was gold, followed by silver and iron. From the point of view of the history, mining and metallurgical activities on the territory of Bosnia can be observed in three separate areas: eastern, central and western Bosnia. In the eastern area with the center in Domavija near Srebrenica, silver was most exploited. In the central Bosnian area, which included the Lašva river basin, the area of the Vranica mountain near Gornji Vakuf and the area of Kiseljak, gold was mostly exploited, and to a certain extent silver, lead and iron. The western area includes the Sana, Japra and partly Una river basins and the areas around the settlements of Ljubija, Stari Majdan, Sinjakovo and Mrkonjić Grad. In this area rich in iron ores, there were also lead and copper ores. It is assumed that in addition to iron, lead and copper were also produced.

Considering the set goal, the paper pays attention to mining and metallurgical activities in the western Bosnian area bordered by the towns of Sanski Most, Prijedor and Bosanski Novi. From the point of view of mining and metallurgy of Northwestern Bosnia, the most important area is certainly along the rivers Sana, Japra and partly Una, the richest in iron ores, and along which there were lead ores and some copper ores. The most important mining sites were located in the areas of Blagaj and Maslovare near Bosanski Novi and Ljubija and Stari Majdan near Sanski Most (Fig. 8).

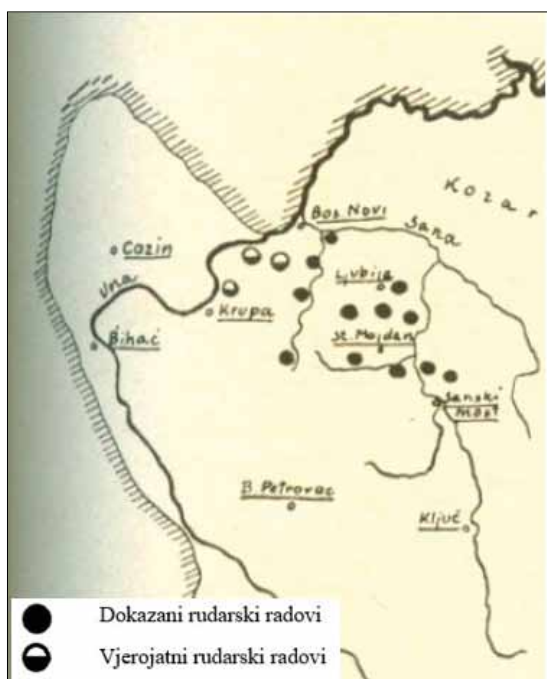


Fig. 8 Map of ancient mining areas in northwestern Bosnia: black circle - proven mining works; black-white circle - probable mining works (according to: Pašalić 1954: 63; map modified by: L. Lazić)

Intensive iron production in this area is evidenced by slag deposits that can be found in a thin layer along almost the entire area. The technology of mining and iron production required constant relocation by building new furnaces in search of ore and forest. The need for wood was especially great because the ratio between the mass of iron ore and charcoal in furnaces was approximately 1:4. Only in a few places the slag was found in larger deposits collected in larger mounds, such as in the lower Japra river basin, near Blagaj, and Stari Majdan on Sana, which are the best known mining sites in Northwestern Bosnia. According to the estimate of the eng. Kubijas, the amount of slag in the Japra river basin is close to one million tons, and it contains 47-48% Fe and 2-3% Mn (Pašalić 1954: 58). That these are the remains of predominantly ancient and not medieval mining

can be seen from the fact that ancient artifacts or Roman money are very often found in this slag. There are remains from pre-Roman time, but remains from Roman time are dominant.

This northwestern area of Bosnia was inhabited by the Illyrian tribe *Mazaei*, who already in pre-Roman time mined and produced iron. A large number of iron and less bronze artifacts were found in cemeteries, settlements on wooden foundation piles and forts from the Hallstatt period. Based on the findings of V. Radimsky and F. Fiala, it can be concluded that iron was mined and produced in the valley of Sana in the 5th and 4th centuries BC, i.e. in the late Iron Age: La Tène culture (Pašalić 1954: 65). In Sanski Most F. Fiala found traces of ancient iron production, even the remains of a bloomery furnace (Sergejevski 1963: 92).

Thanks to its geographical position, communication openness and tame and ore-bearing land in the valleys of the Sana and Japra rivers, the *Mazaei* reached a high level of development even before the establishment of the Roman administration. According to the findings, mining in the Illyrian times was reduced to a number of surface mines. Thus, it can be assumed that mining and metallurgy at the *Mazaei* played an important role in pre-Roman times because they played an important role in defense against invaders passing through the area. Also, it should be emphasized that the Greek colonization of the Adriatic and the Celtic invasion, which began in the 4th century BC, had a great influence on the development of mining and metallurgy in this area (Pašalić 1954: 65). The prevailing opinion is that mining and metallurgical activities had a great impact on the construction of settlements and the intensity of life in the area, which can be concluded from the traces of settlements and roads discovered so far.

There are findings from which it is evident that in that period there was trade with the area of the Apennine Peninsula, so that the *Romans* had data on ore wealth and existing workshops for iron production on Bosnian soil. They needed weapons for their wars of conquest, so they became interested in Dalmatia as early as the 3rd century BC, but then they failed to completely conquer and Romanize it until the beginning of the 1st century AD. They started a war with the *Illyrians* in 229 BC. The importance of metallurgical production of weapons is also evidenced by the fact that it took Rome two and a half centuries to conquer these areas. The greatest resistance was offered by the *Mazaei*, *Iapodes* and *Daesitiates*, who lived in areas rich in iron ores and had developed metallurgical production (Pašalić 1954: 68). In the period from 6 to 9 AD followed by one of the largest uprisings in Dalmatia and Pannonia, the so-called Batonian Uprising (*bellum Batonianum*). So the province of Dalmatia as such can be spoken of only after Baton's uprising. Before Baton's uprising, the whole area of Pannonia and Dalmatia belonged to the province of Illyricum, which was first under the Senate and then under the Imperial Administration (Beželj 2015: 5). The domicile population continued to engage in mining and metallurgy even after the Roman conquests.

Although ancient mining and metallurgy were at a high stage of development, the necessary knowledge is still lacking in order to gain a complete insight. The most important material for filling gaps in the knowledge of ancient mining are archaeological finds, mostly the remains of mining activities and metallurgical workshops, epigraphic monuments and

numismatic finds. The largest concentration of epigraphic monuments (votive stone altars) is located in the valleys of the rivers Sana and Japra, found in cemeteries and in the remains of ancient mining and metallurgical workshops and plants. Although they are mostly dated to the 3rd century AD, the first evidence of their activity dates from the 1st century AD. Also, the first numismatic inscriptions about the activity of the mines on Japra date from the end of the 1st century AD, from the time of the emperors Nerva, Trajan and Hadrian. Emperor Trajan (98–117) advocated for the improvement of mining and metallurgy, so the first data on metallurgy are given by coins from Trajan's time. The coin with the legend "*metalla Ulpiana Delm*" and "*metalla Delm*" were made in the period between 104 and 110, indicating a number of mining plants united in one imperial domain, the so-called *fisk* based on the principle of provincial division. Namely, based on the inscriptions on the found epigraphic monuments points to the fact that the development of local mining and metallurgical plants was closely connected with changes in the Imperial Administration, which is described in more detail by D. Sergejevski (1963: 92–93). From 9 AD, i.e. during the 1st century, the mines have become the property of the Roman people (*ager publicus*) and could be leased to a certain association (*societas publicanorum*). The inscriptions, found in Virunum in the province of Noricum, indicate that in the 2nd century the mines belonged to the state that leased them to private mine leases, *conductors*, who worked under the control of the Imperial procurators. It can be concluded that in the 1st century in the province of Dalmatia there were no significant mining and metallurgical activities under the Imperial Administration. The special development of mining and metallurgy took place at the end of the 2nd and the beginning of the 3rd century. The technology of iron production from the craft level has grown into a higher level of production in iron production plants, the so-called *officinae ferrariae*. At that time, the largest number of mines and the most important metallurgical plants were opened in the lower Japra river basin and in Šehovci and Stari Majdan near Sanski most.

This claim is supported by the most important archeological finds from Roman times: in Šehovci, on the right bank of the Sana, the Roman metallurgical workshop was found, and in it the copper coin of Constantius II (324–350), in Briševo nine epigraphic monuments were found in the cemetery, at the mine in Ljubija a trench in limonite was found, about 300 meters long, and in it about 4 kg of small Roman coins of the emperors from Gallienus to Probus (253–282), and three vessels and some tools. In the lower Japra river basin near Blagaj in the 1930s, during the exploitation of slag, various Roman objects and a lot of Roman small coins from the time of Aurelian were found, while most from the 4th century to Theodosius (Sergejevski 1963: 87).

From the point of view of metallurgy, the most important are the foundations of a larger complex of the Roman buildings in Šehovci, excavated in 1890 by the mining engineer V. Radimsky, next to which he found the remains of two bloomery furnaces with an internal diameter of 0.9 m, typical for that time (Fig. 9).

In particular, a larger scope of research was conducted on the border of the settlements of Blagaj and Maslovare. In Blagaj, at the sites of Crkvina and Bare, the remains of a settlement were found, and in Maslovare, at the site of Majdanište, the remains of a metallurgical plant were investigated (Merdanić 2018: 4). The Majdanište site was the first in Bosnia to provide reliable data on the appearance of the iron production plant complex. Traces of a large ancient metallurgical plant were discovered during the exploitation of slag in the 1930s. Eighteen objects were found in the entire survey, some of which were

more and some less explored. Remains of bricks with the SISC cancel were found on one of the buildings that served as a basilica (Pašalić, Basler 1962: 220).

According to the research of I. Bojanovski, the metallurgical plant (*officinae ferrariae*) in the area of Stari Majdan was significant in terms of the volume of iron production, and it operated continuously from the 3rd century to the middle of the 5th century. The volume of production is confirmed by the slag deposits at the sites of Glavica and Šljačište, which occupies an area of over 6 hectares with 250,000 cubic meters of slag with 48% iron. Parts of the walls were found in the slag, as well as

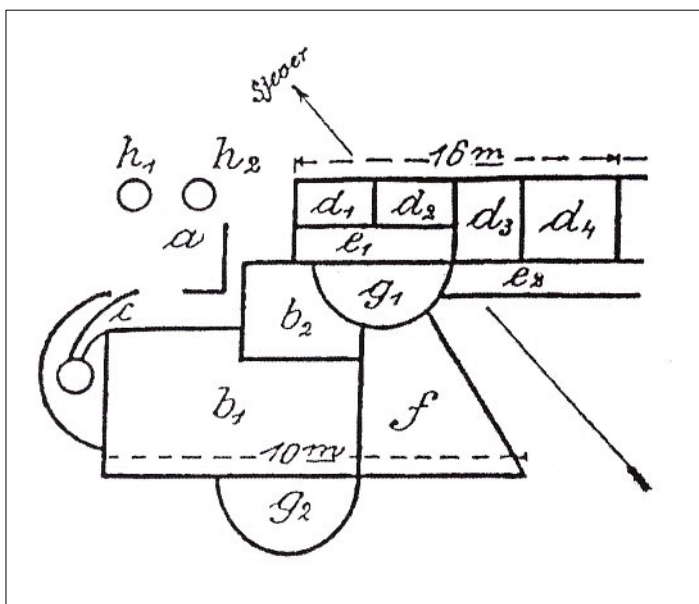


Fig. 9 Sketch plan from the excavation near Sanski Most: showing Roman buildings and locations (h1, h2) of two furnaces, Opus incertum (Radimsky 1891: 437)

the entire building, smaller and larger fragments of clay from a furnace, metal objects in the form of wedges and tools, Roman money, an ingot, fragments of Roman pottery, and fragments of hollow pipes made of baked clay that served as nozzles (tuyeres) for blowing air by bellows into furnaces. I. Bojanovski assumes that the finished products were shipped via the Sana and Una to the Sava, as well as the Danube or along the Salona-Siscia road (Bojanovski 1983; 1984; 1988; Merdanić 2018: 38).

According to archeological findings, it can be concluded that iron was mined and produced in Northwestern Bosnia until the end of the 4th century. In the 5th century, these activities ceased, to end with the invasion of the *Avarians* at the end of the 6th century and the arrival of the *Slavs* at the beginning of the 7th century (Sergejevski 1963: 97).

Only in the area of Ljubija, near Prijedor, seven inscriptions dedicated to the goddess *Terra Mater* were found. There are two interpretations in this regard. One of them is the idea of possibly organizing the Sana and Japra mining basin as *metalla publica*, i.e. *territorium metalli*, or the alleged visit of Emperor Septimius Severus to the mines of the eastern and western Bosnian area, during his travels through Pannonia and Dalmatia in 202 AD. According to the first theory, *Terra Mater* was often viewed as a mining deity, i.e. the connection of ores and mining with the wealth of the earth's womb. With regard to the territorial limits of these inscriptions, more likely is another theory that the worship of *Terra Mater* is related to the ethnicity of the inhabitants of the area who worked in the ore mines and had considerable experience in mining. All the deities, with the exception of the Sedat, in whose honor the epigraphic monuments were erected on the territory of the northwestern *territorium metalli*, have Greek-Oriental origins. It is to be assumed that these monuments were erected by mining officials of the same origin (Merdanić 2018: 27).

To what extent the aforementioned probable arrival of Septimius Severus influenced the development of mining and metallurgy in this area there is no hard evidence, but the fact that by that time the Bosnian mines started to work much more intensively. Namely, the fact that at that time the number of procurators increased due to Severus' concern to give military commanders adequate employment for appropriate merits (Sergejevski 1963: 94).

After the conquest of the province of Illyricum, by suppressing the Illyrian Batonian Uprising in 9 AD, in order to consolidate their power, the *Romans* built strong fortresses which were connected by functional roads. In addition, roads were needed for several reasons: to ensure the shortest possible connections between the Adriatic and the Danube, to protect the northern borders that Emperors Augustus and Tiberius moved to the Danube, and, among other things, to mine ore and transport iron products, especially to metallurgical centers Siscia and Sirmium.

The *Romans* rebuilt the existing roads, and most of the new ones were built during the reign of Emperor Tiberius (reigned from 14 to 37), and continued especially during the reign of Emperor Claudius (reigned from 41 to 54). Most responsible for the construction of the road network, which connected Salona with the interior of the province of Illyricum, was Publius Cornelius Dollabella, the imperial governor of Illyricum (from 14 to 20). From the so-called Salona inscriptions, four square panels that were built into the tower of the Split Cathedral, it is known that in Dollabella's time five new roads were built in Illyricum. The first, most significant, most famous and largest was *colonia salonitana ad fines provinciae illyric* 167 Roman miles (241.8 km) long, and it led from Salona to the northern border of the province of Illyricum (Beželj 2015: 18). It connected the south with the north of the province of Illyricum, i.e. Dalmatia with Pannonia, and from that road all the newly built ones later separated. Judging by the milestone, found in Kopjenica near Ključ, this road passed through Northwest Bosnia in 47/48, during the reign of Emperor Claudius, and then its construction was completed (Sergejevski 1963: 88). The road passed through the valley of Sana, connecting the mining area of Northwestern Bosnia with Salona in the south and Siscia in the north. The main road Salona-Siscia was joined by small local roads that were vital for the mining area in the valleys of the rivers Sana and Japra. The mining centers of the area were also connected by these roads. Near the village of Jablanica, southeast of Mount Prosara, Elagabalus' milestone was found in 1946 (in the third line is the emperor's name M. Aurelius Antoninus p. f., better known as Elagabalus (218–222)). According to I. Bojanovski (1972: 163–174), this finding is a sure proof that the main road Siscia - Salona went through Utolica, Dubica and continued through the valley between the mountains Kozara and Prosara, i.e. it did not come from the mining area on the Sana (Fig. 10: Siscia – Ad Praetorium).

From the river Una to Siscia, on a route about 60 km long, the road led across Mt. Zrin controlled by the Osječnica fortress (Fig. 10). Also, it should be emphasized that for the transport of ores, iron products and semi-finished products and other products in this area, the Roman administration also used the rivers Sana and Una, the navigability of which enabled easier and cheaper transport. The exchange of goods with Siscia took place on the river Sana - Una - Sava - Kupa in both directions on a route of about 220 km. Proof of this is the finding of wrought iron pieces in the Una riverbed near Hrvatska Kostajnica, as well as bricks from Siscia found in the remains of buildings from the Roman times in the area of Northwestern Bosnia.

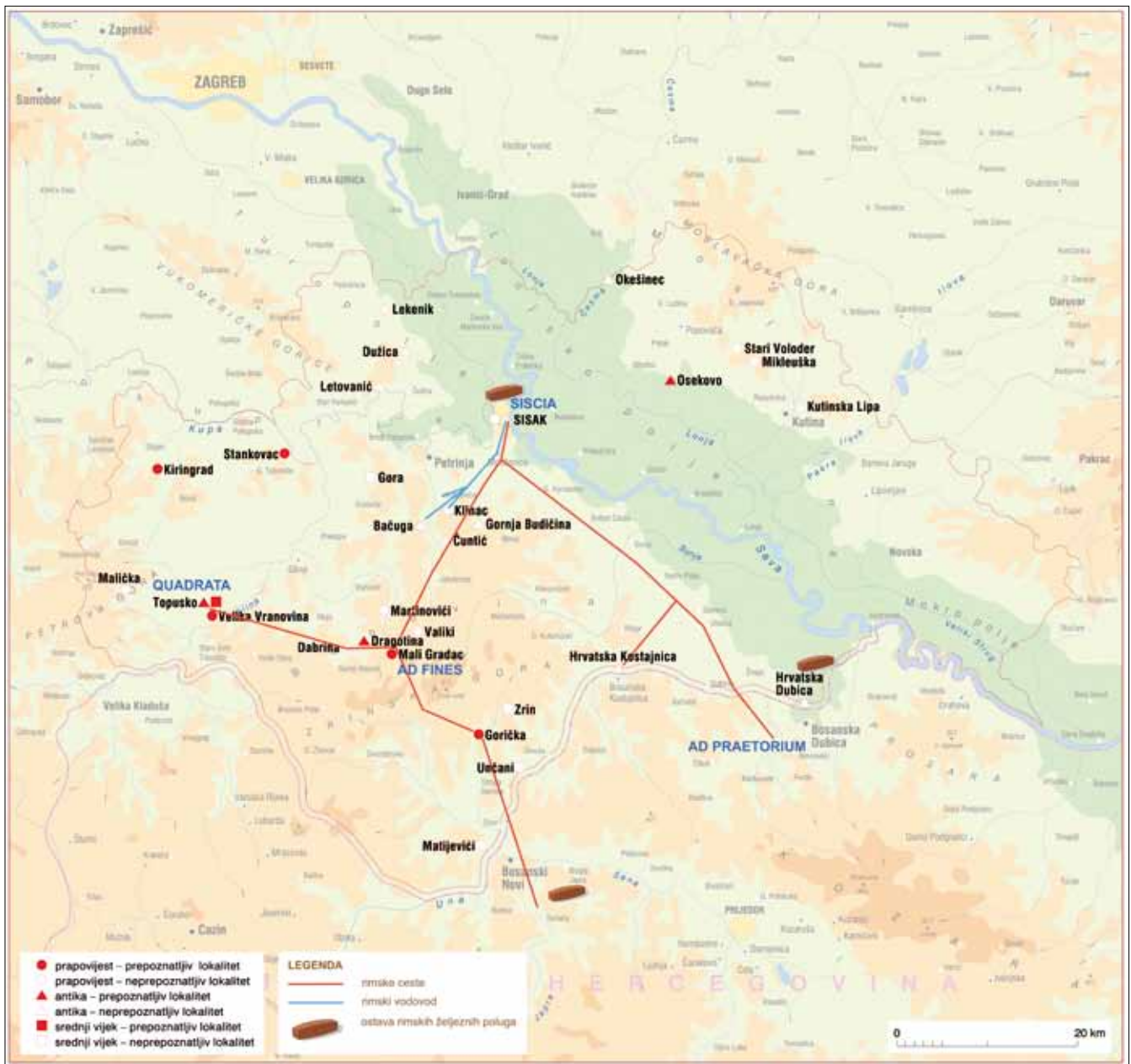


Fig. 10 Roman roads to Siscia and the location of found wrought iron pieces (map drawn by: A. Durman). Circle - prehistory, triangle - roman age, square - middle ages, red - known site, white - unrecognisable site, red line - roman roads, blue line - roman aquaeduct, illustrated wrought iron - deposit of wrought iron bars.

IRON PRODUCTION TECHNOLOGY IN ANCIENT TIMES

The process of iron production, which developed in the Middle East and Asia Minor, through the Mediterranean areas spread to Europe, especially thanks to the *Phoenicians*, *Celts* and *Romans*. At that time, iron was produced in *bloomery furnaces* (Fig. 11), and the technological process of iron production in these furnaces was called *bloomery process* (Wikipedia 2020a).

The process began by alternately stacking rows of charcoal and iron ore forming a furnace nest on a previously formed hearth. The resulting mound is then walled with stone or brick and clay. In some cases, in order to increase the refractory quality, the inner lining was consisted of clay containing sand or crushed baked clay. At the top was an opening for the exit of gases from the combustion of fuel, and at the bottom of the wall was an opening for entry of air-blast. Since the first recorded depiction of the melting process was found on the wall of an Egyptian tomb (from the 15th century BC) in which the fire was intensified by the use of bellows moved by the legs, and bellows was also used in the Vučedol culture (3000–2200 BC), it can be safely assumed that air was blown into such furnaces using bellows. The furnaces had an internal diameter of approximately 300 to 400 mm and were about 1 m high (Sarna 2016).

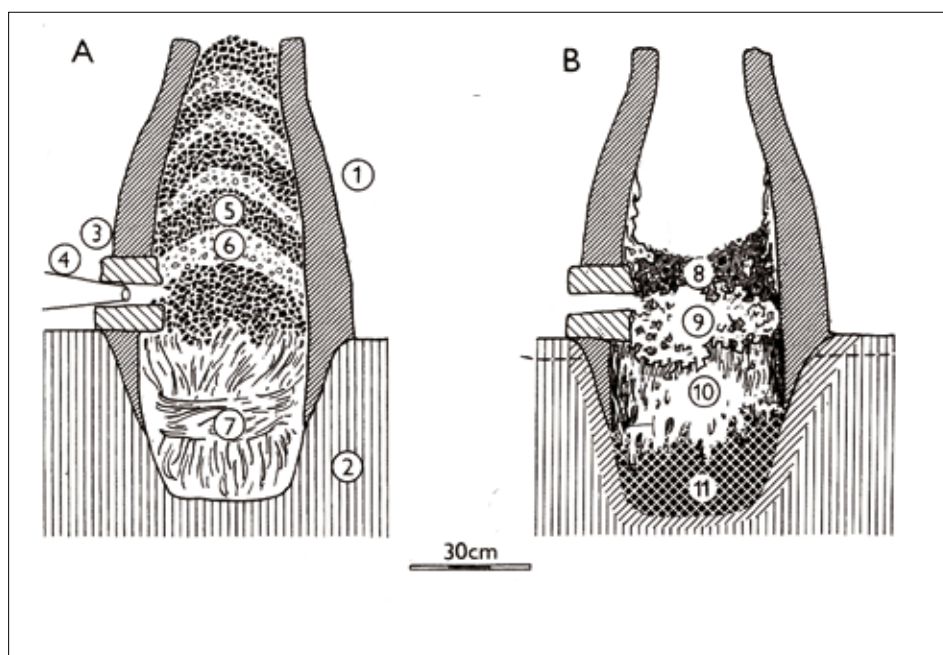


Fig. 11 Bloomer furnace of the type "slag-pit furnace", Opus incertum (after: Pleiner 2000: 372)
 A – Before smelting: 1 shaft, 2 virgin soil, 3 tuyere block, 4 bellows, 5 charcoal, 6 iron ore, 7 straw or brush wood
 B – After smelting: 8 furnace slag, ore residues, charcoal, 9 iron sponge, 10 slag block in the pit, 11 charcoal and ash

At that time, another type of furnace, the so-called *beehive furnace* (Sarna 2016), had a domed form in the shape of a beehive. In these furnaces, a mound made of alternating layers of charcoal and iron ore was covered with a thick layer of clay, and through the lower part of the side wall were installed openings for air supply, which was supplied under pressure from the bellows.

The process of reduction of iron ore corresponded to the process that takes place in the upper zone of the modern blast furnace, i.e. the zone of indirect reduction. This means that the resulting iron was produced without a melting process. It was relatively clean, soft and wrought iron, i.e. suitable for forging, due to its low carbon content, so that various weapons and tools could be produced from it by forging. The process itself took place as follows. After ignition of charcoal through the lower opening of the furnace, combustion gas temperatures above 1000 °C were achieved, so that at these temperatures generated CO reduced iron oxides to wüstite (FeO) and then FeO was reduced to elemental iron. If the ore was from a wetland with increased moisture content, a water evaporation process was previously carried out in the upper part of the furnace. In any case, FeO could not be completely reduced but only to the achieved equilibrium state of the mixture of CO and CO_2 gases. The remaining FeO reacted with individual tailings constituents (especially sands) forming iron olivine (fayalite), which formed the majority of the slag. The achieved temperatures in the hearth of the furnace (slightly more than 1100 °C) were sufficient to melt the slag, but not the fayalite, so that the process of FeO reduction in the slag could not be carried out (Sarna 2016). For this reason, slag contained over 50% of Fe, depending on the iron content in the ore. This process yielded only about 12.5% of iron from iron ore, and the mass of "iron sponge" was up to 70 kg (Wikipedia 2020b). Iron sponge was collected at the bottom of the hearth, and molten slag at the top of the hearth, so that it partly flowed through the lower opening of the furnace.

The analysis of slag is extremely important because it can indicate the places where iron production took place, and its hardened shapes also help to reconstruct the shape and dimensions of the destroyed furnaces. By studying the chemical and mineral composition of slag, data can be obtained on the level of the technological process and on the type of ore used as well as the quality of the iron product.

In the described types of furnaces, it was necessary to destroy the furnace in order to remove the lump of iron sponge. This lump had to be reheated to remove residual slag and impurities by the forging process. In doing so, finished products or semi-finished products were formed, usually of an irregular square shape. Furnaces of this type with the described

bloomery process lasted practically until the end of the first millennium of the new era, and in some cases even longer, for example in Styria and Silesia until the 18th century (Wikipedia 2020b).

The *Romans* helped spread iron production technology. One of the iron-making techniques that the *Romans* spread north all the way to Great Britain was the furnace, which had the shape of a bowl or cylinder 2 m high. Unlike previous furnaces, this furnace is filled through the upper opening with layers of charcoal and iron ore. Air was introduced through an opening in the bottom of the furnace, and was turned in the direction of the wind flow. With a gust of wind, the air flow was introduced into the furnace through the opening. The flow of air through the furnace shaft was aided by the flow of wind above the upper opening creating a pressure below atmospheric pressure, which sucked in air through the lower opening. The disadvantage of these furnaces was the dependence of the process on wind, so it could not be carried out throughout the year. The advantage of these furnaces was that the product, which was also a lump of iron sponge, was extracted through the lower opening and then forged into a certain shape. However, there were no intense air currents in the observed region, so the *Romans* used furnaces with air bellows. Baked clay nozzles were installed in the air inlets, which had the function of accelerating the air flow. This is confirmed by the mentioned finding from Stari Majdan, where such nozzles up to 220 mm long and 10–20 mm thick were found. The inner diameter decreased from 55–65 mm conically to 10–20 mm.

According to archaeological findings of 97 wrought iron pieces downstream from Hrvatska Dubica, it can be concluded that the *Romans* in the furnaces described above produced the so-called "*iron flower*", in fact the lump (bloom) of "*iron sponge*" with admixtures of slag weighing 20–30 kilograms, and then forged it into semi-finished products weighing 3–5 kg intended for further processing. With the described technology, it can be determined that *officinae ferrariae* were metallurgical workshops or metallurgical plants which included *bloomery furnaces* and forges.

Only at the end of the Middle Ages new types of furnaces *Stuckofen* and *Blauofen* are designed, which were forerunners of modern blast furnaces. For the first time in history, in the *Blauofen* furnace molten iron or blacksmith's "*iron sponge*" could be produced. In the 14th century in the Rhine valley, a *Flussofen* type furnace was built on the basis of the *Stuckofen* and *Flussofen* furnaces, which was the first blast furnace for continuous iron production. The product was molten iron which was used, among other things, for casting cannons (Wikipedia 2020b).

Therefore, it is not correct to use the names of smelters (smelters) of iron for *officinae ferrariae*, but it is more appropriate to speak about metallurgical workshops or plants, depending on the size. Also, in the cited works, (e.g. Merdanić 2018: 38), it is claimed that the furnaces reached the temperature required for melting ore of about 1535 °C, which is impossible to achieve with charcoal and blowing cold air. Or that a cast piece of iron weighing 23 kg was found in Majdan near Jajce (Pašalić 1954: 56–57). The only processing of iron shaping at that time was forging, unlike of metals of lower melting point such as copper and bronze, which could be formed by casting.

CONCLUSION

The basic idea of this paper is to point out on the one hand the importance of iron production in the observed areas of the Mt. Trgovi and Northwestern Bosnia, and on the other hand the fact that, apart from the geological connection of these areas with rich iron ores, in ancient times it was a unique area connected by roads and the exchange of goods. The importance of iron production conditioned the emergence of settlements and the construction of roads.

There are no findings to confirm that in ancient times there was communication between tribes living on either side of the river Una. After Rome established administration in these areas, traffic corridors were built, both road and river, which integrated this area. Although there are evidences of iron production in pre-Roman times in the areas of the Mt. Trgovi and Northwestern Bosnia, due to the richness of iron ores and forests, iron is produced mainly in the Sana and Japra river basins with a special intensity of the 2nd century AD. Iron in the form of wrought pieces as semi-finished products were transported to Siscia and then formed there into finished products. Roman Siscia was an important center that connected, by roads and rivers, iron mines and workshops in the areas of Northwestern Bosnia and Banovina. It was mostly iron that connected Siscia with the Adriatic and especially the Danube, as the most important Roman border, by roads and enabled the city to gain a mint (one of a total of five mints of gold money in the Roman Empire).

Also, it is important to point out that the *Mazaei*, as a large and organized people, had developed mining and metallurgy in pre-Roman times. It cannot be ruled out, taking into account their material culture and geographical position, that they were more oriented towards the province of Pannonia even though they administratively belonged to the province of Dalmatia. Even in modern times, especially during the SFRJ, the area of Northwestern Bosnia materially and culturally

gravitated to Sisak. The connection is also seen in iron production. In the 1960s MK Željezara Sisak (Sisak Ironworks) supplied iron ore as well as ancient slag from this area, and many inhabitants of this part of Bosnia found work in this plant.

The paper also briefly describes the technology of iron production in ancient times. The occurrence of high iron content in slag is also explained. The cause of this phenomenon was the transition of fayalite to slag, which could not melt at the achieved temperatures, so there were no conditions for direct reduction of FeO, which normally takes place in the lower part of the modern blast furnace. This was the reason that only about 12.5% by weight of iron was obtained from iron ore.

ACKNOWLEDGMENTS

This work has been supported by Croatian Science Foundation under project "Iron production along the Drava River in the Roman period and the Middle Ages: Creation and transfer of knowledge, technologies and goods" (IP-06-2016-5047).

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TRACES OF IRON PRODUCTION IN THE AREA OF POKUPLJE IN THE 1ST MILLENNIUM BC

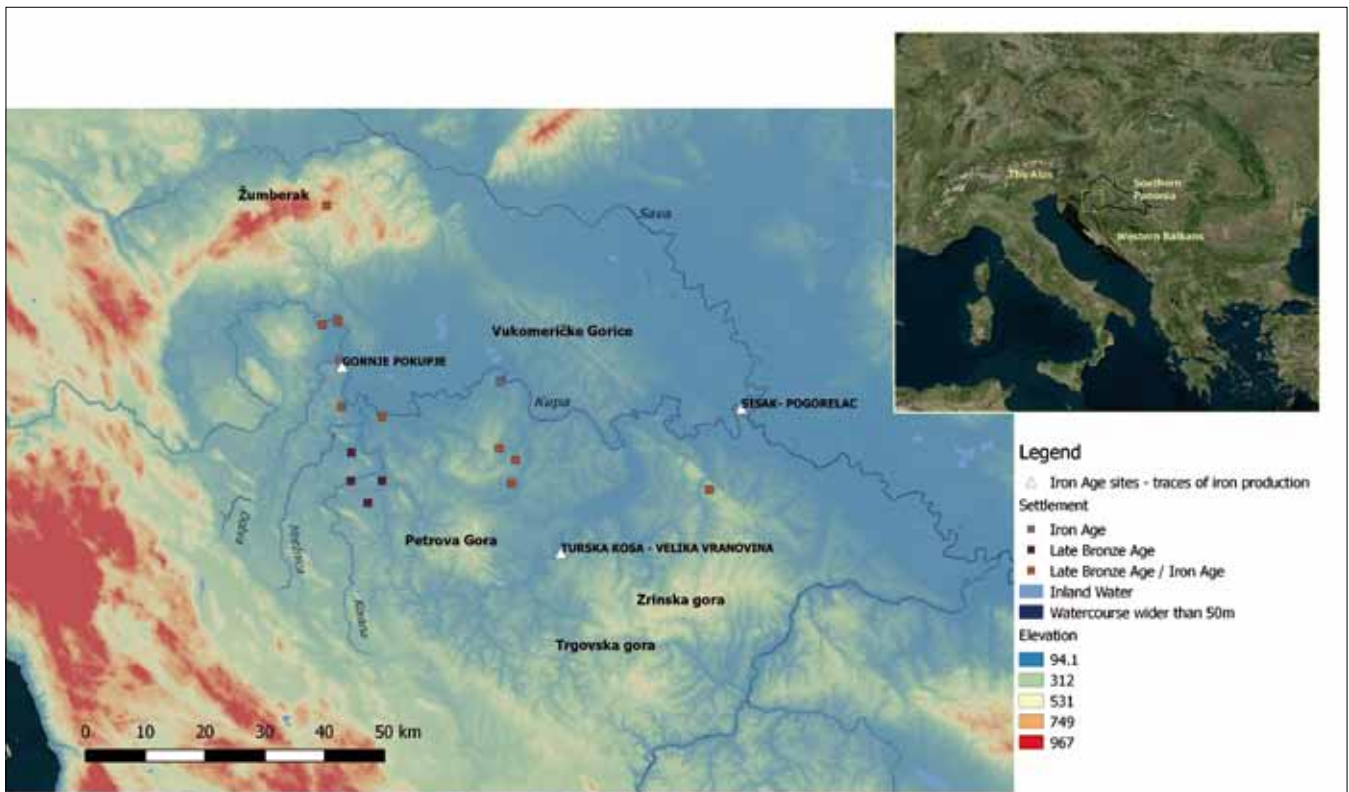
The Pokuplje area (central Croatia) and its mountainous fringe have great potential for the production of iron in archaeological periods, including the Iron Age. The potential results both from the availability of natural resources and from a close cultural and geographical connection with the neighbouring iron-producing regions on the territory of present-day NW Bosnia and SW and central Slovenia. The region is understudied from an archaeological perspective, so finds related to iron production are scarce. This paper discusses rare finds (slag, technical ceramics, iron bloom) related to iron production and processes carried out on two sites, Gornje Pokupje (Late Iron Age) and Sisak–Pogorelac (Late Hallstatt/Early La Tene). The potential for iron production during the Iron Age is discussed on the basis of archaeological traces of iron production processes and ore availability (type of ore, spatial distance, possible mining methods) and suitability for direct reduction. The methods used consist of macroscopic analysis of archaeological finds and the spatial analysis of the relationships between geologically known deposits, historically recorded mining areas and potential areas with occurrences of ore, suspected based on geochemical data on topsoil saturation with iron of geogenic origin.

Key words: bloomery iron production, post-reduction slag, technical ceramics, Iron Age, ore deposits, spatial analysis

INTRODUCTION

The Pokuplje region lies at the crossroads of three geographical and cultural regions - the south-eastern Alps, southern Pannonia and the western Balkans (Map 1) - and as such had a significant role in the Iron Age communication network. Neighbouring regions are known for their iron production during the Iron Age. Early iron production was recorded in the Central Bosnian cultural group (sites Pod near Bugojno, Čolaci near Donji Vakuf, etc.) (Pravidur, Vuković 2011) as well as in the area of the Dolenjska group (Slovenia) (Trampuž Orel 2012; Črešnar et al. 2017). Both cultural groups were present in areas rich in iron deposits, in northwestern and central Bosnia (Bojanovski 1988; Basler 1999; Pravidur, Vuković 2011) and in southeastern and central Slovenia.

The Pokuplje is an area on the lower reaches of the Kupa River in central Croatia (Map 1). The Kupa River valley stretches over 296 km on Croatian territory from its source in the Risnjak National Park near Razloge in the Gorski Kotar region to its confluence with the Sava River near the town of Sisak. The relief features of the area are heterogeneous, as the river flows through the mountainous region of Gorski Kotar into the lowlands in the southwestern part of the Pannonian Basin. Based on the geomorphology of the landscape, the area is divided into the Upper and Lower Kupa River Valley. The Upper Kupa flows through the pre-alpine area of the Gorski Kotar and Kordun regions in Croatia. In a broader geographical sense, this area includes the confluence of the Upper Kupa, the Lower Dobra and the Mrežnica. The valley of the lower Kupa is the area from the town of Ozalj, where the river emerges from the mountainous region of Gorski Kotar and flows into the valleys of the south-western part of the Pannonian Basin, to the confluence with the Sava in the town of Sisak. The region is surrounded by the Žumberak mountain range in the northwest, the Vukomeričke Gorice hills in the northeast and the Slunj karst plateau in the southwest. The area of the Zrinska and Petrova Gora mountains, located south of the Kupa River, should also be considered in the geographical context within this article, as they are iron ore bearing and form the contact zone with the Western Balkans.



Map 1 The Pokuplje region and the surrounding geographical and cultural regions of the Iron Age (base map: Europe DEM, 25 m, www.copernicus.eu; Openlayers map (QGIS 2.14. plugin): Bing satellite map) (made by: T. Karavidović)

The Pokuplje region and its wider geographical framework, especially the adjacent mountain ranges, are known for their iron ore deposits of different types and genesis, which were exploited in historical periods. Traces of iron production in the region are rare and have only been found in relatively recent archaeological investigations.

This paper analyses archaeological finds related to iron production (slag, technical ceramics, iron bloom) from two Iron Age sites, the Sisak–Pogorelac and Gornje Pokuplje, in order to understand the nature of the processes that led to their formation and the activities carried out at the sites. Another objective is to determine the potential for local iron production in the Pokuplje region based on historical and geological data on the availability of resources (ore deposits) and data on traces of mining or iron production in the region assumed for archaeological or historical periods. The methods consist of macroscopic analysis of finds and analysis of potential ore mining areas through spatial analysis (QGIS 3.22). Ore deposits are mapped on the basis of georeferenced geological maps of the area and historical sources on mining activities in the region (which are often not recorded on current geological maps). Based on data on topsoil iron saturation in the region and known archaeological finds of bog iron ore, the potential for the existence of further deposits is presumed. To determine the accessibility of different types of ore, the spatial relationship between the locations of Iron Age sites with evidence of iron production activities and ore deposits is analysed. The likelihood of the use of different ore types is discussed on the basis of the potential technological usability, the presumed accessibility of the deposits and the data on ore types used in the Iron Age in the wider geographical area of Europe. For the latter discussion, previously published geochemical data on ores and the environmental indicators of occurrence are also used.

ARCHAEOLOGICAL SITES WITH TRACES OF IRON PRODUCTION

Analysed archaeological finds related to iron production and/or processing of iron blooms or semi-products originate from the Gornje Pokuplje and Sisak–Pogorelac sites.

The Gornje Pokuplje site is situated in the Lower Kupa river valley at the confluence of the Dobra and Kupa Rivers in Karlovac county (Map 1). During 2018 and 2019 surface field surveys followed by excavation of several test trenches were conducted. The most distinctive feature discovered, was a massive rampart, with orientation east to west (Drnić 2018: 224–230) (Fig. 1). The preserved parts of the rampart reach up to 3 meters in height, although it is almost flattened in the

central part and heavily damaged by recent earthworks in its western part. The rampart is constructed in dry-wall, using middle-sized and small rocks combined with soil. It is a well-known construction technique used for numerous Iron Age ramparts in the territory of Dolenjska in Slovenia (Dular, Tecco Hvala 2007: 79, 84–85, 90–91, 93), but a unique structure in the Pokuplje region, the only known fortified prehistoric lowland settlement. Numerous surface finds were collected in the area south of the rampart and within a test trench,¹ including sherds of typical Late Iron Age pottery (wheel-thrown vessels, graphite-tempered pots, etc.) (Drnić 2018: 244–245, T. 109–110) and debris from iron production, represented by fragments of technical ceramics and slag. North of the rampart, the field survey yielded a large quantity of late mediaeval/early modern pottery sherds, including several pieces of green-glazed kiln tiles. Based on the results of the field survey and the excavation, two phases of occupation can be distinguished: (1) the Late Iron Age phase, a settlement with a rampart on the northern side and (2) the Late Mediaeval/Early Modern phase with historically affirmed structures (Fig. 1).²

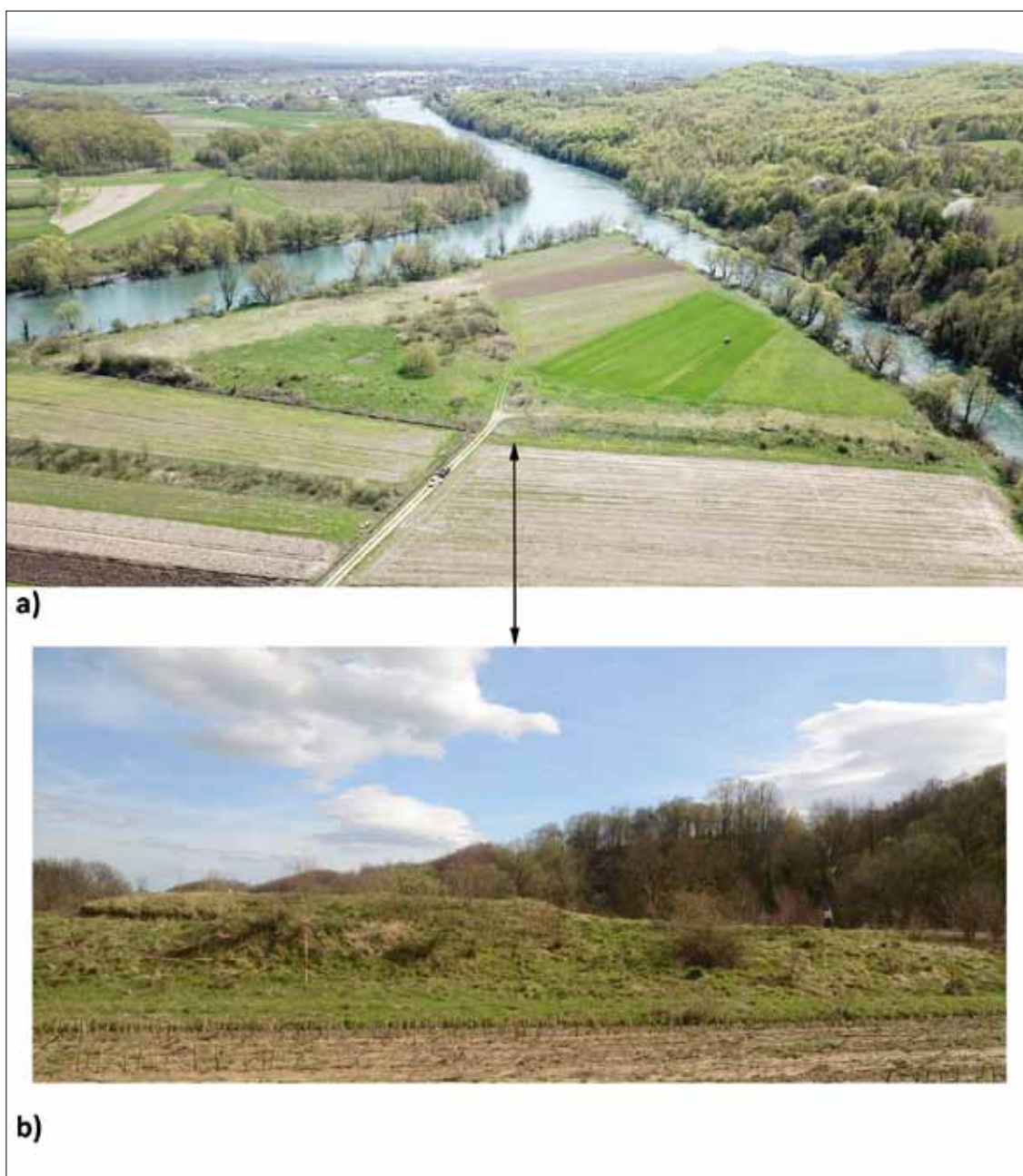


Fig. 1 a) Aerial view of the Gornje Pokuplje site, b) side view of the preserved part of the rampart, surrounding the Iron Age settlement on its northern side (photo by: L. Bogdanić, I. Drnić)

- 1 Fragments of the typical Late Iron Age pottery, spindle - whorls, grindstones and several iron objects were found in Trench 3 (dim. 50 m²), located next to the rampart on the south side, within the settlement area. The remains of three hearths with stone constructions were investigated in the habitational layers.
- 2 In the First Military Survey map from the late 18th century (<https://maps.arcanum.com/>), a building is recorded on the site.

The Pogorelac site is located in the modern town of Sisak, near the confluence of the Kupa and Sava rivers (Map 1). This Iron Age settlement is well known in the archaeological literature, although systematic research began only 15 years ago (Drnić, Miletić Čakširan 2014; Drnić, Groh 2018; Drnić 2020). With the current state of research, it can be assumed that the core of the prehistoric settlement, which is dated to the later phase of the Late Bronze Age (Ha B), was located on the right bank of the Kupa, in what is now the riverbed. In the late Hallstatt period (6th–4th century BC), the settlement expanded considerably on the right elevated bank and became an important centre of southwestern Pannonia. Another important settlement phase, characterised by territorial growth, took place in the 2nd and 1st centuries BC, when the settlement on the left bank of the river Kupa expanded towards the river Sava (Fig. 2).



Fig. 2 Aerial view on the position of Sisak – Pogorelac site (photo by: L. Bogdanić)

Rare traces indicating ironworking activities were found in Trenches 2 and 5, located in the middle of the Late Hallstatt/ Early La Tene settlement, where the remains of several above-ground structures were found (Fig. 3). Although traces of ironworking are sparse at the Sisak–Pogorelac site, several other finds confirm the processing of non-ferrous metals and the production of metal objects (Drnić 2020: 125–127). These are various clay moulds, semi-finished products and crucibles with traces of copper alloys. In addition, two structures interpreted as bronze smelting furnaces were excavated in Trench 5 during the 2018-2019 excavation campaign (Fig. 3). Numerous bronze drops were found in the filling of the collapsed dome of the first structure, while a crucible and half of a ceramic tuyere were found in front of the furnace. Toreut production has been confirmed in the Iron Age settlement of Sisak - four bronze matrices for the production of silver pendants (Drnić 2020: 125, fig. 80).

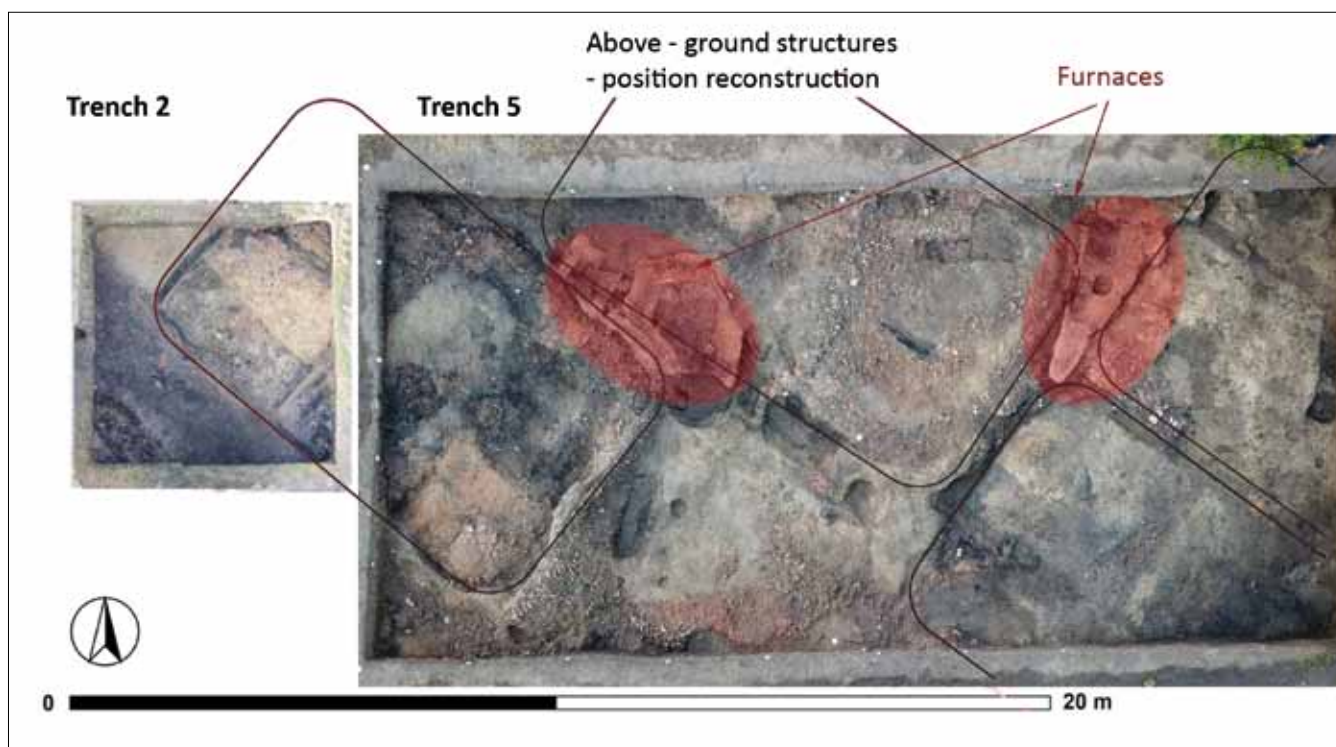
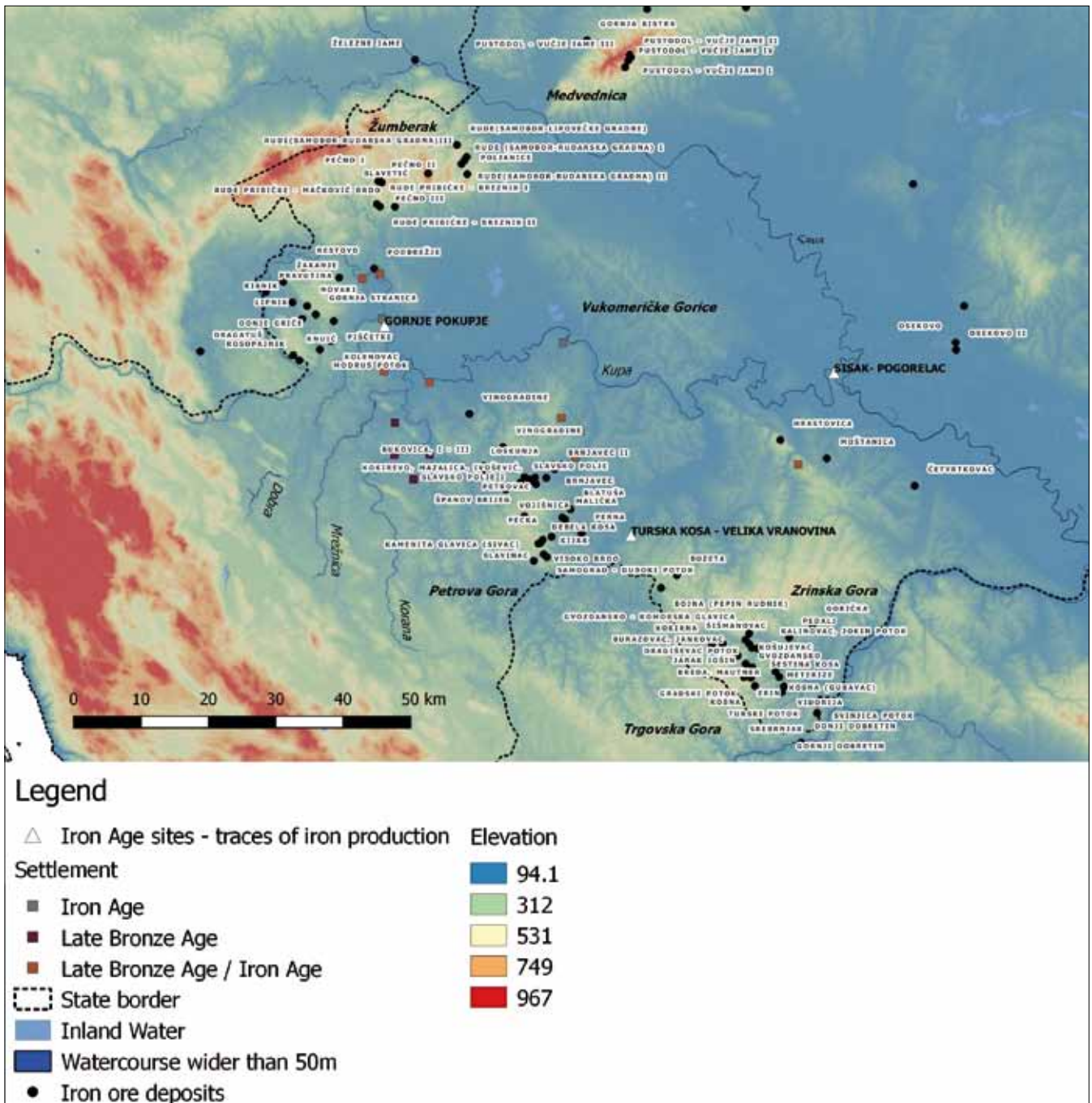


Fig. 3 Sisak – Pogorelac site, trench 2 and 5 where slag and iron bloom samples were found. Traces of several above-ground structures and bronze melting furnaces are seen in the archaeological record (modified according to: Drnić 2020: 42, fig. 18; made by: T. Karavidović)

IRON ORE DEPOSITS AND THE HISTORY OF MINING IN THE BROADER AREA OF POKUPLJE

The Pokuplje area and surrounding mountain ranges are characterized by significant iron ore presence, concentrated in several mountainous and lowland areas (Map 2). The economically significant deposits are present on the Petrova, Zrinska, Trgovska Gora and Žumberak mountains and occurrences of iron ore are present in the broader lowland area (within the Pliocene - Pleistocene clays, silts, sands and sandy gravels). Ore deposits are diverse in terms of origin and mineral paragenesis, as well as the type and age of rocks in which mineralization occurred and the period of formation (Marković 2002). The basic types of iron ore are haematite, siderite and limonite.

Different types of ore deposits whose mineral paragenesis is diverse and complex occur on Trgovska Gora (Jurković 1958; 1993; Šikić 1988a; 1988b; Marković 2002; Dedić, Kruk 2016). According to Marković (2002), it is possible to distinguish five genetic groups of deposits: 1) wire type deposits in the form of quartz - siderite wires with limonite occurring as a result of secondary oxidation of siderites, 2) iron mineralization of ankeritized limestones and limestone dolomites in the form of sheets and lenses, where oxidation of ankerite surfaces formed deposits of quality limonite (SI slopes of Trgovska Gora), 3) mineralization (wires, veins, lumps) in the Middle Triassic deposits probably formed by submarine volcanic exhalations (NW part of Trgovska Gora, occurrence of haematite, limonitized haematite, limonite and specularite), 4) sedimentary deposits of the Hunsrück type (interlayers of lenses or irregular bodies within clay and sand deposits) partly formed by precipitation from iron hydrosol and partly as clastic sediment, by flooding and accumulation of hard limonite from the oxidation zone of siderite and/or ankerite deposits, 5) limonite concretions, nuggets and/or crusts (Trgovska and Zrinska Gora) of smaller dimensions found in sands and clays and formed partly by precipitation due to increased concentration of iron solution in soils and partly as clastic sediment, mechanically transported. Deposits on Trgovska Gora are the most economically significant iron ore deposits in Croatia, as evidenced by data on numerous mining districts and intensive exploitation from the end of the 18th century, and especially during the second half of the 19th century and the first half of the 20th century (Jurković 1993; Šebetić 2000; Marković 2002: 81–82). Significant amounts of ore, mostly limonite, measurable in tens of thousands of tons were extracted from deposits such as Gvozdansko (30–50 000 t), Šestina Kosa



Map 2 Geologically mapped iron ore deposit positions and assumed positions according to historical sources on exploitation in the Pokuplje region and surrounding areas (base map: Europe DEM, 25 m, www.copernicus.eu) (made by: T. Karavidović)

(50 000 t), Kosna (40–50 000 t), Jokin Potok–Komorska glavica (83 000 t), Gradski Potok (75 000 t). Some deposits like the Šestina Kosa were almost depleted.

Petrova Gora mountain is also historically and economically significant due to numerous iron ore and coal deposits (Map 2) that were exploited since the 19th century (Šebetić 2000). Iron ore deposits on Petrova Gora can be characterized as hydrothermal and sedimentary (Korolija et al. 1980; 1981; Marković 2002; Benček et al. 2014; Magaš et al. 2014). Hydrothermal deposits are extremely zonally distributed and located in the eastern part of the Upper Paleozoic complex. These are the wire types of deposits (quartz - siderite, barite - siderite and barite wires). The basic minerals are siderite and limonite (formed in the oxidation zone of siderite wires and the sedimentary type). The sedimentary deposits are located along the northern and eastern rim of Petrova Gora and beyond, in the north part of the Banija region. The basic minerals

are (1) haematite (Bukovica deposit), (2) Hunsrück type limonite (Vojišica, Slavsko Polje), (3) limonites of various origins (south and east part of the Petrova Gora and the wider Banija area) formed as a syngenetic or later precipitate and/or clastic deposits formed by wearing of the oxidation zone (limonite) of quartz-siderite wires and redeposition. At Trgovska, Petrova and Samoborska Gora (Žumberak mountain range) mountains copper, zinc, lead and silver occurrences are also present (Marković 2002).

In the area west of Ozalj and Karlovac, limonite deposits within the Pliocene - Pleistocene clays, sands and sandy gravels, formed as layers 0.5 – 3 m thick or spherical formations (Podbrežje) with a diameter of about 1 m and as individual boulders of various sizes have been recorded (Marković 2002: 67). These ores are formed by precipitation at increased concentrations of iron ions in the soil solution or as clastic sediments. This type of ore was exploited in the 19th century, and the paper "Pregled rudarske djelatnosti za 1859" (Review of mining activities until 1859) (Laszowski 1944) mentions mining companies, suggesting the existence of mines in several spatially close positions near the villages along the Kupa River and nearby tributaries, from where the ore was transported for further processing to Samobor (Croatia) and Graz (Austria). Field surveys conducted during recent history (1954) have indicated lower concentrations of ferrous sandstones and limonites in the broader observed area and the low possibility for the existence of sizeable reserves (Marković 2002: 67). The latter is a possible consequence of the mentioned intensive exploitation and probably one of the reasons for the lack of the exact positions of deposits on the geological map (Bukovac et al. 1984b: 47–49; 1984a) of the observed area.³

Another part of the region, the Žumberak mountain range, is known for deposits of iron ore, primarily haematite, siderite and limonite as well as copper ores (Pleničar et al. 1976; Pleničar, Premru 1977; Šikić et al. 1978; 1979; Marković 2002: 67–68; Kastmüller et al. 2009). Haematite and siderite deposits in the Samobor hills belong to the exhalation-sedimentary type, and they are genetically, paragenetically and spatially related to siderite-sulphide wires. Haematite and limonite deposits are also known in the Krašić area (positions in the wider vicinity of the villages of Ruda Pribička and Pečno). According to Marković (2002), hematite deposits are associated with carbonate Triassic deposits, while limonite could be formed by oxidation of haematite while the deposit formation is partly related to erosion and redeposition and the formation of clastic deposits. Historical data indicate the possibility that the exploitation of ore deposits in Rude began in the 13th century, while the earliest written evidence directly related to mining in Rude dates to the 16th century (Vasiljević, Fabijanec 2016: 74). Intensive exploitation was carried out during the 19th and 20th centuries (Marković 2002: 67).

Although the ore resources in this area are abundant, archaeological research has not been conducted systematically yet and archaeological evidence of ore exploitation is lacking. In the literature, the area of Zrinska, Petrova and Trgovska Gora is often associated with the exploitation of iron copper and/or silver ores in antiquity and/or pre-Roman times (Bojanovski 1988: 277; Durman 1992; 2002; Koščević 1995: 23). These associations are based on the natural spatial connection with the Japra, Sana and Una valleys (NW BiH) and numerous pre-Roman and Roman sites with clear traces of iron production near deposits (Pašalić 1954; Bojanovski 1988; Basler 1999: 94–96) but also the geostrategic and the administrative significance of ancient *Siscia* (Sisak) and its role in production processes, management of the production and distribution of iron in the Roman province of Dalmatia and Pannonia (Koščević 1995; 1997; Škegro 1999: 101, 103–104; Durman 2002). Although there is a strong implication that the deposits in these areas were exploited as early as the iron age, there is still no direct archaeological evidence of mining, primary iron production or provenance studies to support this claim. Available data is often fragmented and has several major issues. Archaeological and geological literature includes toponyms of positions where, according to the authors, traces of mining iron ores and silver and/or production processes (slag accumulations) were carried out and which are most often associated with the pre-Roman or Roman period. However, the data is often inconsistent, the source of individual data is not put forward, or it is not clearly defined based on which parameters were these theses adopted. Bojanovski (1988: 277) mentions the positions of Gorička, Gvozdansko, Topusko and attributes traces of ancient mining to them but does not provide direct archaeological evidence that supports this thesis. R. Koščević transmits the latter data (1997) and mentions (1995) Zrinjska, Petrova and Trgovska Gora in the context of pre-Roman iron production, citing as a source the geological study of the area of Trgovska Gora (Tučan 1941). The latter study (Tučan 1941: 151–153) mentions "old abandoned limonite trenches" (Jokin Potok–Ljubina site) and "large slag deposits as remnants of ancient, primitive iron ore smelting" (a site near Vrlanda stream, on the road to Maidan and Jokin Potok–Ljubina), without a

3 Map 2 shows the positions according to Marković (2002) and deposit locations assumed through the historical data (topographic data, village names) mentioned in the "Survey of mining activities until 1859" (Laszowski 1942). The positions are not plotted precisely, given that the existing data does not allow it. The main reference for positioning the potential, geologically unmapped deposits, was topographic data from the historical sources compared to names of today's villages and in relation to the geological base in which occurrences of ores of similar genetic types from this area are recorded (Marković 2002). A georeferenced geological map (scale of 1:10000) (Bukovac et al. 1984a) and a topographic map of Croatia (1:25 000) (State Geodetic Administration Portal, geoportal.dgu.hr) were used in the preparation of the map.

more detailed description. Other, more detailed geological studies (Jurković, Durn 1988; Jurković 1993: 42; Marković 2002: 77) and historical surveys of mining activities (Šebetić 2000: 103) mention the position of Komorska glavica⁴ in relation to ancient mining and the Španov Brijeg⁵ to iron production processes (Map 1). In addition, sites with traces of mining (trenches) or iron production are known to exist before the time of the first historical sources from the 17th century, and are presumed in the area around the village Hrastovica along with sites known before sources from the 18th century in the area of Malička and Perna, Kosna and Vinogradina and Gvozdanski–Majdan Brdo (Šebetić 2000: 102–103, 110, Table 1; Marković 2002: 77),⁶ all situated on Trgovska and Petrova Gora mountains (Map 1). The period in which these deposits were originally mined is difficult to predict given the long-term intensive exploitation in the area. Historical data implies that on the Samoborsko Gorje, Trgovska and Zrinska Gora mountains, the earliest mining activity could have started as early as the 13th century, but probably from the middle of the 15th century and in the 16th century when silver-bearing galenite, iron and copper-bearing ores were exploited (Vasiljević, Fabijanec 2016). The exploitation continued at an intermittent pace until the 20th century (Jurković, Durn 1988; Kolar Dimitrijević 1991; Jurković 1993; Šebetić 2000; Marković 2002).

Circumstances that do not allow the unquestionable adoption of these positions as evidence for ancient and/or pre-Roman and early medieval iron mining or production are: 1) lack of material archaeological evidence and/or professional/detailed descriptions or documentation, 2) lack of revision archaeological field surveys or excavations, 3) uneven and general terminology based on toponyms and multiple occurrences of the same toponyms in a broad geographical area, 4) matching names of deposits and mines in different sources with different interpretations of the period of origin, 5) high intensity of exploitation over a long period, especially in the early modern times that could potentially erase or degrade traces of earlier mining activity.⁷

RESULTS AND DISCUSSION

IRON PRODUCTION AND PROCESSING REMAINS: SLAG, TECHNICAL CERAMICS AND AN IRON BLOOM

Gornje Pokupje site

During the field survey at the Gornje Pokupje site, a total of 2.5 kg of debris related to iron production was found. Based on macroscopic analysis, the waste can generally be divided into two main categories: bloomery iron production/processing slag and technical ceramics. A total of 2,066 g of iron production slag and a 24 g fragment of an iron bloom were found. Based on the macroscopic analysis, the slag can be divided into two major groups. The first group is quite uniform and can be considered as post-reduction slag. It consists of the slag cakes that are formed during the refining and purification of iron blooms, that is semi products with entrapped slag. The second group is not very diagnostic and consists mainly of highly fragmented samples, making the identification of the processes that produced the slag uncertain. The latter samples could have been formed by post-reduction processes, such as compaction or bloom purification, but some features could also indicate smelting processes. Theoretically, post-reduction processes involving the processing of bloom can be divided into two main phases: consolidation/compaction of the bloom and refining/purification of the excess slag (Pleiner 2000; Bayley et al. 2001: 34–35), although these two processes are not necessarily carried out separately. The latter can be referred to as primary smithing (Jouttijärvi 2015: 43) or bloomsmithing, as it involves successive reheating and hammering to remove excess slag from an iron bloom. Under these circumstances, a slag cake can form inside the forge or hearth under the bloom, often with a plano-convex cross-section (Serneels 1993). This type of slag is called smithy hearth

4 Jurković (1993) describes the position of the deposit and traces of mining and states that the deposit on the southern slopes of Komorska Glavica was opened in Roman times and mined via smaller surface mines, 500 m long and 30 m deep. According to the data on the deposit, the hard limonite formed by oxidation of the anchorite and siderite ore bodies would have been mined. At the end of the 19th century because of the undermining and exploitation of the deeper layers, the deposit was almost depleted.

5 Marković (2002) mentions that based on the type of slag it was concluded that iron was produced in Roman times, without citing the source of the data. He further states that in the earliest written records of mining activity (from 1969), old iron ore mines were recorded around the nearby village of Hrastovica.

6 Trenches and ancient smelting furnaces are mentioned for the area of Perna and Malička, discovered during the geological survey conducted upon the order of Maria Theresa in 1770 (Marković 2002: 77). According to I. Kruhek (1999), on the map of Ivan Nepomuk Sgarget from 1776, on the Majdan hill, there is a hill of slag, crushed ore, smelting workshops, churches and mills attributed to the Saxons. Other mentioned locations (Hrastovica, Kosna and Vinogradine) are marked as positions of mines.

7 Examples are: 1) the position of Komorska Glavica near Gvozdansko, which is mentioned in the context of ancient (and earlier) mining in geological studies and was actively exploited in the 19th and 20th centuries and probably exhausted (Jurković 1993: 103; Šebetić 2000: 104, Table 2; Marković 2002: 78), 2) Jokin potok, a toponym that appears in the context of mining from archaeological periods (pre-Roman period according to Koščević 1995; Tučan 1941: 153) and later mining, in the 19th and 20th centuries (Jurković 1993: 40, 42–43; Šebetić 2000: 102–103, 105, Tables 1, 2; Marković 2002: 81), 3) Majdan–Vrlanda stream / Majdanski stream which is interpreted as a pre-Roman or Roman site (Koščević 1995) and is close to the assumed position of the production complex attributed to Saxons and the positions of mines from the 20th century (cf. Tučan 1941: 151–152; Jurković 1993: 40, 42; Kruhek 1999; Šebetić 2000: 104, Table 2), 4) the Španov Brijeg position, where the remains of iron slag attributed to antiquity have been said to exist, and the ore was subsequently excavated in three trenches (Marković 2002: 74–77).

bottom or plano-convex bottom (Serneels 1993: 47–49; Bayley et al. 2001: 34–35) and is a subtype of post-reduction slag. At the Gornje Pokuplje site there are several samples of primary smithing slag (Pl. 1). The upper surface of most samples is unevenly consolidated, while the lower surface is very similar in all samples, with an uneven, medium-rough surface. One sample has traces of unburnt charcoal, indicating that it was formed in a charcoal bed (Pl. 1: 1). The cross-section of these samples is plano-convex or concave-convex (Pl. 1: 1, 2) and lenticular (Pl. 1: 3, 4). The samples are porous, with numerous regularly and irregularly shaped porosities and rusty parts visible in the structure. They are slightly magnetic and the surface is partially covered by a layer of rust, indicating a high iron content in the slag. Two of the samples (Pl. 1: 3, 4) are stratified, which could indicate that the slag was formed in at least two phases, in other words, the slag mass could have cooled and solidified during the reheating process, which would suggest that the rhythm of the primary smithing was intermittent. An interesting feature is that three of the samples are semi-circular (plan view), with the straight side possibly indicating the placement of the slag adjacent to the furnace walls of the reheating hearth (Pl. 1: 1, 2, 3; Fig. 4). The formation of slag directly on the furnace walls is related to the design of the furnace and the position of the bloom within the furnace and its relationship to the air input. Theoretically, the airflow has a direct influence on the volume of the hot zone, so the positioning of the bloom and the resulting formation of slag underneath, close to the edge of the hearth or on the walls, may indicate a lower airflow (Serneels, Perret 2003). The upper surfaces are uneven and different in all samples and one of them has traces that may indicate that the air supply (tuyere) was placed directly above (horizontally or at a slight angle) the upper surface of the slag (Pl. 1: 2; Fig. 4). Two samples (Pl. 1: 1, 2) are overall very similar (dimensions, shape and total mass)⁸ which can be attributed to the slag content of the refined product and the way the process was carried out. Consequently, these two finds can be taken as evidence that a similar semi-finished product was processed at least twice at this site and that even the workflow was similar. Other finds show different characteristics, such as a layered structure (Pl. 1: 4), a presumably greater weight and possibly a different shape (Pl. 1: 3). The latter may indicate greater variability in terms of the characteristics of the processed blooms or semi-products or the way that the process was carried out. The analysis of post-reduction slag needs to be considered preliminary, as the processes that led to its formation are complex and the level of investigation (surface survey) and the quantity and degree of preservation of the finds are low.

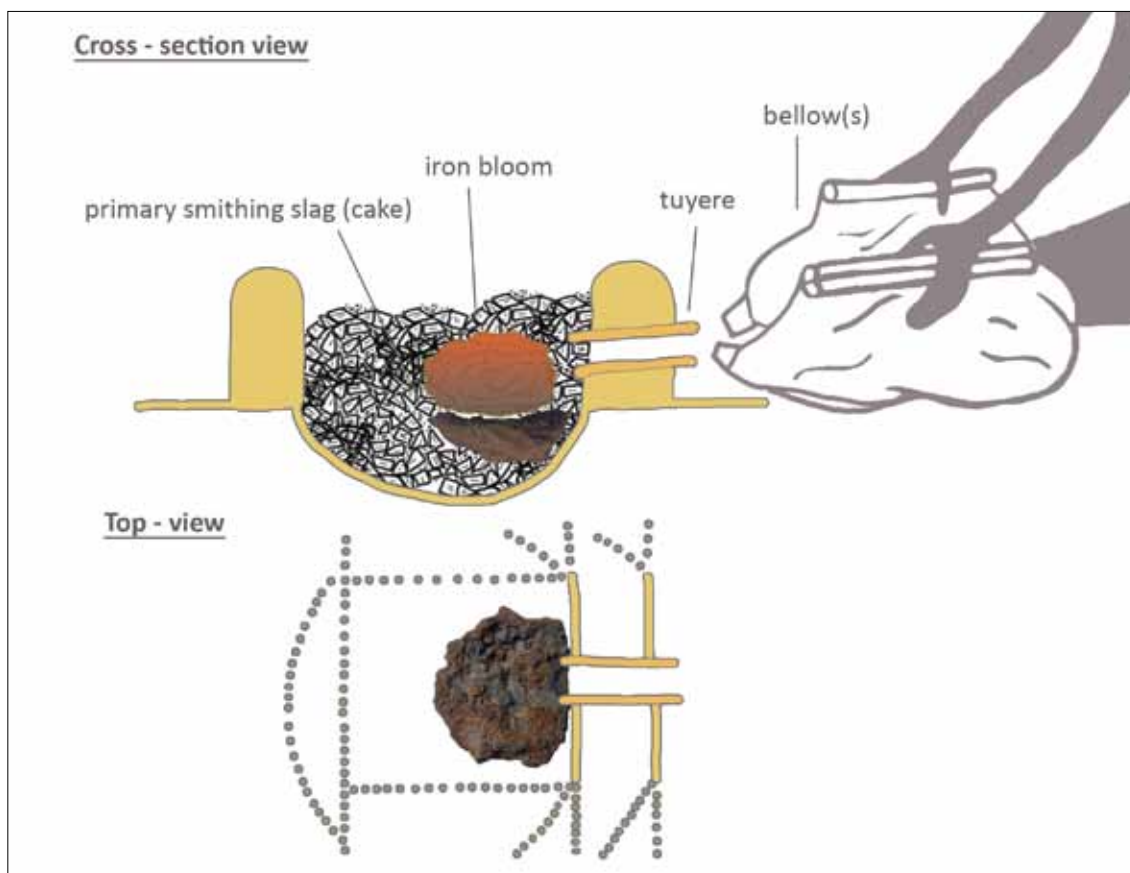


Fig. 4 Reconstruction of the reheating hearth and the position of the slag cake with one straight side (top view) that indicates its placement at the walls or edge of reheating hearth (sample - Pl. 1: 1) (made by: T. Karavidović)

⁸ Sample cat. nr. 1 (Pl. 1: 1) is fully preserved and weighs 326 g while the total mass of the sample cat. nr. 2 (Pl. 1: 2) has been calculated based on the reconstructive presumption of the preserved part percentage (289 g – 85 % = 340 g – 100%).

Other samples are more difficult to assess by macroscopic analysis, partly because they are highly fragmented and because possible processes involved in their formation tend to leave macroscopically similar forms. They are generally more fragmented, irregularly shaped, the structure of the slag is denser, as if it had been deposited in a molten state for a longer period of time, which would be a more likely environment in a smelting furnace than in the smithing/reheating hearth, if we assume that the inside of a smelting furnace is a more thermally insulated and stable environment and the cooling process takes longer. Alternatively, the slag density could be related to the nature of the materials, i.e. the chemical and mineralogical composition of the slag and the way the process is carried out in the reheating hearth (Serneels, Perret 2003). A sample of the slag (Pl. 2: 5) has a flow texture on the upper surface, which may be characteristic of smelting slag (slag from inside the furnace with flow texture or tap slag), but primary smithing is not excluded. The fragment is very small and the flow shows no signs of regular rivulets, as would be the case with typical tap slag (Bayley et al. 2001), which may suggest that it is molten slag from inside the furnace (smelting or bloom refining-reheating). A single, highly magnetic, amorphous fragment (gromp) completely covered with rust may be considered a detached or unsintered fragment of an iron bloom. In cross-section (Pl. 2: 6), remnants of slag can be seen, concentrated mainly on the edge of the fragment, while the iron is not fully compacted and voids are present. This type of debris may be an unsintered piece of iron bloom, indicating smelting at this site, but it could also be a trace of the post-reduction procedures. In the latter case, the fragment could have become detached from the bloom during compaction, directly after the smelting process, or during consolidation and purification, i.e. primary smithing.

The technical ceramics are represented by several small fragments with a strongly burnt, vitrified and deformed inner surface as well as traces of adhering slag (Pl. 2: 7–10) and one fragment with a slightly vitrified inner surface (Pl. 2: 11). On a macroscopic level, it can be seen that the clay mass is saturated with sand, which may have been added to improve the refractory properties of the structure, which was intended to withstand high temperatures. On the other hand, the soils in the vicinity of the site consist mainly of clay, silt and silty clay (Benček et al. 2014; Magaš et al. 2014), so the raw material available near the site is already saturated with sand to some extent and could be refractory without other materials having been intentionally added. The vitrification of ceramics and the traces of slag adhering to the surface may be characteristic of the inner walls of bloomery smelting furnaces, where temperatures of up to 1100–1250 °C are reached (Pleiner 2000: 133; Charlton et al. 2010: 353; Karavidović 2020: 149–150) (Fig. 4) or even higher in the lower, active zone near the hearth and air input. The fragments could also belong to simpler installations for reheating, primary and/or secondary smithing, where high temperatures are also reached under more oxidising conditions. Depending on the details of the hearth design, the position of the air supply, the air flow rate and the placement of the iron bloom in the hearth, it is possible for slag from the iron bloom to adhere to the walls of a reheating hearth/furnace. A strong indication of such an event is that most of the post-reduction slag cakes found at the site have a straight edge, indicating that they were formed by the edge of the furnace hearth, which means that the iron bloom was placed very close to the air intake hole or tuyere (Fig. 4). It is also possible that the clay walls of a reheating furnace deform or even melt to some extent under the temperatures reached during reheating/primary smithing. In bloom refining, i.e. the removal of slag by reheating, the temperatures reached must ensure that the fayalite is melted from the bloom (1200–1300 °C) and that the iron is in an austenitic state (above 900 °C) (Pleiner 2000: 215). The temperatures reached in the experimental horseshoe-shaped reheating hearth were up to 1100–1250 °C, and the walls of the smithing hearth were glazed and lined with adhering slag.⁹ Fragments with a heavily burnt and deformed or slagged inner surface (Pl. 2: 7–9) belong to a part of the wall around the most active zone, near the air inlet of the hearth or furnace, while a fragment with a slightly vitrified inner surface (Pl. 2: 11) would be placed away from the most active zone.

The Pogorelac site

Several finds discovered in the habitational layers of the Sisak–Pogorelac site prove that metallurgical activities took place in the Iron Age settlement. Features that could be interpreted as smelting or smithing furnaces were not recorded during the research conducted so far. However, one interesting find is an amorphous, exceptionally magnetic ferruginous mass physically associated with fired clay (Fig. 5; Pl. 3: 14). It has a very irregular shape and on one side traces of unburned charcoal are visible, imprinted in the slag. Imprints of charcoal may be characteristic of slag from inside smelting furnaces, which may have been removed and cooled before the charcoal was burned. The surface of the sample is unevenly magnetic, suggesting some degree of slag inclusions. The latter could indicate that this is not a fully consolidated and purified iron bloom but one that was taken directly from a smelting furnace and possibly compacted. Based on the appearance of the

⁹ The experiment was conducted by the author during 2020. The results are a part of a Phd thesis and have not been published yet.

outer surface, some degree of compaction may also be suspected. There are occasional, relatively flattened areas on the top surface of the bloom that could indicate compaction/consolidation or even reheating and purification to some degree (Fig. 5). The surface texture suggests that a wooden hammer was used, which would be a functionally appropriate tool for compaction and removal of adhering and trapped slag, as it allows a gentler approach than the use of an iron hammer. The latter is often required for the initial stages of post-reduction processing of the bloom after it has been removed from the smelting furnace, since the iron bloom at this stage is a spongy mass that is only partially sintered and still saturated with slag, so that the use of a heavier hammer could result in fractures and disintegration of the bloom. The adhered clay fragments show no signs of severe burning, vitrification, or slagged surfaces, as would be the case with the interior walls of a smelting furnace near an active zone where the bloom is formed, so they cannot be considered adhered furnace walls with certainty. It is possible that the curious appearance of the adherent clay fragments on this ferruginous mass is related to the destroyed structure in which it was found, or to post-depositional changes (agglomeration due to progressive rusting and surrounding soil), and is not directly related to the process of iron production, meaning that it is a secondary occurrence. The find was recovered from the destroyed above-ground structure (Structure 6/10 in Trench 2), which is dated to the late Hallstatt and early La Tène periods (Fig. 2). Archaeological record showed a pile of wall clay daub on the interior floor made of compacted clay that could be interpreted as a collapse of a massive wall structure. The event was likely caused by fire, as suggested by burn marks. The above-ground structures/houses in this and the previous settlement phase were built in the so-called postpad construction method (Drnić, Groh 2018: 93–94, fig. 21; Drnić 2020: 47–49, figs. 22–24).

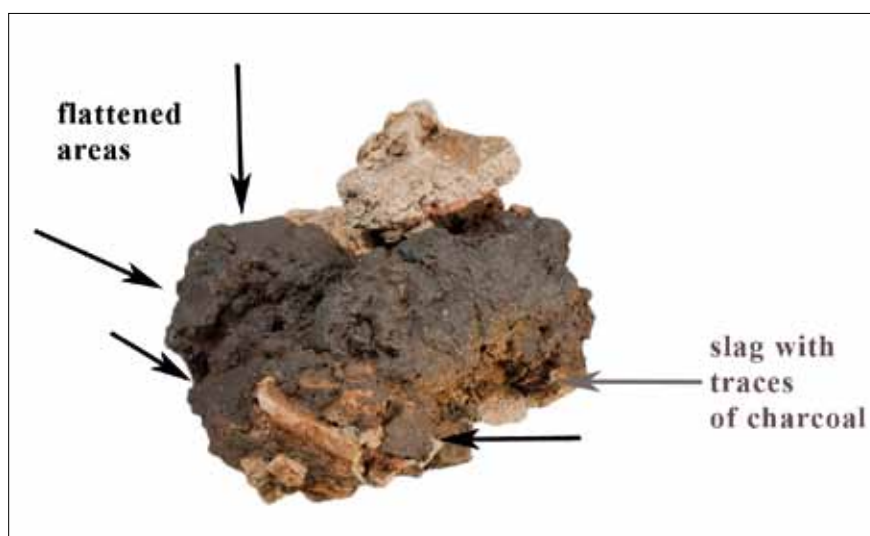


Fig. 5 Iron bloom with adhering ceramic fragments from the Sisak – Pogorelac site (Pl. 3: 14)

Other finds related to iron production are two slag cakes (Pl. 3: 12, 13), which could be defined as post-reduction slag, created through iron bloom refining, the process of consolidation and/or purification, i.e. primary smithing. They are of different sizes, circular and semicircular (top view) and plano-plano and plano-convex (cross section). If we assume that they were formed in two separate events, the variety in size and mass could indicate the processing of semi-products of different size and amount of entrapped slag. As with the samples from the Gornje Pokuplje site, the straight edge seen on one sample (Pl. 3: 13) indicates that it was formed at the edge of the reheating furnace/hearth. The latter sample shows signs of stratification on one edge. This could indicate that the process by which it formed was interrupted, with a certain amount of slag having cooled to some degree before the upper layer of slag was deposited on it. On the other hand, the stratification is only seen on the outer edge of the sample (opposite the straight edge closest to the furnace walls, i.e., the air input) which could indicate that the temperature in the hearth was slightly lower at the edges, allowing the slag to cool faster than in the centre and before additional slag was deposited. There are impressions of unburned charcoal on the sample, suggesting that the slag was surrounded by charcoal during its formation. The latter could theoretically support the assumption that the uneven distribution of heat (close to the air input and on the outer sides of the slag mass) caused the layered appearance, since the imprints of unburned charcoal are found only at the edges and sporadically at the bottom of the slag sample.

ACTIVITIES RELATED TO IRON PRODUCTION IN THE POKUPLJE REGION

Most of the slag and furnace wall fragments found at both sites can be interpreted as the remains of post-reduction processes, i.e. the refining and purification of iron blooms by reheating and hammering, a process that follows the smelting of iron ore and the production of iron bloom. Slag or furnace walls characteristic of smelting were not found or could not be identified with certainty, although some finds at the Gornje Pokuplje site are ambiguous (Pl. 2: 6). If we consider the representation of finds with uncertain attribution against the diagnostic finds, it is more likely that all finds reflect post-reduction processes involving compaction and refinement (purification) of the bloom. Nevertheless, smelting cannot be ruled out at this site. All the debris at the Gornje Pokuplje site was found in close spatial association with fragments of Late Iron Age pottery and other finds, south of the rampart within the enclosure of the presumed settlement, suggesting that these processes were carried out within the settlement grounds. A similar conclusion can be drawn from the context of the finds from Sisak–Pogorelac site, where post-reduction slag cakes and a semi-worked iron bloom were found within the settlement context. Here, a close spatial connection with finds of furnaces related to bronze production can serve as an indication of metal production and processing activities carried out within the investigated area of the site. Specialisation within the individual steps of iron production in connection with the placement of the workplace was assumed at some Late Iron Age sites, although these sites are often temporally and spatially distant. Specialised bloomsmithing and forging within or in close spatial relation to settlement areas has been suggested at sites in present-day France (Berranger, Fluzin 2014), Germany (Alpine highlands, Schaefer 2014: 49–50), Switzerland (Serneels, Perret 2007), etc. On the territory of today's Dolenjska region (Slovenia), in the lowlands of the Krka river valley, which is geographically and culturally connected to the Pokuplje region, numerous sites with traces of iron production are known (Črešnar et al. 2017: 85, Fig. 4). At the Cvinger site (Braždevec position) near Dolenjske Toplice, an iron production complex extending over 5000 m² is presumed (Mušić, Orenko 1998: 179), where remains of smelting furnaces have been discovered (Dular, Križ 2004: 228–230; Črešnar et al. 2017: 83, Fig. 3; 2020: 539–547). The smelting area is located nearby but outside the enclosed settlement area, which, according to the current state of research, seems to indicate a closed workshop environment. A similar organisation of iron production, i.e. the placement of the smelting area outside the settlement, could be a possible explanation for the lack of clear traces of smelting activities in the currently investigated archaeological record on sites in Pokuplje, since the finds are mainly related to post-reduction activities and were found within the settlement grounds. The semi-worked iron bloom, found in a settlement context is an interesting and ambiguous clue. On the one hand, it could have been produced and slightly worked at another place where smelting and immediate compaction took place. In this sense, it could testify to the form of a semi-product transferred from a smelting area for further processing, i.e. smithing. On the other hand, we cannot say with certainty that the bloom was not produced in the vicinity of find, as research has not yet covered the area of the archaeological site to any great extent. The only site in the Pokuplje region where smelting activities have been suspected, based on archaeological finds and record, is the Turska Kosa–Velika Vranovina site near Topusko. It is a smaller hillfort, situated at the elevated position above the river Glina (Map 1). To the east of the settlement, the remains of the birital cemetery and a cultic area have been excavated. According to a brief excavation report (Čučković et al. 2009: 6, 16, 23–24, 38, Fig. 18), traces of simple pits interpreted as iron ore smelting furnaces and dated to the late phases of the Early Iron Age were found at the edge of the settlement (Pogledalo position). Interestingly, excavation director Lazo Čučković mentions the presence of iron production remains in an area marked as Cultic place 1, where hundreds of anthropomorphic and zoomorphic figurines were found, in addition to numerous pottery sherds, textile tools and others. In the short report, he mentions the presence of a layer of burnt sand along with the iron slag pieces. According to the author, the finds that could confirm the connection of the cultic place with metallurgy are also short ceramic tubes that could have served as the openings of the bellows. The finds related to the presumed iron production have not yet been published or studied, so this interpretation is still uncertain. At a theoretical level, it seems important to stress out that ceramic tubes, as the excavator calls them, could be ceramic tuyeres used as air input instruments that were a part of furnace construction (smelting, reheating, smithing furnace/hearth).

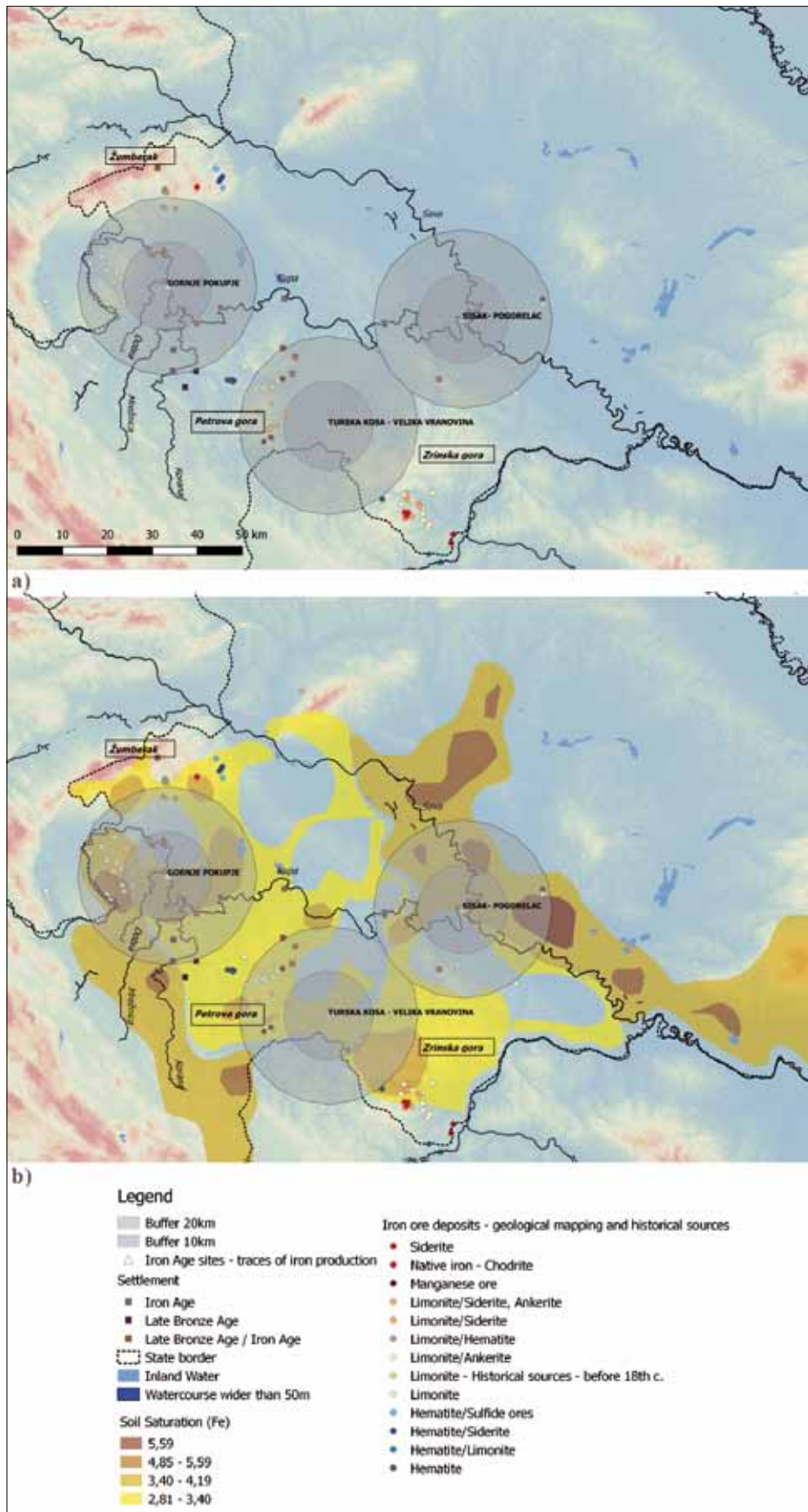
IRON ORE EXPLOITATION POTENTIAL IN THE IRON AGE

Evidence of historical mining in the wider area of the Pokuplje region is numerous, but there is as yet no direct evidence of mining in prehistoric period. Nevertheless, the natural conditions for local iron production are present in the region and all the sites mentioned in the study are located in close proximity to iron deposits and extensive forest areas, two elementary conditions for iron production. If we look at the distance of the iron ore deposits from the sites under discussion,

the majority of the deposits are located within 10–20 km as the crow flies from the sites (Map 3a). Predominately, the nearest deposits are limonitic ores of different geological origin and paragenesis.

Different types of deposits bearing iron ores of variable quality and paragenesis were actively and extensively exploited in the 19th and 20th centuries, depending on the economic needs and requirements of technology in use. The iron was extracted in blast furnaces by indirect reduction. Although the data on the locations of exploited iron ore deposits and mines in historical periods are valuable, the adoption of the potential areas of iron ore exploitation in the Iron Age should take into account that the manner and purpose of exploitation and the technology of iron production in historical and modern periods differ greatly from those in archaeological periods. The technological requirements for producing bloomery iron by direct reduction method and pig iron/cast iron in blast furnaces are not the same and are directly reflected in the composition (ore grade, ratio of iron oxide to gangue) and other properties (pre-reduction preparation, especially size of ore grains, porosity, etc.) of the ores that can be used. While modern production methods can consider ores with lower Fe content of up to 20–30 % mass (Joosten 2004: 11), R. Pleiner (2000) has set a boundary value of 79–86 % mass Fe_2O_3 (50–60 % mass. Fe) based on empirical knowledge, for ores used in bloomery iron smelting, which is often higher than the iron contents of limonite and siderite ores for which data are available and which have been historically exploited and geologically mapped in the Pokuplje region (Jurković 1993: 42–43; Marković 2002: 67, 75, 77, 79–81). On the other hand, haematite and siderite ores found on the slopes of Petrova Gora and Žumberak (Samobor Hills) mountains are classified as 50–59 % mass. Fe (Marković 2002: 67–70). However, archaeological experiments have shown that bog iron ores with much lower iron contents of up to 49 wt.% Fe_2O_3 or even less could have been used for bloomery iron production in combination with higher grade ores (Crew 1991a; 1991b; Crew, Salter 1991; Seernells, Crew 1997; Crew, Charlton 2007; Crew et al. 2011; Thiele 2010), so potentially most ores found on Petrova, Trgovska and Zrinska Gora mountains and in the lowlands of river valleys may have been used as a resource for iron production in the Iron Age. As far as technological usability is concerned, ore content is not the only important parameter for successful direct reduction used in archaeological periods. Oxide ores such as limonite, haematite and goethite are easily reduced, while other types such as carbonate ores (siderite) would theoretically require a preparation process to turn the metal components into oxides that can be reduced (Pleiner 2000: 88–90). Other characteristics such as the level of porosity, the amount and the nature of gangue constituents may also be important for effective reduction.

Another important issue is the accessibility of the ores in relation to the mining techniques required for exploitation. The rare archaeological traces of ore mining dating to the Late Iron Age are usually described as opencast workings, consisting of relatively shallow pits scattered more or less regularly across the landscape (Pleiner 2000: 93–94). This method would be best suited for the exploitation of limonite ores, which occur as secondary products of surface oxidation of ore bodies or sedimentary types in the lowland areas and on the foot slopes of the hills in the wider area of Pokuplje. The latter occur as concretions, nuggets and lenses or irregular bodies within clay and sand deposits, formed partly by precipitation from the iron-saturated hydrosol (i.e. bog iron ores) and partly as clastic sediments accumulated in the lowland areas by redeposition of hard limonite from the weathered oxidation zones of siderite, haematite and/or ankerite ore bodies (Marković 2002). These types of deposits were often not considered economically beneficial in modern times and could easily have been fully exploited in the 19th and early 20th centuries, which is why they are not always geologically mapped. The potential for the formation of iron ore and the existing deposits in the lowland areas today as well as in the past can to some extent be presumed from the results of geochemical analysis of the saturation of iron in the upper soil levels (Halamić, Miko 2009). Detailed research into possibilities of iron ore formation in similar alluvial sediments was carried out in the Podravina region, a lowland region of the upper Drava catchment, which also has a similar or lower degree of saturation with iron of geogenic origin in the soil (Halamić, Miko 2009: 48–49). The results of the study (Brenko et al. 2020) indicate that the Podravina region is a suitable area for the formation of bog iron ore, although the current conditions are likely to inhibit the formation of bog iron ore to some extent, due to long-term agricultural activities in the area and land reclamation activities that may have a negative impact on precipitation, mainly by changing the groundwater table. In this area, the local bog iron ore was actively exploited in late antiquity and the early Middle Ages and processed for iron extraction using the direct method (Brenko et al. 2021; Sekelj Ivančan, Karavidović 2021). Another example of bog iron ore usage comes from the Roman site of Okuje I (Nemet et al. 2018), located in the Sava river valley, extending from the Pokuplje area, where occurrences of iron ores in the alluvial deposits have not been recorded in geological surveys, although the soils in the downstream area of the Sava River near the site have high iron saturation (Halamić, Miko 2009: 48–49). Elevated values of iron saturation in the Pokuplje region, at a relative aerial distance of 10 – 20 km from the Sisak–Pogorelac and Gornje Pokuplje site (Map 3b), are found in the lowland, alluvial sediments of river valleys (valley of the Sava



Map 3 The spatial relation between iron age site positions, relief features and watercourses and (a) locations of different iron ore deposits present in the region and beyond (b) levels of topsoil saturation with iron (georeferenced according to: Halamić, Miko 2009) - indicating a potential for the formation/existence of other ore deposits (base map: Europe DEM, 25 m, www.copernicus.eu) (made by: T. Karavidović)

downstream from Zagreb and around Sisak, riverbeds of the Kupa, Korana and Mrežnica from Ribnik to Slunj), where the presence of iron is of geogenic origin (Šorša, Halamić 2004: 93, 95; Halamić, Miko 2009: 48–49). Scarce data on the ores exploited in the 19th century mention the ores found in loam not far from the village of Pravutine (Laszowski 1942) as the best quality ore for exploitation, and the chemical analysis of the ore samples shows that the ores around the villages of Ribnik, Žakanj, Pravutine, Reštovo and Novaci contain 44.15 % mass. Fe (63.12 % mass Fe_2O_3), and around the village of Podbrežje about 60–63 % mass. Fe_2O_3 (Marković 2002) (Map 2, 3). These sites are spatially close to the Gornje Pokuplje site, while other documents on surface exploitation of limonitic ores mention sites near Sisak–Pogorelac and Velika Vranovina (Šebetić 2000: 104) (Map 2, 3). Bog iron ores often have a very variable iron content, but are naturally very porous and can be easily reduced by the method of direct iron ore smelting (Pleiner 2000: 88). The potential occurrences of bog iron ores, redeposited limonitic clastic sediments or weathered surface layers of limonite are easy to identify and exploit, as they tend to occur in hillfoots and lowland areas relatively shallow below the ground surface or on the surface of haematite or siderite ore bodies. Sufficient quality of the bog iron ores or hard limonite and accessibility (possible mining technique, lowland location, relative distance from the sites) of these ore deposits could have played an important role in the exploitation strategy of an Iron Age community. It is also interesting to note that in the geographically and culturally connected Dolenjska region (Slovenia), where numerous iron production sites have been discovered (Črešnar et al. 2017: Fig. 5), a common ore is limonite, often found in various forms (such as layers and concretions in clayey and sandy soil – possibly bog iron ores (?)) and of different quality (Trampuž Orel 2012: 19–20; Črešnar et al. 2017: 88, fn. 14), in lowland and slightly hilly areas. Finds of limonite ores were discovered at the Iron Age sites Cvinger (Braždevec position) near Dolenjske Toplice (Črešnar et al. 2017: 85, fn. 4) in the Dolenjska region and beyond, at the site Podboršt near Trebnje (Hrovatin 2013: 97). At both sites, pieces of raw (limonite) and/or thermally processed – roasted (haematite) ores were found, in addition to other finds characteristic of iron smelting, leading to the assumption that the local limonite iron ores were exploited and used for iron production. For the sites in the Pokuplje region, there are not yet sufficient data on iron smelting or mining to exclude other possible ore deposits such as hematite or siderite ores in the mountainous parts of the Pokuplje region. At other Iron Age sites in the wider European area, high-grade ores such as haematite, limonite, siderite were used together with bog iron ores for iron production during the Iron Age (Pleiner 2000: 40; Gassman, Schäfer 2014: 23–24; Schäfer 2014: 33; Stöllner et al. 2014: 45–49; Thelleman et al. 2017; Lehnhardt 2020; Pravidur, Vuković 2011). Apart from primary and/or secondary smithing activities at the Pogorelac site, there is evidence of local bronze production (Drnić 2020: 125–126) and copper ores are present in the mountainous parts of the region on the Samoborsko Hills (Žumberak mountain range), Trgovska and Petrova Gora (Marković 2002: 42–45). These deposits are often paragenetically connected to siderite ores or spatially close to iron ore deposits, which should be taken into account when locating possible exploitation area(s) on a theoretical level. Production of the silver objects is assumed in Sisak, and mountainous parts of Trgovska and Petrova Gora hills have historically been known for exploitation of silver-bearing galenite and limonite (Marković 2002: 55–56). Some positions, such as Slavinac, are both silver and iron ore bearing.

CONCLUSION

The Pokuplje region and its mountainous borderline have a great potential for the production of iron during archaeological periods, including the Iron Age. The potential comes both from the availability of natural resources and a close cultural and geographical connection to the neighbouring, iron-producing regions, areas where Dolenjska and Bosnian cultural groups were present, on the territories of today's NW Bosnia and SW and central Slovenia. The region is understudied from an archaeological perspective, so finds connected to iron production are scarce. Nevertheless, three sites (Gornje Pokupje, Sisak–Pogorelac, Turska Kosa–Vranovina) have yielded finds that imply some iron production processes were carried out. Finds analysed in the present paper testify that iron blooms (semi-products) were processed within the settlement grounds in the Late Iron Age (Gornje Pokupje) and late phases of the Early Iron Age and beginning of the Late Iron Age (Sisak–Pogorelac). Iron ore smelting at the sites was not confirmed but cannot be excluded, as for some slag finds the processes involved in their formation cannot be defined with certainty and the scope of archaeological field research provides limited potential for interpretation. Archaeological excavation has only covered small portions of the Iron age site in the case of Sisak–Pogorelac and, in the case of Gornje Pokupje site, the finds originate from surface field surveys. Archaeological data from previous studies imply that smelting was carried out at the edges of a settlement on the Turska Kosa–Vranovina (Pogledalo position) site dated to the late phases of the Early Iron Age, where the connection

between iron production finds and the cultic context is also assumed. The finds were not studied in detail, so the character of processes they testify to and whether these are evidence of smelting is still uncertain. Based on the research presented and analogous examples of iron production process organisation during the Iron Age, it is possible that the workspaces where different stages of iron production (primarily smelting, primary and secondary smithing) have been carried out, were not the same, further implying organisation of iron production activities and the possibility of specialization within the context of Iron Age sites in the Pokuplje area. On the Sisak–Pogorelac site, a close spatial connection between the position of archaeological finds related to primary smithing and the semi-worked bloom with finds implicating bronze production is present. The latter could imply that both metals were processed in a relatively narrow area within the settlement grounds, although there could be a slight difference in time when the activities were undertaken as stratigraphy on the site suggests.

The evidence of historical mining in the broader area of the Pokuplje region are abundant, but there is no direct evidence of mining in the prehistoric period so far. The sites mentioned in the study are located in close vicinity to iron ore deposits and vast woodlands, two elementary resources needed for iron production. The current state of geological research shows that ores of different mineralogy, geological origin and paragenesis as well as quality are present throughout the mountainous borderline of the region. The occurrence of ores in lowland parts of the region is also assumed through historical data on mining, an archaeological find of bog iron ore (Okuje I site) and the geochemical data on soil saturation with iron. The majority of deposits, located in the mountainous part and the lowland areas, are in the vicinity of the sites, at an aerial distance from 10 to 20 km. Predominately, the closest and most frequently occurring deposits are of limonitic ores of various geological origins and paragenesis. The potential for the formation of bog iron ores that are known only from one archaeological context in the region, and not the geological mapping, also needs to be taken into account, as areas marked as potential formation zones are in close vicinity of all iron age sites in the region.

Chemical data on the quality of ores from deposits located near the sites indicate that almost all ores were of sufficient quality, i.e. technologically usable for the production of iron by direct reduction, a process used during archaeological periods. However, if we take as an argument the accessibility of ores, in terms of distance of ore sources from archaeological sites, the potential level of mining complexity and the method of mining known from sites in the wider European Iron Age as well as the type of ore used in the nearby Dolenjska region and the most common ore in close vicinity of sites under study, it seems that limonite ore deposits show the greatest potential for exploitation. The potential deposits of bog iron ores, redeposited limonite clastic sediments or weathered surface layers of limonite can be easily recognized and exploited, as they tend to occur in hillfoots and lowland areas relatively shallow beneath the soil surface or on the surface of haematite or siderite ore bodies. Sufficient quality of bog iron ores or hard limonite and the accessibility (possible mining technique, lowland location, relative distance from the sites) of these ore deposits could have played an important role in the exploitation strategy of an iron age community. However, Iron Age communities across Europe used different types of ores, so the use of haematite and siderite cannot be excluded. The type and quality of ores, determine the technological usability of ores to some extent and can consequently condition the method of preparation of ores and the way that the smelting process is performed. Technological usability of ores smelted by direct reduction is best with oxide ores, such as limonite, haematite and goethite. Siderite would be uneasy to smelt as it is a carbonate ore, and would require additional preparation (such as roasting) to convert metal compounds into oxides, and still may not be usable. Apart from primary and/or secondary smithing activities on the Gornje Pokupje and Pogorelac sites, there is an indication of local bronze production and teneutics in silver on Sisak–Pogorelac position and in the earlier investigations of the iron age phases of the Sisak site. The connection between the processing and production of various metals should be taken into account when locating possible exploitation areas on a theoretical level if we presume a common exploitation strategy. The copper ores present in the mountainous parts of the region on Samoborsko Gorje hills (Žumberak mountain range), Trgovska and Petrova Gora are often paragenetically connected to siderite ores (and weathered layers of limonite) or spatially close to iron ore deposits. Mountainous parts of Trgovska and Petrova Gora have historically been known for exploitation of silver-bearing galenite and limonite and some positions are both silver and iron ore bearing.

The Pokuplje region is generally understudied, and direct evidence for iron production in the Iron Age is somewhat scarce, but there are many indirect implications of potential for iron production as early as the Iron age and its longevity, so this paper aimed to bring forward new data in the hope of future, more detailed research into iron metallurgy within the region.

CATALOGUE

1. Description: Post-reduction, primary smithing slag. Upper surface uneven, bottom surface traces of unburned charcoal (dim. 1.2 x 0.7 cm – 0.5 x 0.6 cm). Top view semicircularly shaped, one side relatively straight. Cross-section plano-convex. Structure unevenly porous, traces of limonitisation on the upper and bottom surface and in the porosities of the cross-section.
Site: Gornje Pokupje
Field mark: D-P 2018, N – 1
Material: slag
Level of preservation: 100%
Dimensions: 9.4 x 8.3 x 2.3 cm
Weight: 325 g
2. Description: Post-reduction, primary smithing slag. Upper surface uneven and porous, bottom surface uneven, mildly rough. Top view semicircularly shaped (?), one side relatively straight. Cross-section plano-convex. Structure unevenly porous, traces of limonitisation on the upper and bottom surface and in the cross-section. Layered.
Site: Gornje Pokupje
Field mark: D-P 2018, N – 6
Material: slag
Level of preservation: 85% (?)
Dimensions: 8.2 x 7.3 x 2.3 cm
Weight: 289 g
3. Description: Post-reduction, primary smithing slag. Upper surface uneven, bottom surface uneven, mildly rough. Top view semicircularly shaped (?), one side relatively straight. Cross-section lenticular - irregular. Structure unevenly porous, traces of limonitisation on the upper and bottom surface and in the cross-section. Layered.
Site: Gornje Pokupje
Field mark: D-P 2018, N – 2
Material: slag
Level of preservation: 60% – 80% (?)
Dimensions: 11.9 x 7.8 x 5.3 cm
Weight: 593 g
4. Description: Post-reduction, primary smithing slag. Upper surface uneven, bottom surface uneven, mildly rough. Top view semicircularly shaped (?), one side relatively straight. Cross-section lenticular. Structure unevenly porous, traces of limonitisation on the upper and bottom surface and in the cross-section. Layered.
Site: Gornje Pokupje
Field mark: D-P 2018, N – 7
Material: slag
Level of preservation: 60%(?)
Dimensions: 6.8 x 5.6 x 3.0 cm
Weight: 156 g
5. Description: An amorphous fragment of iron (bloom). Surface covered in rust. The cross-section shows relatively compacted iron with some porosities and slag inclusions. Slag concentrated on the edges of the fragment.
Site: Gornje Pokupje
Field mark: D-P 2018, N – 12
Material: iron/slag
Level of preservation: fragment
Dimensions: 3.5 x 2.5 x 1.1 cm
Weight: 21 g
6. Description: Fragment of smelting / primary smithing slag (?). The upper surface shows flow texture, the bottom surface is rough and uneven.
Site: Gornje Pokupje
Field mark: D-P 2018, N – 11

Material: slag

Level of preservation: ?

Dimensions: 5.4 x 3.4 x 2.4 cm

Weight: 48 g

7. Description: Fragment of furnace wall, inner surface heavily burned, vitrified, traces of adhering slag.
Site: Gornje Pokupje
Field mark: D-P 2018, N – 4a
Material: clay/slag
Dimensions: 5.4 x 3.7 x 2.8 cm
Weight: 35 g
8. Description: Fragment of the furnace wall, inner surface vitrified, heavily burned and slightly deformed, traces of adhering slag. Clay paste saturated with sand.
Site: Gornje Pokupje
Field mark: D-P 2018, N – 5
Material: clay/slag
Dimensions: 6.0 x 4.1 x 2.5 cm
Weight: 40 g
9. Description: Fragment of the furnace wall, inner surface vitrified, heavily burned and deformed, traces of adhering slag.
Site: Gornje Pokupje
Field mark: D-P 2018, N – 10a
Material: clay/slag
Dimensions: 4.5 x 3.5 x 1.5 cm
Weight: 34 g
10. Description: Fragment of the furnace wall, inner surface slightly vitrified.
Site: Gornje Pokupje
Field mark: D-P 2018, N – 9
Material: clay/slag
Dimensions: 5.2 x 4.2 x 2.5 cm
Weight: 28 g
11. Description: Fragment of the inner furnace wall surface, vitrified, slight traces of adhering slag.
Site: Gornje Pokupje
Field mark: D-P 2018, N – 4b
Material: clay/slag
Dimensions: 4.3 x 2.7 x 1.3 cm
Weight: 17 g
12. Description: Post-reduction, primary smithing slag. The upper surface is uneven, the bottom surface has an imprint of the furnace bottom, uneven. Top view circularly shaped. Cross-section plano - plano, slightly lenticular. Structure unevenly porous, traces of limonitisation on upper and the bottom surface, sporadically in the cross-section.
Site: Sisak–Pogorelac
Field mark: U – 51
Material: slag
Level of preservation: 100%
Dimensions: 6.0 x 5.5 x 2.9cm
Weight: 145 g
13. Description: Post-reduction, primary smithing slag. Upper and bottom surface uneven, mildly rough. The top view is semicircularly shaped, with one straight side. Cross-section plano-convex. The structure is unevenly porous, with traces of limonitisation on the upper and the bottom surface. Traces of unburnt charcoal by the edge of the sample and bottom. The layered structure is seen on the edge.
Site: Sisak–Pogorelac
Field mark: U – 151

Material: slag

Level of preservation: 100%

Dimensions: 9.5 x 9.8 x 3.4 – 3.3 cm

Weight: 420 g

14. Description: Block of ferrous mass of iron and slag with adhering ceramic fragments, irregularly shaped – iron bloom. Surface unevenly magnetic, partially very magnetic. Sporadically traces of unburned charcoal on one side (dim. 1.5 x 0.9 x 0.2 cm).

Site: Sisak–Pogorelac

Field mark: U – 151

Material: iron/slag/ceramics

Dimensions: 18.5 x 17.0 x 15.0 cm

Weight: 4497 g

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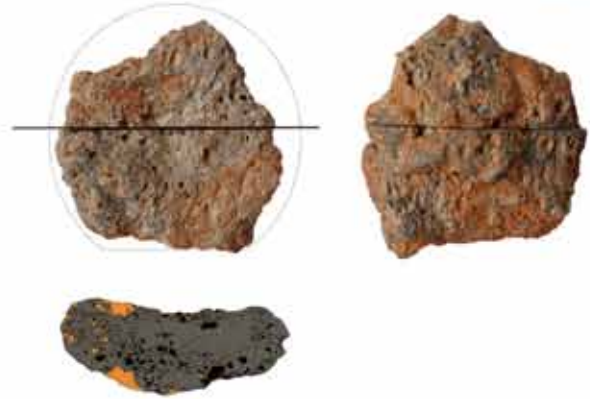
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PLATE 1

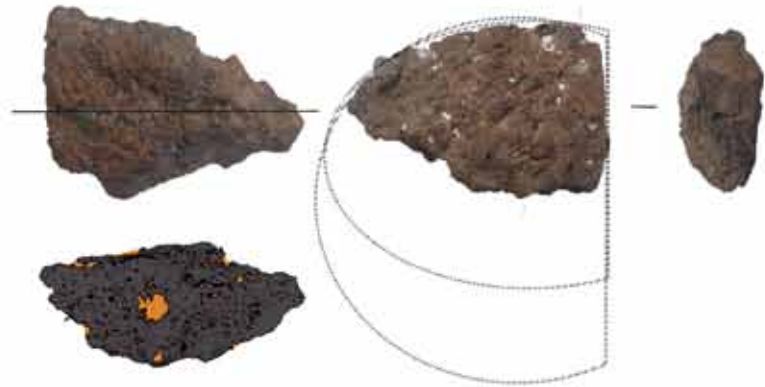
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■ Porosity
 ■ Slag
 ■ Rust



PLATE 2

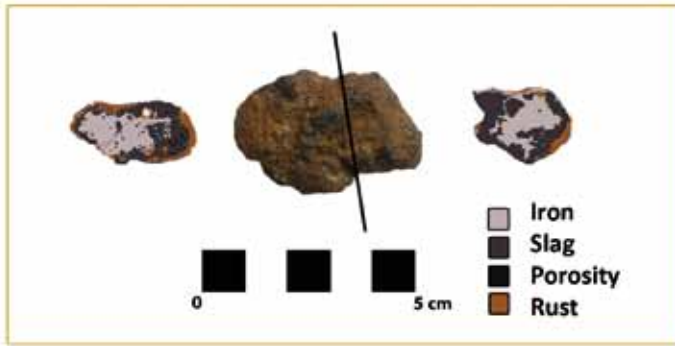
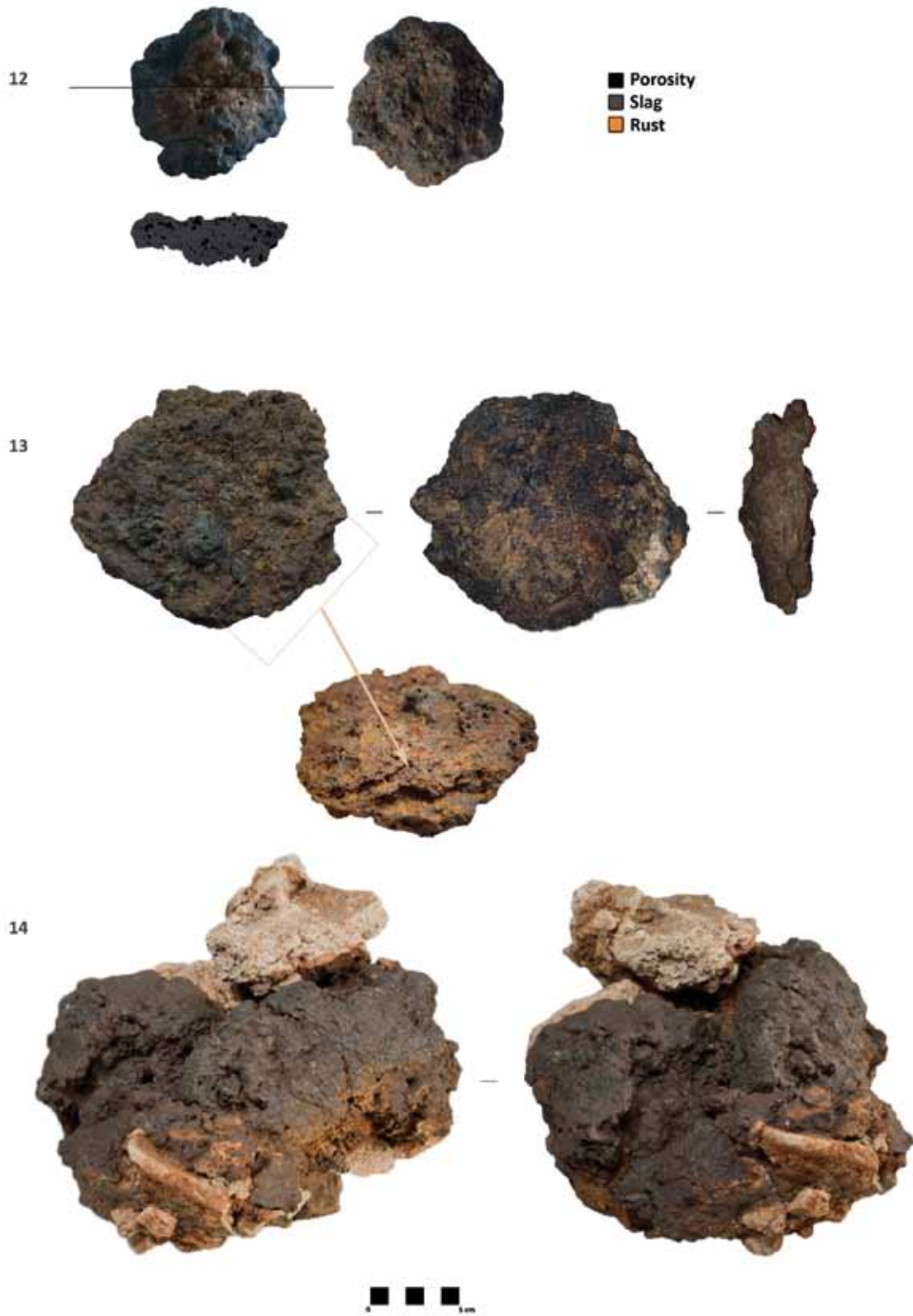


PLATE 3



THE OKUJE SITE – TRACES OF EARLY IRON PRODUCTION

This paper presents the results of the archaeological excavations at the Okuje Site conducted between 2008 and 2009 which formed a part of the protective excavations that took place during construction of the Zagreb – Sisak motorway. The Site is located in Turopolje, a region south of the City of Zagreb. The total area investigated at the Site amounts to 80 000 m². It is a multi-layered site with traces of life from the Early Bronze Age, La Tène, Roman, Early and High Middle Ages, and the Modern periods. The predominating medieval settlement finds date from the 13th to 15th centuries. The finds of the Roman road and the remains of Roman settlements and graveyards are also significant. This paper emphasises the traces of metallurgical activity identified in the group of interconnected waste pits in which c. 500 kg of metallurgical waste produced through the production of bloomery iron was found. This is probably the edge of a workshop complex where metallurgical waste was disposed of after melting and processing. Iron production is assumed to appear in the late Antiquity and into the Early Middle Ages.

Key words: The Okuje site, Turopolje, iron production, bloomery iron, late Antiquity, Early Middle Ages

INTRODUCTION

The Okuje Archaeological Site is geographically located in the Turopolje Region and, in administrative terms, is part of Zagreb County (Fig. 1). It is located around 4 km south of the Town of Velika Gorica on either side of the local road that leads from the settlement at Okuje to Mraclin. The Site includes agricultural areas that belong to the cadastral districts of these aforementioned settlements. The archaeological excavations were carried out between 2008 and 2009 as part of the protective archaeological research during construction of the Zagreb – Sisak Motorway (Velika Gorica jug – Lekenik Section). The Contracting Authority was the Ministry of Culture and the Investor was Hrvatske autoceste. Intensive archaeological field survey (Burmaz, Vujnović 2009) and geophysical research (Mušič 2008) determined the location of the Okuje Site and, due to the density and size of the findings, the Okuje Site was administratively and operationally divided into several individual units (Fig. 2).¹ An area of 80.000 m² was investigated and numerous archaeological remains from different eras were found – the Early Bronze Age, La Tène, Roman, Early and High Middle Ages and Modern periods. An extremely large number of findings were discovered during this research. The preliminary results from some of the archaeological aspects of the Okuje site have been published several times (Bugar 2012; 2021; Bugar, Mašić 2013). Here we present a part of the Okuje Site, i.e. traces of metallurgical activity. It was identified in the form of c. 500 kg of metallurgical waste that was found in several interconnected waste pits and some nearby pits. Individual and smaller fragments of

¹ The Okuje I, Ia, II, IIa and IIIb Sites amount to 49.000 m² and were researched by Zagreb City Museum (Bugar 2009; 2012). The Okuje III, IIIa and IIIc Sites amount to 29.854 m² and were researched by the Archaeological Company Kaducej d.o.o. (LLC) (Vujnović, Burmaz 2010). Along the southernmost edge of the Okuje Site there is also the Mrkopolje Site that amounts to 2040 m² which was researched by the University of Zagreb's Faculty of Humanities and Social Sciences' Department of Archaeology (Miloglav, Demicheli 2010).

slag were also found elsewhere across the site in the waste pits of Roman and High Medieval settlement objects. This type of metallurgical waste indicates pre-industrial production of bloomery iron on this site. Judging by the context of these findings, this production took place in Late Antiquity and, as indicated by a fragment of charcoal found in the core of a slag sample that was radiocarbon dated, in the Early Middle Ages. The character and type of iron slag finds are the reason for the inclusion the Okuje Site in the TransFER research project (Sekelj Ivančan, Karavidović 2021). According to the many features of the lowland relief near the Sava and its tributaries (in addition to other characteristics) the Okuje Site's environment might be compared to that of other archaeological sites in Podravina which form the core of the TransFER project.

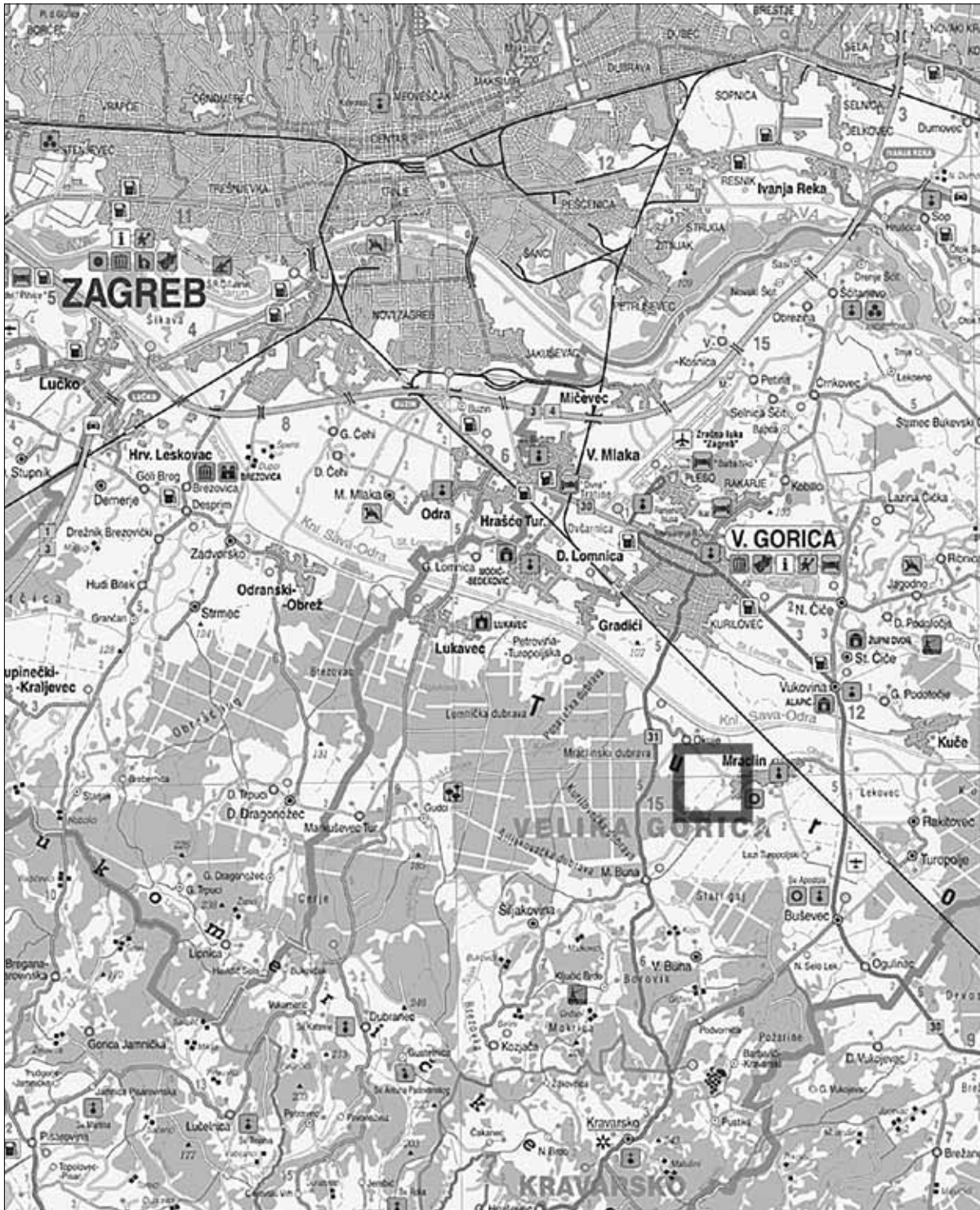


Fig. 1 The position of the Okuje site (made by: M. Gregl)

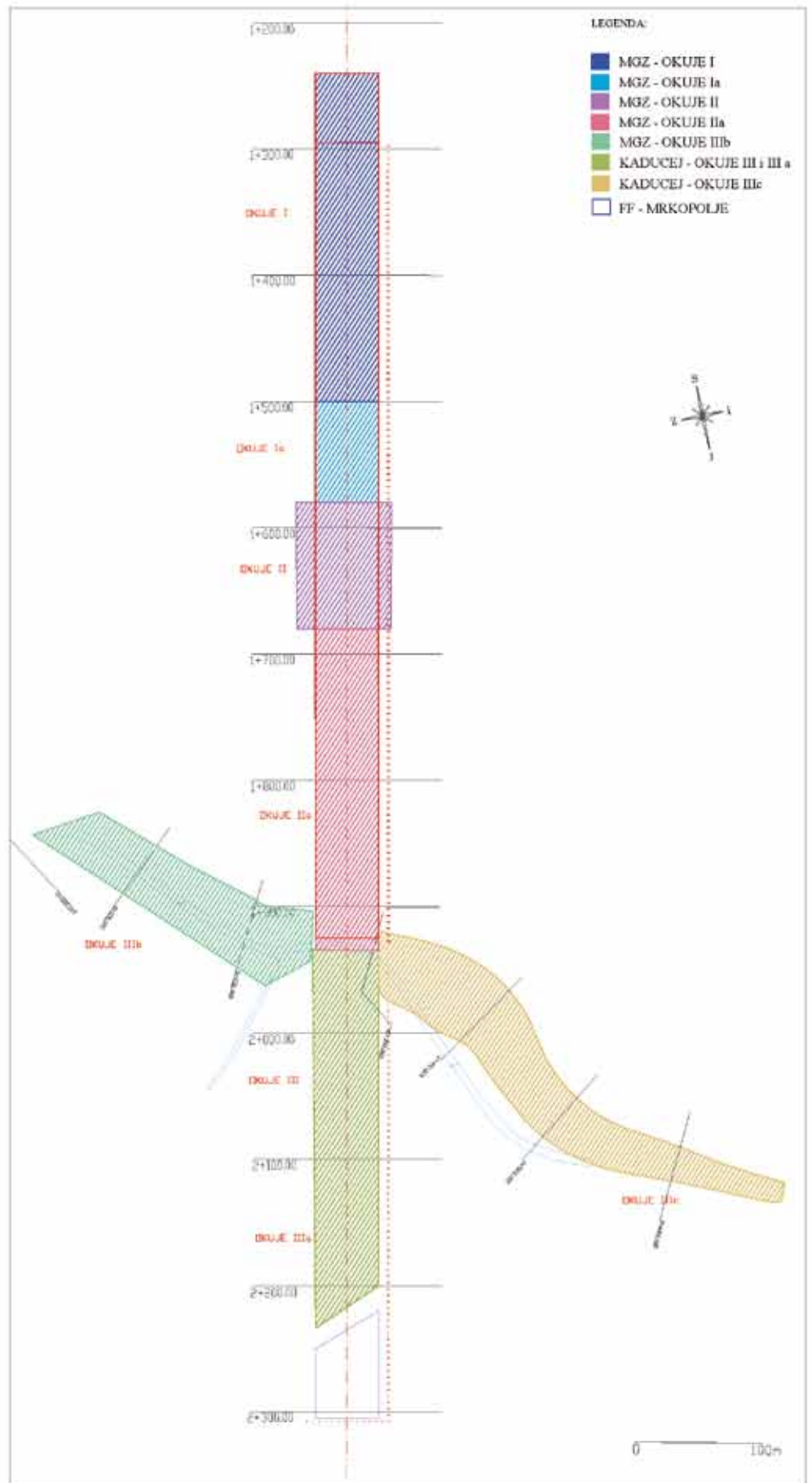


Fig. 2 The layout of the Okuje site with the position of individual units (made by: A. Sičić, A. Bugar)

THE WIDER AREA SURROUNDING THE OKUJE SITE – RELIEF CHARACTERISTICS

The traditional Turropolje Region was named after the 'tur', now extinct aurochs (*Bos primigenius*). In Medieval written sources is referred to as *Campus Zagrabienensis* and *Campus Nobilium Zagrabienensis* (Laszowski 1911, Vol. I: 36; Fürst-Bjeliš 1996: 10). The connection of Zagreb via the Sava River to its southernmost valley, which was primarily used as a natural resource or agricultural base, was thus recorded in its historical title. An understanding of the relief, the geological and hydrological characteristics of space and the conditions for economic development are necessary as a prerequisite for all human activities. They are also indispensable tools for interpreting archaeological periods.² Turropolje encompasses vast lowland encircled by natural borders – hills and rivers – the Sava River, the slopes of Vukomeričke Gorice (hills) and the confluence of the Kupa and Sava River. In a broader sense Turropolje is a part of the Pannonian geographical region and, in a narrow sense, is part of the Southwest Croatia Basin. It is characterised by a complex relief structure with fluvial accumulations and fluvial denudated relief types (Fürst-Bjeliš 1996: 10–11, 33–34). The Sava River is an important factor in the Turropolje Region's geomorphological and relief characteristics. Although it originates in mountainous areas, near Zagreb it takes on all the features of the lowland river, whose meandering profile is its main characteristic (Riđanović 1983: 35). Furthermore, due to the depositing of gravel in the slower lowland parts of the Sava River's path its riverbed is up to 5 metres different in height from the surrounding area and slightly changes its course which causes flooding of the lowlands along the Sava River. On the other side, the riverbeds of the Sava's tributaries are lower and deposit mud that settles on the plains and forms an impermeable layer where water is more easily retained, thus creating floodplains and marshes (Roglić 1974: 51; Fürst-Bjeliš 1996: 40–41). It is an extremely wetland area with a moderate continental climate with relative humidity and areas that were previously covered with forests (mostly oak and hornbeam) that today has been partially turned into agricultural land (Fürst-Bjeliš 1996: 44). The occasional flooding of the Sava and Kupa Rivers and their numerous tributaries have largely determined the environment and the living conditions, which is why water flow regulations have been implemented over the last hundred years. These also include the construction of the Sava-Odra Canal which has greatly altered the natural water mechanisms (Fürst-Bjeliš 1996: 41).

FIELD SURVEYING AND GEOPHYSICAL RESEARCH RESULTS

The Okuje Site was determined on the basis of intense field survey (Vujnović, Burmaz 2008; Burmaz, Vujnović 2009). A 100% sample was collected of a network of 10 x 10 m quadrants and, given the degree of visibility, 40 x 40 cm test trenches were dug every 10 or 20 metres (Burmaz, Vujnović 2009: 243). The entire area of the Zagreb – Sisak Motorway Second Section was field surveyed, with the highest concentration of archaeological finds being observed between Okuje and Mraclin settlements, from the Sava – Odra Canal in the northernmost part of the section (mileage 1+250) to the Mrkopolje Site in the southernmost part of the section (mileage 2+320) (Burmaz, Vujnović 2009: 243). Throughout the Okuje Site the finds were predominately medieval, yet it was observed that Roman period finds made up a larger percentage in the northern part of the site between mileage 1+250 and 1+800. From mileage 1+800 to 2+300 and to the east and west of the road there was a quantitative predominance of medieval material. A significant amount of metallurgical waste (slag) was collected in the area between mileage

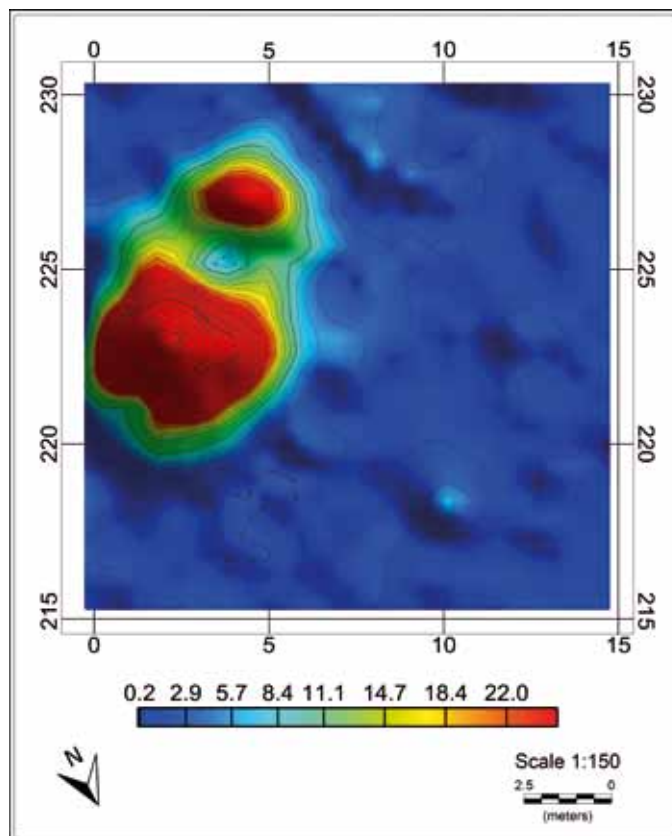


Fig. 3 Magnetometric image of the complex of waste pits related to iron production at the Okuje site (made by: B. Mušič)

² The starting point and indispensable work for the study and understanding of the Turropolje Region and its aspects is Borna Fürst-Bjeliš's 1996 doctoral dissertation entitled '*Historijsko-geografska analiza prostornog pojma tradicionalne regije Turropolje*' ('A Historical-geographical Analysis of the Spatial Concepts of the Traditional Turropolje Region').

1+400 and 1+500. An examination of the quadrants revealed the largest part was located north of the old stream and in the area of the stream bed, i.e. north of the area that was later excavated as a concentration of pits containing evidence of metallurgical activity (defined between mileage 1+500 and 1+600). It was later concluded that most of the slag found in the field survey was dragged by plowing further north of the stream to the area of the subsequently excavated Roman settlement and cemetery. The target areas were later geophysically examined. Of the three geophysical survey methods applied – magnetic, geoelectric resistance and georadar – the best results were provided by the magnetic method (Mušič 2008). Thermoremanent anomalies were most evident and, even prior to the archaeological excavation, an object related to metallurgical activity was clearly observed (Fig. 3).

AN ANALYSIS OF THE NATURAL POSITION AROUND THE OKUJE SITE IN THE CONTEXT OF THE ARCHAEOLOGICAL RESEARCH RESULTS

The Okuje Site spread in the direction from the north to the south and was 1070 m long and 50 m wide. It started in the immediate vicinity of the Sava – Odra Canal and ended where the Mraclin Toll Booth on the Zagreb – Sisak Motorway is situated today. About halfway along its length the Site was intersected by the Okuje – Mraclin local road, alongside which two narrower belts of a total length of c. 620 metres were investigated, which gave the ground plan of the excavation Site the appearance of an elongated cross (Fig. 2). The microlocation of the Okuje Site is characterised in the north by lowland prone to flooding and smaller hills with smaller watercourses to the south which flow into the Obdina Stream located to the north of the Site. The lowest elevation is about 104.3 m at the northernmost edge and rising to 109.6 m Above Sea Level in the south. Geomechanical probes have identified three types of geological substrates based on sediment granulation: clay/sandy clay, sand/gravelly sand and gravel/sandy gravel (Mušič 2008: 7, Figure B). During the archaeological excavation ten so-called geological probes were dug to determine the Site's basic geological and archaeological stratigraphy. Geological-engineering expertise determined that all layers at the Okuje Site are fluvial in character and, from a hydrogeological aspect, three categories of deposits have been defined, namely highly permeable (gravel and sand deposits), poorly permeable (mixtures of gravel, sand, clay and powder) and impermeable clay and powder deposits (Novosel 2011).³ Several meters thick layers of high-quality clay were observed in a geological probe in the centre of the Site (Fig. 4). Archaeological research also revealed old stream beds and a group of drainage canals which indicate that the environment was treated and adapted to season flood and humidity. The foundations of wooden buildings with pillars and raising the floor level is characteristic of traditional wooden Turopolje and Posavina architecture adapted to areas prone to flooding (Duić, Šimunović 1980: 21; Salopek et al. 2006: 11, 23). This concept can also be observed in certain types of archaeologically researched objects at the Okuje Site. The geological probes also determined the former groundwater level on which the wooden structures of six Roman wells have been preserved. These are also characterised by techniques that connect the corners of the wooden planks, which in turn directly indicate the methods used in the construction of above-ground level wooden buildings in the Roman settlement. An analysis of the type of wood used to produce the well construction determined that oak predominates in most samples.⁴ Due to its exceptional technical characteristics – durability, strength, elasticity and ease of processing – oak was used for constructions. It is also excellent for the production of charcoal (Sekelj Ivančan et al. 2019: 52, 65). An analysis of animal bones found in the settlement pits (mainly from medieval pits) revealed that, in addition to domesticated animals, numerous bones were found that belonged to forest-dwelling animals. The numerous remains were those of deer, the bones of wild boar and roe deer were also evident in addition to sporadic, but significant, examples of aurochs bones (*Bos primigenius*) (Hincak 2010). This most certainly additionally proves that the area surrounding the site was at one point much more forested, even today it is not far from the Mraclinska and Okujaska Dubrava and the Turopoljski Lug (forests). By sublimating all the natural characteristics from the environment in which the technical solutions used to design the buildings reveal environmental adaptation and the use of natural resources originating from the Site itself, we are able to briefly list the archaeological results of the research at the Okuje Site. Here there were many of the preconditions not only for habitation but also iron production, which is well evidenced by the Okuje toponym which, once heard, is a place associated with metalworking or forging. The technical term 'okujina' (also ogorina, cunder, kovarina, kovačina, engl. 'steel mill scale, mill scale') is by-product in steel production (Sofilić, Brnardić 2013: 141–144).

3 Geological expertise was provided by the late Tomo Novosel MSc Eng. from the Zagreb Engineering Institute who, as an exceptionally experienced field geologist, significantly contributed to our understanding of the Site's geological characteristics, for which we are extremely grateful.

4 Preliminary analyses was provided by Prof. Jelena Trajković from Faculty of Forestry and Wood Technology of the University of Zagreb.

At the lower northern part of the Site, running alongside the old stream bed, several settlement pits were identified which date from the Early Bronze Age. Here, to the south and north of the old stream, the largest part of the Roman period rural settlement has been preserved. It dates mainly from between the 3rd and 5th centuries. The smaller cremation cemetery dates from between the 2nd and 3rd centuries which, at least in part, is contemporaneous with the nearby settlement. The older cemetery is located to further south, and was used, judging by the radiocarbon dating samples, in the last third of the 1st century. It is a modest autochthonous cremation cemetery. La Tène Age pottery was found sporadically within the Roman period pits, and it is possible that the core of the La Tène Age settlement is located in the immediate vicinity of the excavated site. Only about half of the Site is on slightly raised terrain, which forms a kind of terrace about 3.5 metres higher than the surrounding terrain and is ideal for tracing a Roman road. In part it overlaps with the route of today's road. Although it was only preserved in the traces of gravel 'pavimentum', with remains of wheel ruts and side ditches alongside the road, 286 m of the road was defined. It is believed that this is the Emona – Siscia Road, the remains of which were previously thought to be between the area between Okuje and Mraclin (Klemenc 1938: 29). To the south of the road there is a web of smaller hills, where most of the large High Medieval-era settlement has been explored.⁵ For the most part this settlement dates from between the 13th and 15th centuries. It also extends to border the modern (and thus Roman) road route to the north. This settlement comprehensively destroyed almost all previous Roman period objects in the vicinity of the road. Also, judging by the pottery finds, a few pits can be approximately dated to the 10th and 11th centuries. Evidence that there was even an earlier Medieval settlement on this Site dating from the 7th or 8th centuries has been subsequently confirmed only by radiocarbon-dated charcoal found in one slag sample.



Fig. 4 Layers of clay in a geological probe in the centre of the Site (photo by: B. Rožanković)

⁵ This covered an area between 150 000 and 200 000 m², which was confirmed in part by the excavation itself and in part by the extensive field surveying (Vujnović, Burmaz 2010: 245).

A DESCRIPTION OF METALLURGICAL ACTIVITY AT THE SITE

The so-called metallurgical facility, which was also defined by geophysical research (Fig. 3), was positioned between mileage 1+500 and 1+600, on the southern side of the excavated old stream bed (Fig. 5). The stream stretched from NE to SW, was about 10 metres wide and was about 80 metres in length. The stream was certainly flowing during Roman period and later, and pieces of roman brick and pottery fragments were found in layers of backfill. Several fragments of smelting waste were also found in the backfill of the stream bed. Inside an area of approximately 100 m² (11 x 10 m) a group of shallow connected waste pits filled with metallurgical waste were found about 25 metres from the edge of the old stream (Figs. 6, 7). Immediately below the arable land, on a slightly rounded surface, an excavation collected about 500 kg of assorted metallurgical waste – smelting slag, the burnt walls of smelting furnaces and ceramic tuyeres – a highly specific waste later associated with the production of bloomery iron. The course of the excavation was very complex and impractical due to the rainy, muddy and snowy conditions. The defined deadline for completion of the protective research did not work in its favour either. Given the character of these findings the waste was discovered in a secondary position, i.e. deposited in pits away from the area where the production took place. Namely, traces of the smelting furnace were not found, but the amount of slag and technical ceramics, and the fact that the pits were located relatively close to the eastern edge of the excavation, probably indicates that only the edge of the workshop complex was revealed by the excavations. This would be a fairly common picture of findings relating to smelting activities in which a large amount of waste was deposited in the marginal areas of the workshop as at the Virje – Volarski breg/Sušine site (Sekelj Ivančan 2014; 2020: 3). The fact that this activity at the Okuje Site took place near the stream bed indicates the importance of water in the process of iron preparation and production. It is also worth pointing out the proximity of two investigated Roman period wells which were respectively 17 and 21 m away from the metallurgical facility. It is not entirely clear whether they were contemporaneous with the time of iron production, as there were no pieces of slag in the backfills. Between mileage 1+500 and 1+600 slag was also found in a several waste pits in the immediate vicinity or away from the so-called metallurgical facility, although in smaller quantities and without accompanying ceramic finds. However, 21 kg of smelting waste was revealed in a small pit some five metres away from the main complex of waste pits, including a piece of charcoal that was noticed inside one compacted piece of slag. This was found during the later stages of the TransFER Project analysis (Fig. 8). Radio-carbon dating placed it from between the 7th and 8th



Fig. 5 A view of an old stream bed at the Okuje site (photo by: A. Bugar)

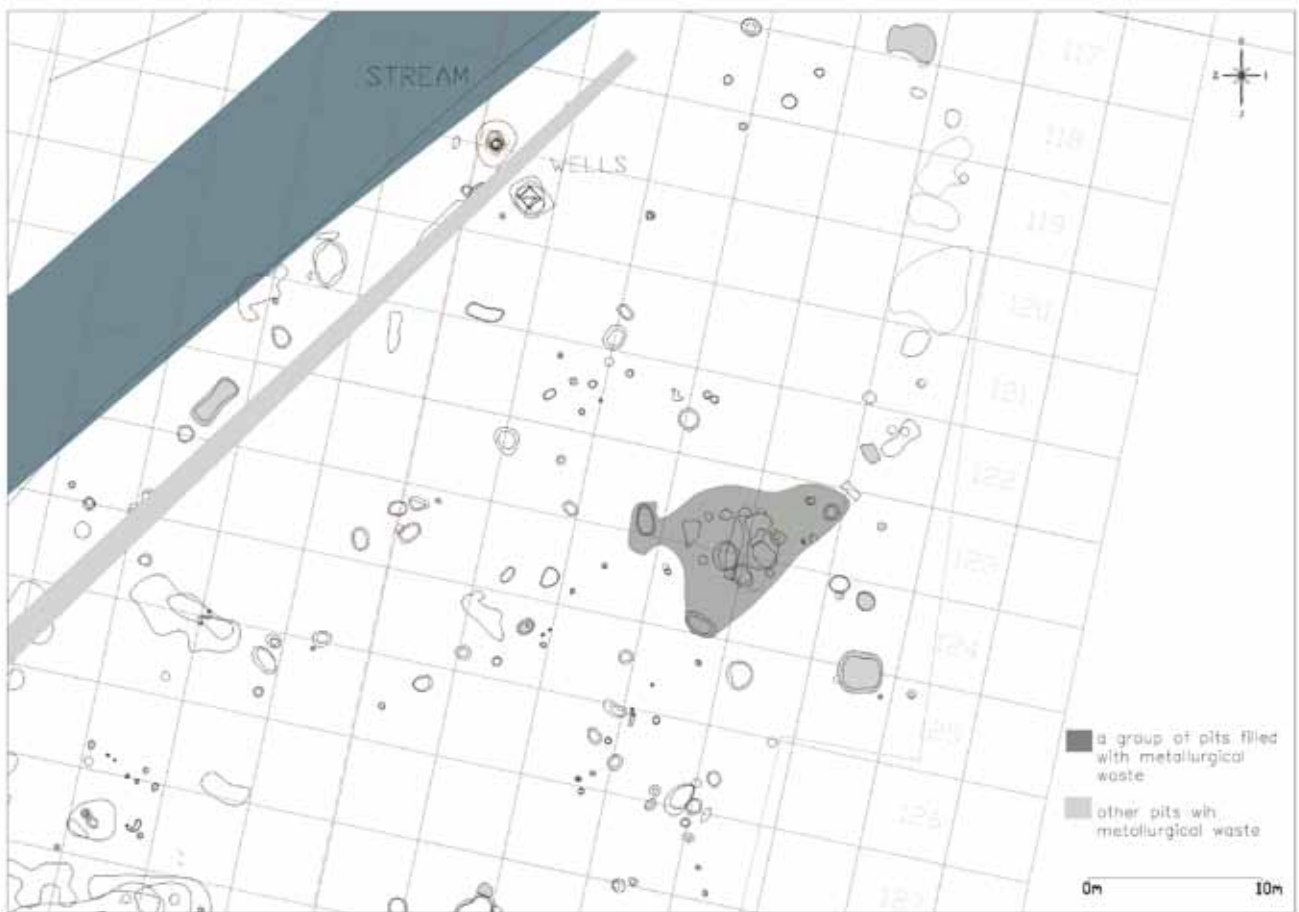


Fig. 6 Plan of the excavated features of the part of the Okuje site where the metallurgical activity was observed (made by: A. Sičić, A. Bugar)



Fig. 7 Remains of the complex of waste pits related to iron production (photo by: G. Đurić)



Fig. 8 A post-reduction slag with a piece of charcoal in the slag mass (photo by: M. Gregl)

centuries. Slag was also found individually and in small quantities in the backfill of a few Roman period pits. Also it was found in High Medieval-era pits, yet additional secondary roman-era material also appears in the backfill. As we explained earlier, the large High Medieval-era settlement thoroughly destroyed the Roman period settlement along the Roman road, and also the earlier Medieval settlement. The area used for iron production was relocated from Roman period settlement objects, and the first Medieval-era objects were around 250 metres away. Given that it was, in all probability, a proper workshop with a great deal of waste, fire and smoke, it would have been desirable to site it at a greater distance from the settlement.

METALLURGIC WASTE ANALYSIS

The first field-phase interpretation revealed that these finds are related to bloomery iron production, for which I thank Professor Aleksandar Durman (Bugar, Mašić 2013; Bugar 2021). During the initial attempts of interpretation there were no conditions or space for a comprehensive review of half a tonne of metallurgical waste. Therefore the samples used to define the chemical composition required to prove or disprove the bloomer iron thesis were accordingly selected by appearance, differing colour or surface appearance and slag compactness or porosity. Chemical analyses (XRF, ICP-AES and ICP-MS) defined the main chemical elements, the medium and the trace elements, and the measured amount of iron, manganese, cobalt and nickel present in the trace element concentration range undoubtedly associated the finds with iron production (Rončević et al. 2013). A more detailed review of the specific type of waste took place during the TransFER Project and primary classification took place.⁶ In addition to the fragments of clay furnace walls, ceramic tuyeres, slag from inside furnaces, liquid slag, and plain convex forging slag (Figs. 9–11), very small fragments of lumps of ore were found. It was initially assumed that the iron ore used in the production of bloomery iron dating from the Late Antiquity Period at the Okuje Site was brought in from a mine somewhere around Siscia (today's Sisak), but an analysis of hematite ore from the ore-bearing areas near Sisak showed no similarities with the Okuje Site's analysed slag's chemical composition.⁷ On the other hand, the microstructure of one of the analysed slag samples from the Okuje Site revealed predominant quartz and mineral goethite, which are characteristic of iron oxyhydroxides. This sample was also characterised by increased iron, silicon and nickel content, which is comparable to bog iron ore analyses from other sites that were presented in recent publications (Thelemann et al. 2016). Therefore we can most likely associate this Okuje Site sample with bog iron ore (Nemet et al. 2018: 33). These data were further supported by an analysis of unmelted ore that utilised the Powder-X-ray diffraction (PXRD) method. An ore sample was preserved on the surface that was interpreted as part of a clay furnace wall (Fig. 12). A Powder-X-ray diffraction (PXRD) analysis of this sample revealed that the main phase in the sample was alpha-Fe(OH)-goethite. Quartz minerals, epsilon-phase FeO(OH), as well as other quartz minerals were also present in a sample but in a much smaller part.⁸

Pre-industrial iron production required certain requisite preconditions, namely a sufficient amount of wood for the production of charcoal, clay for the construction of smelting furnaces, water for preparation and post-production processing

6 After the archaeological excavation the material was stored for a decade and was only partially investigated. By moving these findings to improved museum depot the conditions for more thorough investigation were created. I would like to personally thank Tajana Sekelj Ivančan and Tena Karavidović who performed the tedious overview and performed the primary classification of metallurgical waste from the Okuje Site during the TransFER Project.

7 Relating to this detail, I would like to thank Sanda Rončević PhD who performed a comparative analysis.

8 This analysis was made by the Institute of General and Inorganic Chemistry of the Department of Chemistry at Zagreb University's Faculty of Natural Sciences (Prof. Dubravka Matković-Čalogović PhD).



Fig. 9 Fragment of slag from inside furnace (photo by: H. Jambrek)



Fig. 10 Liquid slag from the Okuje site (photo by: H. Jambrek)



Fig. 11 Fragments of ceramic nozzles from the Okuje site (photo by: M. Gregl)



Fig. 12 The fragment of furnace wall with attached slag and solid particles of iron ore from the Okuje site (photo by: H. Jambrek)

of bloomery iron and, the most basic prerequisite of all, iron ore (Pleiner 2000: 270). The environment around the Okuje Site was certainly wooded, intersected with streams and the former inhabitants would have been able to dig up high-quality clay at the site. Given that it was a humid environment prone to flooding, which would have been far more pronounced in the past, and given that the analysis results of a sample were associated with bog iron ore, it is possible that the Turopolje area, like the Podravina region, could create the conditions for natural bog iron ore in the past.

ACKNOWLEDGMENTS

I would like to thank our Professor Aleksandar Durman, PhD for the initial insights into bloomery iron production. I would also like to thank Professor Sanda Rončević and her team from the Division of Analytical Chemistry at the University of Zagreb, Faculty of Natural Sciences with whom it was a pleasure to work. I would like to thank Tajana Sekelj Ivančan for her enviable persistence, work and, above all, her patience. I would like to thank Tena Karavidović for her sharp mind. I would like to thank the whole team that excavated the Okuje Site, especially my colleagues Dženi Los, Nikolina Antonić, Iva Marochini, Nikša Vujnović and Josip Burmaz.

Translation: Snježana Husnjak Pavlek, Robert Jenkins

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ARCHAEOLOGICAL FINDS OF METALLURGICAL ACTIVITIES ON THE TERRITORY OF THE RIVER DRAVA BASIN DURING IRON AGE AND ANTIQUITY

In the period from 2016 to 2020 extensive field surveys and perambulations of the River Drava Basin area, aimed at recording archaeological sites containing finds connected to the production and/or processing of iron, were undertaken. The results of the surveys showed that a surprisingly large number of settlements, dated to the Iron Age and Antiquity, contained some type of finds connected to metallurgy. This conclusion was also confirmed by a recent discovery of a larger lump of slag found within an excavated Early Iron Age settlement context. Furthermore, during an extensive review of the Study Archaeological Collection of the Koprivnica Town Museum a small number of finds connected with metallurgical activities, originating from Early Iron Age and Roman period sites, excavated between 1979 and 1990, was found. Upon their examination, it was realised that only brief and scarce mention of these finds as well as their interpretation, was noted within the excavation publications if any.

The first aim of the paper is to present and give a preliminary interpretation of the “forgotten” pieces of slag from the Koprivnica Town Museum Study Archaeological Collection and the recently conducted excavation. The second part of the text gives a preview of positions containing metallurgical finds collected during the mentioned surveys. Based on the collected information, the author discusses the type and intensity of metallurgical activities within the two periods. The results presented were gained through the activities within the TransFER project (IP-06-2016-5047), financed by the Croatian Science Foundation.

Key words: Iron Age, Antiquity, archaeological excavation, field survey, iron metallurgy, River Drava Basin

INTRODUCTION

During 2019 and 2020, in the course of photographic documentation, rearrangement and construction of a database of the complete Study Archaeological Collection of the Koprivnica Town Museum,¹ new finds associated with metallurgical activities in Antiquity and Iron Age on the territory of the River Drava Basin emerged. The finds originate from several archaeological excavations conducted between 1979 and 1990. The publications, which followed the excavations, gave very little or even no information at all regarding the type of these finds or their interpretation, besides their attribution as pieces of slag.

About the same time, in the course of a small-scale excavation of the Prehistoric and Early Medieval settlement at the site Međuriće VI near Torčec in 2019, a clod of slag was found on the bottom of an Early Iron Age dugout. Even though this find may not seem as much, it gave a new perspective to the examination of pieces of slag originating from the above-mentioned older excavations, especially the ones dated to the Hallstatt period. The reason for this lies in the fact that during the TransFER project, which is the first Croatian project that deals with the production of iron, due to its short duration and limited funds metallurgical activities on the territory of the River Drava basin were archaeologically confirmed

¹ The Study archaeological collection contains unpublished material (pieces of pottery, glass, construction ceramic) and samples (animal bones, slag, charcoal) from all the archaeological sites on the territory of the River Drava Basin which were excavated or recognised during field surveys by the Museum's archaeologists since its foundation in 1951.

only during Late Antiquity (Sekelj Ivančan, Mušić 2014: 179; Valent, Sekelj Ivančan, Šoštarić 2021) and Early Medieval period (Sekelj Ivančan 2010; Sekelj Ivančan et al. 2019: 48).

Therefore, even though one might think that the finds presented further in the text may not be considered as representative, their interpretation in connection with the processing of a semi-finished product and/or the production of bloomery iron gives an important insight into metallurgical activities in the River Drava Basin during Iron Age and Antiquity. And that is what this paper is about.

OLD EXCAVATION, NEW INFORMATION

As an introduction, it is important to mention that none of the pieces which will be presented, was found within the context of any kind of a metallurgical workshop. Some of them were discovered within the settlement context, while most of them were found during the excavation of graves.² Based on the preliminary macroscopic analysis, the finds are divided into technical ceramics that could be related to metallurgical activities (vitrified smelting/smithing furnace walls, tuyeres) and bloomery iron production and/or processing (primary smithing) slag.³ Given their fragmentation level, i.e. the poor state of preservation, it was not possible to give a unison interpretation of each piece. In such cases, two interpretations are given. All the presented pieces are listed in the Table (Tab. 1) with the context of their discovery and interpretation, as well as in the accompanying Plates (Pl. 1–3).

The overview of metallurgical finds found during the work on Study archaeological collection of the Koprivnica Town Museum will start with pieces of slag collected during excavations of the Kunovec Breg – Kod poklonca site (Map 1: 1), the presumed position of the roman station *Sonista* (Tab. Peut.) i.e., *Sunista* (Itiner. Hier.) (Fulir 1967: 180–183; Marković 1990: 125–131; 1997d: 177). The site was excavated during three preventive campaigns, in 1979, 1980 and 1990, during which parts of a settlement and 11 graves, dated between the late 1st and second half of the 2nd century, were unearthed (Demo 1980a; 1980b; 1981; 1982a; Marković 1990). In total, twelve pieces of slag were found in nine different contexts (Tab. 1: 1–9, Pl. 1: 1–9), and all of them on the area of the cemetery.⁴ The finds were not mentioned in any of the publications, but the results of the 1990 campaign record the find of several pieces of “iron oxide lumps” found within the ditch surrounding the cemetery (Marković 1990: 129), which were unfortunately not preserved.

The second site is Delovi – Grede I (Map 1: 2). It was excavated during a preventive archaeological campaign conducted in 1981 and 1982. During the course of the research, 49 pits were investigated, dated in the late phase of the Late Bronze Age, Late Iron Age, Early, High and Late Medieval period (Marković 1984; 1997a: 149–150). The publication in which the finds were published mentions large amounts of slag, interpreted as forging slag, within the High Medieval context (Marković 1984: 302, Pl. 11: 1–4). These finds should however be dated in a somewhat later period (Valent 2019b).⁵ However, in the listing of the finds discovered within Pit 7, dated in the late phase of the Late Iron Age, i.e., in the second half of the first century BC, the author does not mention the discovery of one piece of slag found within the Koprivnica Town Museum Study archaeological collection (Tab. 1: 10; Pl. 2: 10). This information is significant due to the author’s suggestion that a scraper found in the same context as the slag might be of local production. The premise behind his conclusion and the interpretation of the scraper’s origin lies in the lack of parallels for such a scraper in any known excavated Late Iron Age sites at that time (Marković 1984: 298).

The next site on which a piece of slag was found is Draganovec (Map 1: 3) (Marković 1997b: 152). This site is also presumed to be the position of another roman station, the *Piretis* (Tab. Peut.) i.e., *Peritur* (Itiner. Hier.). It was excavated in 1981 and 1982 (Demo 1982b).⁶ The only collected piece of slag, interpreted as slag from the bottom of a furnace (Tab. 1: 11; Pl. 2: 11), was found as a surface find and it is not mentioned within the publication, or in the excavation documentation. Even though the site was not dated, the change in the orientation of the excavated building, which can be compared with similar changes in building orientation in the nearby site of Ludbreg, i.e., *Iovia* (Vikić-Belančić 1983–1984: 161), suggests that it functioned at least until the fourth century.

2 The sites will be presented chronologically by the year in which the metallurgical finds were discovered.

3 I would like to express my gratitude to my colleague, PhD student Tena Karavidović from the Institute of Archaeology in Zagreb for her knowledge and assistance in determining the pieces presented in this paper.

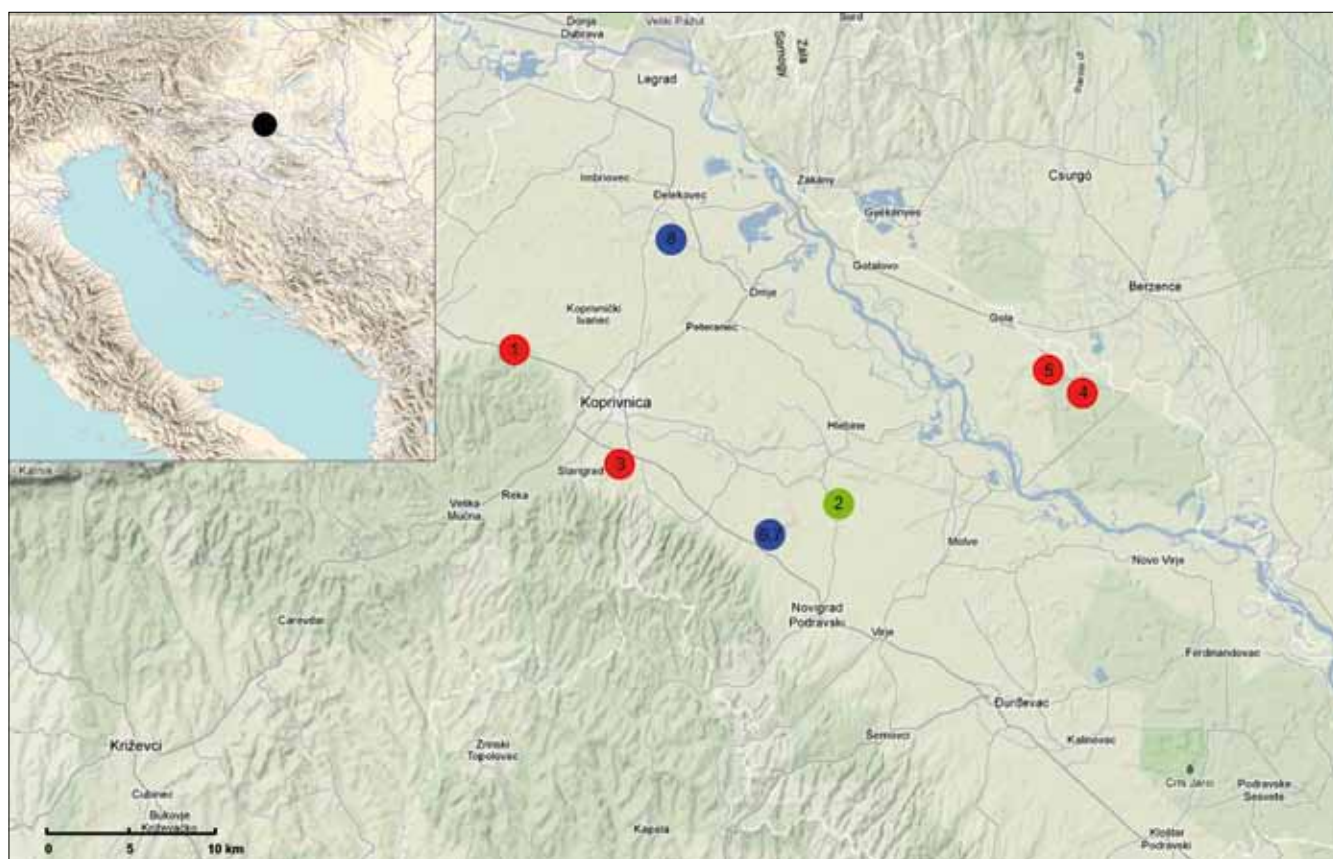
4 The context of finds and the dates when they were excavated allows this conclusion: In 1979 Trench Ia and Ib were placed on the area of the cemetery, while Trenches II and III were set on the area of the settlement. In 1980 five trenches were excavated on the area of the settlement, during January, while the cemetery was excavated in May – the trench was named Trench 2 (of the cemetery). The campaign conducted in 1990 was focused only on the cemetery.

5 It is not clear what happened with the majority of the collected slag from the Medieval context because only several pieces found within Pits 35 and 42 remained in the Koprivnica Town Museum.

6 The results of the 1982 campaign were not published. They are known only from the field journal records which are stored in the Koprivnica Town Museum (Marković 1978–1997: 108).

Table 1 Finds connected to the metallurgy of iron in the River Drava Basin during Prehistory and Antiquity, archaeological excavations context (made by: I. Valent)

No.	Site	Context	No. of pieces	Weight (g)	Interpretation	Datation
1	Kunovec Breg 1979	S-Ia, □ II; 50-70 (-20) cm; 2nd level; 8.5.1979.	1	13	Vitrified furnace wall with slag remains (vicinity of the nozzle)	Antiquity
2	Kunovec Breg 1979	S-Ib, □ I; 1st level; 30-50 cm; 8.5.1979.	2	145	Unidentified; Possibly smelting slag	Antiquity
3	Kunovec Breg 1979	Franjo Seretin's parcel; 50 cm; 10.5.1979.	2	49	Furnace wall with some vitreous slag	Antiquity
4	Kunovec Breg 1980	S-II; □1/2; Step 1; 29.5.1980.	1	13	Vitrified furnace wall with vitreous slag	Antiquity
5	Kunovec Breg 1980	S-II; □14,15; 78-98 cm; Pyre (?) 29.5.1980.	2	20	Tap slag; Unidentified piece	Antiquity
6	Kunovec Breg 1980	S-II; □20; 30-50 cm; 21.5.1980.	1	37	Forging slag / Slag from the bottom of a furnace	Antiquity
7	Kunovec Breg 1990	□D/4; 90-100 cm; 5.3.1990.	1	75	Extremely vitrified furnace wall	Antiquity
8	Kunovec Breg 1990	Grave; □C-D/8-9; 80-100 cm; 12.3.1990.	1	32	Vitreous slag alongside the furnace wall	Antiquity
9	Kunovec Breg 1990	□F/6; 80-90 cm; Grave	1	34	Unidentified; Possibly forging slag	Antiquity
10	Delovi - Grede 1982	Pit 7	1	57	Forging slag / Slag from the bottom of a furnace	La Tène
11	Draganovec 1982	Surface finds	1	68	Slag from the bottom of a furnace	Antiquity
12	Novačka - Gradina 1985	Tunnel; Tumulus S; 1st - 2nd shovel; 21.5.1985.	2	9	Geological/Pedologica formation of sandy-iron composition	Antiquity
13	Gola - Vlaško polje 1985	Tunnel; Grave1; 3rd shovel; 28.5.1985.	1	37	Forging slag / Slag from the bottom of a furnace	Antiquity
14	Vlaislav - Mulji 1985	S-II; 50-70 cm; 17.6.1985.	1	138	Forging slag / Slag from the bottom of a furnace	Hallstatt
15	Vlaislav - Mulji 1985	S-II; 80-100 cm; 8.7.1985.	1	29	Magnetic piece of (forging ?) slag	Hallstatt
16	Vlaislav - Mulji 1988	From the edge of the cannal	1	63	Smelting slag	Hallstatt (?)
17	Vlaislav - Mulji IIA 1988	1st shovel; □ABC/1-10; 15.11.1988;	3	143	Mildly vitrified furnace walls	Hallstatt
18	Vlaislav - Mulji IIA 1988	S-I, □A/1-5; 5th shovel; 17.11.1988;	2	47	Vitrified furnace walls	Hallstatt
19	Vlaislav - Mulji II 1989	Vlaislav - Mulji II 1989; S-I; 2nd level; 27.6.1989.	7	188	Furnace walls; Furnace walls with deposited slag; Vitreous slag	Hallstatt
20	Torčec - Međuriće VI 2019	SU 3; Sample No. 31	1		Forging slag	Hallstatt



Map 1 Position of archaeological sites listed in Table 1: 1) Kunovec Bege – Kod poklonca; 2) Delovi – Grede; 3) Draganovec; 4) Novačka – Gradina; 5) Gola – Vlaško polje; 6, 7) Vlaislav – Mulji, Vlaislav – Mulji II, IIA; 8) Torčec – Međuriće 6 (Blue: Hallstatt; Green: La Tène; Red: Antiquity) (made by: I. Valent)

The two following sites on which three pieces of slag connected to iron production/iron processing were found are located in the region of Prekodravlje, north of the Drava River i.e., between the river Drava and the Croatian – Hungarian border. Both of them are positions of tumulus cemeteries dated within the second and the beginning of the third century AD. The excavation documentation and publications do not mention any finds connected to iron metallurgy. The first site is Novačka – Gradina (Map 1: 4), excavated during four campaigns, in 1978, 1980, 1982 and 1985 (Šarić 1979; Marković 1997e).⁷ The only two pieces, which can be connected to iron metallurgy, were found during the excavation of Tumul S in 1985 (Tab. 1: 12; Pl. 2: 12a, b). The second site is Gola – Vlaško polje (Map 1: 5), also excavated during four campaigns, of which three were conducted between 1971 and 1973 and the final one in 1985 (Kolar 1971; 1972; 1973; 1976: 107–108; Marković 1997c: 158).⁸ The only known lump of slag from the four campaigns of this site was found during the excavation of the Tumul G-1 in 1985 (Tab. 1: 13; Pl. 2: 13).

The last two archaeological sites which fall into the “old excavations” preview are Vlaislav – Mulji 1 and Vlaislav – Mulji 2 / 2A (Map 1: 6, 7). Both of them were found during a pipeline preventive field survey (Marković 1985: 37–38). The Mulji 1 site was excavated in 1985 (Marković 1988: 186–188; 1997f) and Mulji 2A in 1988 / 1989 (Marković 1997g; 1978–1997: 164–173).⁹ Only the results of the 1985 campaign of Mulji 1 and the results of the 1987 field survey on positions Mulji 2 A-D were published.

⁷ Only the first excavation campaign results were published (Šarić 1979). The documentation of the following campaigns is stored in the Koprivnica Town Museum (Marković 1978–1997: 51–53, 109, 145–146).

⁸ The first three campaigns were conducted by the Koprivnica Town Museum curator Sonja Kolar, while the last season was managed by Ivan Šarić, Regional Institute for the Protection of Monuments in Zagreb (RZZSK). Results of the 1985 campaign were not published. They are known only from the field journal records which are stored in the Koprivnica Town Museum (Marković 1978–1997: 147).

⁹ The site Mulji 2 was first found during the preventive excavation of Mulji 1 in 1985. It was recognised as a multilayered site with occupation during Antiquity and Middle Ages (Marković 1988: 187). During the course of field surveys conducted in 1987, it was realised that the site is larger than it was previously thought. In order to separate the newly discovered area of the site, on which the later trenches in 1988 were placed, and distinguish it from the part noted in 1985, the newly defined positions were marked with capital letters A-D, signifying occupation during different periods.

The results of the Mulji 1 excavation mention the discovery of one piece of slag (Tab. 1: 14; Pl. 2: 14) and a lump of iron (Tab. 1: 15; Pl. 2: 15) (Marković 1988: 186).¹⁰ The excavated Iron Age ceramic finds found alongside the two mentioned iron pieces were preliminary dated to a wide time frame between early Ha C (maybe Ha B3) and early Ha D phase i.e., between 8th and 6th century BC (Marković 1988: 187, 195, Pl. 5).

As it was mentioned, the Mulji 2A site was recognised during a survey in 1987. Most of the collected material originated from two Late Iron Age pits, while some pieces could be attributed to the late phase of the Late Bronze Age (Marković 1988: 188). The first possibility to excavate this site appeared in 1988, but due to lack of funds, the campaign was finished the following year. During the course of the campaign, several finds connected to the metallurgical process were found (Tab. 1: 16–19; Pl. 2: 16–17; Pl. 3: 18–19). The excavation trench was placed alongside an artificial canal in close proximity to two Late Iron Age pits recognised in 1987.¹¹ Some finds collected in the 1988 campaign originate from a disturbed context but some were found in a closed context. The only known piece of smelting slag (Tab. 1: 16; Pl. 2: 16) was found on the edge of an artificial canal alongside pieces of Eneolithic, Late Bronze Age, Early and Late Iron Age ceramic. The same time frame applies for the context within which three pieces of mildly vitrified furnace walls were found (Tab. 1: 17; Pl. 2: 17 a–c) – Marković states that the finds collected within the first 40 centimetres originate from the canal which was then spread through a wider surface on the parcel by the excavator and agricultural machinery (Marković 1978–1997: 164–165). The only two pieces found in excavated context during this campaign were two fragments of vitrified furnace walls (Tab. 1: 18; Pl. 3: 18 a, b) found within the fifth shovel level.¹² During the following year, seven more pieces of furnace walls and vitreous slag (Tab. 1: 19; Pl. 3: 19 a–g) were found in a layer recognised as Level 2: light grey soil with finds, dated to the Early Iron Age. The level stretched between 20 and 80 cm of depth with bottoms of pits reaching approximately 120 centimetres (Marković 1978–1997: 171). Based on the available documentation (field documentation with sketches) it is possible to conclude that the finds from the 1988 fifth shovel level can be connected with the 1989 Level 2 and dated to the Early Iron Age.

The last piece of slag, which will be presented in this preview, was found during a trial excavation of the Torčec – Međuriće 6 site in 2019 (Map 1: 8) (Tab. 1: 20; Pl. 3: 20). Based on the collected surface finds the site was long ago recognised as the position of a settlement from the Early Iron Age and Early Medieval period, and it was excavated for the first time in 2007 (Kovačević 2009). The mentioned piece of slag was found on the bottom of a large but shallow Early Iron Age dugout (Fig. 1), situated in close vicinity to Early Iron Age features excavated in 2007. Given the close relationship of



Fig. 1 Torčec – Međuriće 6. Lump of forging slag at the bottom of an Early Iron Age dugout (photo by: I. Valent)

10 Both finds were also mentioned within the field diary (Marković 1978–1997: 149, 150).

11 The 1988 documentation mentions the Late Iron Age pit 2 recognised a year earlier. Some new finds were collected from it. Marković mentions that they plan to excavate the pit if there will be enough time and financial resources.

12 There is no reference of depth in the documentation but the pieces were found within a level that was not disturbed and full of ceramic (Marković 1987–1997: 166).

the contemporary objects excavated during both campaigns, as well as the similarities in collected material, the 2019 excavated dugout can be dated within the same time frame as the pits excavated in 2007, which according to Kovačević corresponds to the Ha C1b - Ha C2 period (Kovačević 2009: 66) i.e., within the 7th century BC.¹³

RESULTS OF THE FIELD SURVEYS

One of the primary objectives during the first year of the TransFER project was to establish a database of archaeological sites with finds connected to metallurgical activities (slag, tuyeres, furnace walls). In order to do so, extensive field surveys and perambulations of the River Drava Basin were undertaken during 2017 and 2018, as well as reviews of the Koprivnica Town Museum archaeological collection, Zvijerac family archaeological collection in Torčec (AZoZ) and Josip Cugovčan archaeological collection in Podravske Sesvete. As a result of these activities, a preliminary database of sites was established, which continues to grow with almost every new field survey.

In order to have a better understanding of metallurgical processes conducted on the territory of the River Drava Basin during the Iron Age and Antiquity, besides the finds presented in the previous paragraph, it is important to present and analyse the results of the conducted surveys (Tkalčec 2017; Krznar 2018; Valent 2018; 2019a), as well as the publications which followed (Valent et al. 2017; 2018; 2019). Unfortunately, extracting reliable conclusions about the period to which the surface finds belong is sometimes not an easy task.

Even though surface finds will reveal the existence of a metallurgical activity on the site, the problem appears when the position is occupied during two or more different periods. In these cases, it is not possible to connect the collected metallurgical finds with a specific period. One might argue that the pieces of pottery found in the same area as the slag provide a solution to this doubt but this may not be so due to the dispersion, i.e., mixing of finds from different contexts during agricultural works. Furthermore, even though the position of the workshop is usually situated slightly remote from the settlement (Sekelj Ivančan, Karavidović 2021: 81), large quantities of slag are often found within the features in the settlement (Valent, Tkalčec, Krznar 2021: 5, no. 9). Therefore, considering only the surface finds sometimes it is not possible to distinguish if the collected slag originates from the position of the workshop or the settlement. Moreover, this doubt increases with every new factor – what if the workshop is situated on the area of a settlement from an earlier period or *vice versa*, or what if the collected finds were secondarily deposited (older finds found within younger features). So, due to multiple variables in analysing all the possibilities of surface finds connected to metallurgy and their connection to a specific period, especially on a multi-layered archaeological site, I believe that the best approach in their interpretation, until future excavations prove otherwise, is in presenting all the contextual parameters which might lead to a conclusion concerning their potential datation.

During the conducted surveys and perambulations, 167 archaeological sites¹⁴ containing iron-connected metallurgical finds were recognised on the territory of the River Drava Basin (Tkalčec 2017; Krznar 2018; Valent 2018; 2019a; 2017; 2018; 2019) in total.¹⁵ Since the paper deals with finds connected to metallurgical activities during Iron Age and Antiquity, single layer archaeological sites dated only to the Medieval and Early Modern Period will be omitted from the following preview, as well as the sites mentioned above. The analysis of the results is therefore as follows: based on the accompanying pieces of pottery 4 sites¹⁶ are dated to Late Iron Age,¹⁷ 13 to Antiquity,¹⁷ 8 to Late Iron Age and Antiquity,¹⁸ 5 to Late Iron Age and Medieval period,¹⁹ 27 to Antiquity and Medieval period,²⁰ 11 to Late Iron Age,

13 I would like to thank the colleague PhD Saša Kovačević from the Institute of Archaeology in Zagreb, director of the 2007 excavations, for the preliminary examination of the Iron Age finds collected during the 2019 campaign.

14 The term position is used due to a fact that some broad and multi-layered archaeological sites are divided into smaller positions based on different representations of material i.e., different occupation periods of the site, just as is the case with the Mulji 2 A-D site.

15 The majority of sites have been published in the mentioned references, but some still have not.

16 Peteranec – Novi krči I (Učoš's parcel), Peteranec – Novi Krči I (Josip Kolesar parcel), Peteranec – Novi Krči III (Joja's parcel), Sigetec – Ogradine IIC (Valent 2018: 166–167, 172–173, 176–177, 226–227).

17 Field surveys: Bakovčice – Veliko polje, Đelekovec – Močvar 1A, Đelekovec – Vidak II, Koledinec – Koledinski lug I, Koledinec – Koledinski lug IIA, Koledinec – Koledinski lug III, Peteranec – Novi krči I (Ivica Varga parcel), Sigetec – Moždanci I, Sigetec – Moždanci IV, Sigetec – Moždanci V, Sigetec – Ogradine IIB, Ždala – Telek III (Valent 2018: 13–14, 36–37, 46–55, 106–107, 110–113, 170–171, 204–205, 216–219, 224–225, 301–302). Excavation: Virje – Sušine (Sekelj Ivančan, Mušić 2014: 179, fn.8).

18 Delovi – Poljane 4, Delovi – Poljane 8, Imbriovec – Berek II, Koledinec – Brezovice I, Koprivnički Ivanec – Log I, Peteranec – Novi krči I (Ignac Milić parcel), Torčec – Dožine IIIB, Torčec – Međuriće III (Valent 2018: 20–21, 28–29, 71–72, 104–105, 125–126, 168–169, 243–244, 249–250).

19 Kladare – Lasci, Sigetec – Moždanci IIA, Sigetec – Ogradine IIA, Torčec – Međuriće II, Valentovci – Mrzla voda II (Valent 2018: 96–97, 206–207, 222–223, 247–248, 273–274).

20 Bakovčice – Nađbarice I, Bakovčice – Nađbarice 3, Bakovčice – Veliko polje, Draganci – Bokčev grob 3, Peteranec – Jablanec I, Peteranec – Jablanec II, Imbriovec – Vujčec II, Kladare – Orešje 2, Koprivnički Bregi – Gorice I, Koprivnički Bregi – Seče, Legrad – Donja šuma, Miholjanec – Pod goricom 2, Molve – Jandrotine I, Peteranec – Cerine 2, Peteranec – Cerine 2A, Peteranec – Vratnac 2, Podravske Sesvete – Popovice (position 3), Podravske

Antiquity and Medieval period,²¹ 1 to Early Iron Age, Antiquity and Medieval period,²² and 2 to Early Iron Age, Late Iron Age, Antiquity and Medieval period.²³ Pieces of pottery were not found on two sites,²⁴ while one site remains undated.²⁵

If one would extract only Iron Age and Antiquity sites from the above-mentioned,²⁶ as well as the combination of the two, and combine them with the sites from which the material is presented within Table 1, the number of sites on which some sort of iron production or processing might have occurred on the territory of the River Drava Basin within the two periods is 33: three sites can be dated to Hallstatt, five to La Tène, 17 to Antiquity and eight to either La Tène or Antiquity.

CONCLUDING REMARKS

The information presented allows us to bring forward certain conclusions related to the fulfilment of the objectives of this paper. These conclusions, if brought only based on the results of the field surveys, could certainly be placed under consideration if there was no “forgotten” and newly discovered archaeological finds presented within Table 1. Even though one might doubt the affiliation of finds from sites Mulji 1 and Mulji 2A, the Međuriće 6 site undoubtedly provides evidence that the beginnings of metallurgy of iron in the area of the River Drava Basin in the Podravina region can be dated to the Hallstatt period. As it is seen from the results of the field surveys, as well as from a closed archaeological context of the Delovi I excavation, some level of iron production and/or processing also occurred in the La Tène period.

On the other hand, the majority of the finds and information presented, which are still preliminary results considering the extent of the conducted research, tells us that the intensity of this economic activity gradually increased during the Roman occupation. This is not at all surprising given the fact that iron ore mining and smelting was one of the most important economic activities governed by the Roman State, either personally or through leases, on which taxes were paid. The reason for this lies in the fact that iron was crucial for supplying weapons to Roman troops, especially the ones situated on the frontiers of the Empire (Škegro 1999: 101–103).

The macroscopic analysis of the iron metallurgy finds presented (Tab. 1; Pl. 1–3) could be divided into two main groups: 1) technical ceramics - vitrified furnace walls with or without slag which might be connected with iron production furnaces (smelting/forging); 2) slag that was formed during the production of bloomery iron i.e., smelting, or (additional) smithing processes. Unfortunately, their analysis, as well as their amount, do not allow us to draw up exact conclusions on the type of the metallurgical activity which was performed, as well as its intensity, during the period the finds are dated to.

Taking into account that the presented pieces of slag found within the Early Iron Age context, consist (mainly) of (vitrified) furnace walls and smithing slag (Tab. 1: 15–20),²⁷ one can conclude that the Early Iron Age population on the territory of River Drava Basin did (sporadically?) engage in some form of smithing. But, what about smelting? The existence of bog iron ore deposits was proven on the territory of the River Drava Basin in the Podravina region and exploitation is implied by finds of ores in late antique and early medieval archaeological context as well as provenance studies and the overall number of smelting sites (Sekelj Ivančan, Marković 2017; Valent et al. 2017: 21; Brenko et al. 2020; 2021; Karavidović 2020; Valent 2020: 7). So, to answer the question of whether the Hallstatt community in the River Drava Basin engaged in smelting activities we can analyse the available information concerning Early Iron Age settlements in the area and compare them with Early Iron Age centres in the nearby regions. Taking that approach the answer to this question imposes by itself.

Given the fact that no large and strong settlement complex which would undoubtedly arise based on the prosperity that a smelting centre might enable, exist on the territory of the River Drava Basin, one can conclude that large scale iron smelting was not conducted here. Furthermore, the amount of slag such a centre, or even a smaller (occasional) workshop, would produce is unquestionably greater than the few known pieces of finds connected to iron metallurgy that originate

Sesvete – Ravnice, Sigetec – Moščanci I, Torčec – Blaževo pole IV, Torčec – Međuriće IX, Torčec – Vratno II, Ždala – Telek 7C (Valent 2018: 7–8, 13–14, 32–33, 73–76, 81–82, 100–101, 115–116, 119–120, 135–136, 146–149, 154–157, 184–185, 196–199, 202–203, 232–233, 251–252, 257–258, 269–270, 313–314), Jeduševac – Staro Selo 2, Kalinovac – Vuglenice I (Valent et al. 2018: 143; 2019: 9, 12), Molve – Jandrotine III (Valent et al. 2019: 18).

21 Đelekovec – Močvar II, Imbriovec – Berek I, Kladare – Orešje I, Kladare – Orešje-Lasci (meandar), Koledinec – Koledinski lug II, Đelekovec – Jegeniš, Legrad – Šoderica, Podravske Sesvete – Popovice (positions 1 and 2), Sigetec – Moždanci IIB, Valentovci – Mrzla voda III (Valent 2018: 38–39, 69–70, 98–99, 102–103, 108–109, 137–140, 192–195, 208–209, 275–276), Đurđevac – Kopčice I (Valent et al. 2019: 15).

22 Đelekovec – Močvar 1 (Valent 2018: 34–35).

23 Imbriovec – Rasko pole (Valent 2018: 77–78), Jeduševac – Stari Jeduševci 1 (Valent et al. 2018: 143).

24 Delovi – Poljane 6, Delovi – Poljane 7 (Valent 2018: 24–27).

25 Đurđevac – Kopčice III (Valent et al. 2018: 143; 2019: 16).

26 By doing so one diminishes the possibility that the metallurgical finds on the site do not originate from the medieval context which is not examined within this paper.

27 The piece of smelting slag (Tab. 1: 16) found at Mulji site in 1988 has a secondary and unreliable context so its connection with the accompanying pieces, as well as their datation, is questionable.

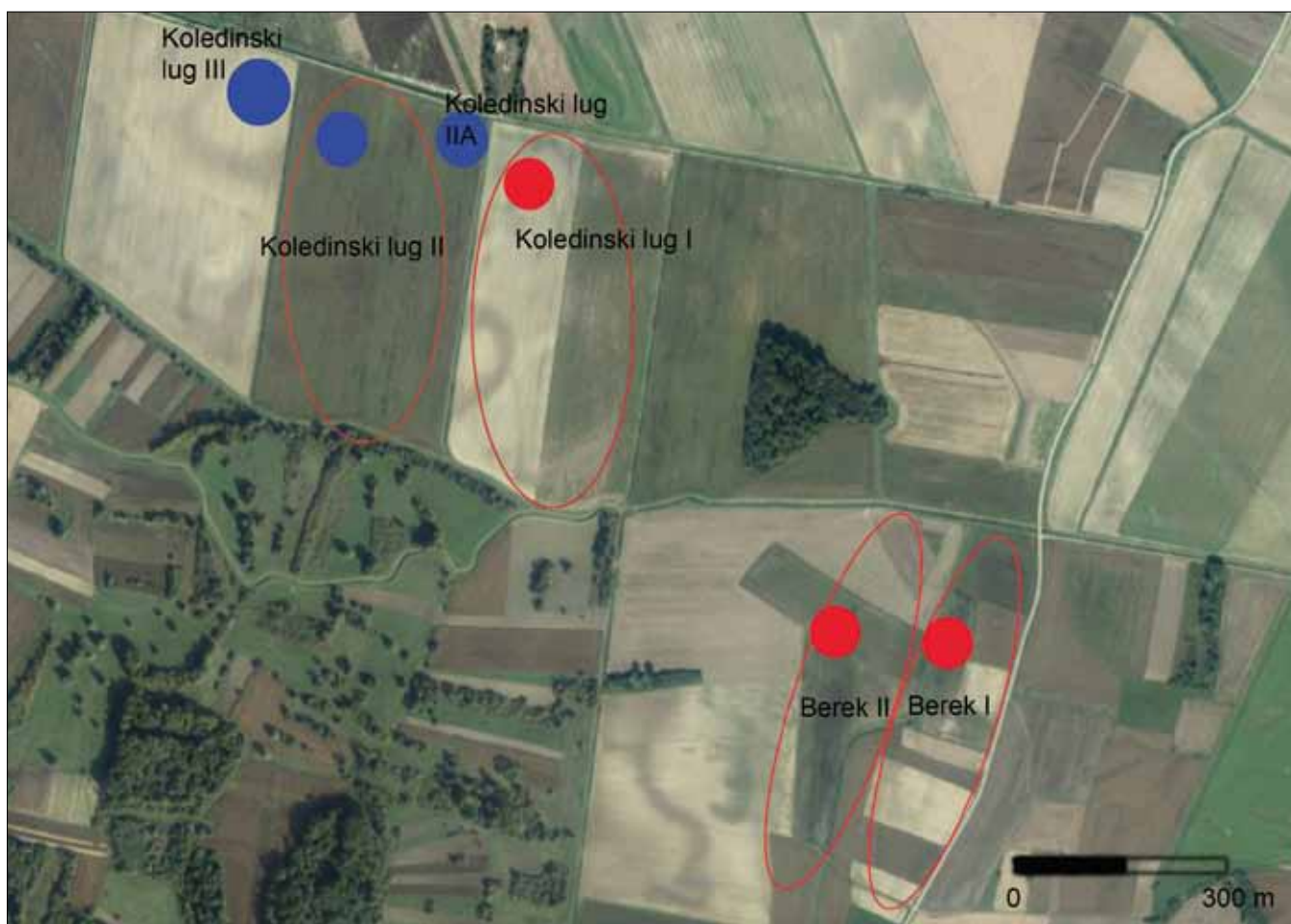
from several different sites presented here. On the other hand, an example of such a large centre on the territory of today's Slovenia is the fortified settlement Cvinger near Dolenjske Toplice (Črešnar et al. 2020). Taking all of the above into account we can conclude that the Early Iron Age population in the River Drava Basin most probably acquired iron objects from a larger remote centre, such as the mentioned Cvinger, and that the metallurgical processes which did take place here were probably limited to small-scale forging and/or repairing.

At first glance, a similar conclusion could be brought for the Late Iron Age settlements as well. The preliminary analysis of the material collected on five single-layer La Tène sites indicates that all the finds can be interpreted as smithing slag. The number of pieces recovered at these sites is quite scarce - only 17 in total. On the other hand, the interpretation of finds collected during field surveys from eight multi-layered sites dated to the Late Iron Age and Antiquity gives a slightly different perspective. Pieces of smithing slag were recovered on four sites and three sites contain smelting slag. The last site contained only a part of a tuyere. Taking all the above into perspective it is clear that only future research will provide information on whether the La Tène population in the River Drava Basin engaged in extracting and smelting the local bog iron ore, as it is presumed for some other settlements (Pleiner 2000: 90; Tankó 2014: 148–149) or they also acquired raw material or (semi)finished products from some larger smelting centre in the Carpathian Basin or the Eastern Alps (Czajlik 2014: 141–143, Fig. 1) and conducted only smithing within the settlements.

As far as the interpretation of the metallurgical activities on the territory of the River Drava Basin during Antiquity is concerned, that task is somewhat easier due to a larger number of sites from which the material was collected, as well as due to numismatic, literal and epigraphic sources regarding mining and smelting throughout the Empire. During the time of Roman occupation, the territory of the River Drava Basin was within the province of Pannonia. After the first provincial division, it fell under Pannonia Superior and finally it was within the Pannonia Savia province. It is considered that the centre of the Pannonia Savia province, *Siscia*, was the main metallurgical centre for the Pannonian and Dalmatian mines. The reason for this conclusion lies in the fact that it was the place in which all the tax from Dalmatian and Pannonian iron mines was collected. Moreover, it was in the vicinity of the main Pannonian mines, situated on the territory of today's central and northwestern Bosnia and Croatian Banija i.e., on the wider area of the Japra, Sana and Una rivers (Škegro 1999: 100–103). The extraction of iron ore, as well as its smelting, within the Pannonian mines, occurred between the late 1st and 6th centuries, with its peak during the 3rd and early 4th centuries (Škegro 1999: 105, 111, 115–117, 119). Taking into consideration the fact that the mentioned abundant mines were places where the Roman State extracted and smelted the iron ore, and wherein some cases final products were produced as well (Škegro 1999: 117), the question which arises here, concerning the territory of the Drava valley, is as following - was the extraction of the bog iron ore in the Drava valley during Roman time profitable or not, and therefore, did it occur?

Upon examination and interpretation of all the metallurgical finds presented within Table 1, originating from four different sites, it is clear that the majority of pieces belong to parts of the furnaces and smithing slag. Only two pieces might be interpreted as smelting and tap slag. A similar situation is with surface finds – pieces of slag from nine sites are interpreted as smithing slag and only three as smelting slag. The first site with solely smelting slag and tuyere find is Ždala – Telek III (Valent 2018: 301–302), but the following two sites belong to a vast archaeological complex, which, besides occupation in Antiquity, has Late Iron Age and Early Medieval surface finds on one part. In order to document the site more specifically, the area is divided into several positions (Koledinec – Koledinski lug I, II, IIA, III) based on the character of various finds which were found on each of them (Valent 2018: 106–113). Vast amounts of both smithing and smelting slag were found on all positions, but the concentration of smelting slag on two positions (Koledinski lug IIA, III) and smithing slag on one position (Koledinski lug I), accompanied only by Roman period pottery might indicate that these activities took place during the same time. Furthermore, the nearby Late Iron Age / Antiquity positions Imbriovec – Berek I and Berek II on which forging slag is also identified (Valent 2018: 69–72), were once situated along the same creek as the Koledinski lug complex, but are currently separated from the Koledinski lug by an artificial canal (Map 2). One more factor which might prove a larger smelting/smithing operation on the site during the Roman period is the architectural remains of a larger complex that stretches over Koledinski lug I position.

As it is visible from the presented results the majority of the metallurgical finds from the Roman period belong to smithing slag. The reason for this probably lies in the fact that iron metallurgy was a state-managed economy, based on large scale mining and smelting within the Pannonian mines, and that iron objects arrived as finished or (semi)finished products to local settlements. These products could have also been repaired or recycled by the local blacksmiths. Hence the smithing slag finds. Consequently, one can assume that the local/low scale (bog iron ore) mining was probably not regarded profitable enough during the first centuries of the Roman rule over the River Drava Basin area, or was simply



Map 2 Position of sites Koledinski lug I, II, IIA, III and Berek I, II (red: forging slag; blue: smelting slag) (made by: I. Valent; base map: DOF (Digital orthophoto), 2017/2018, <http://geoportala.dgu.hr>)

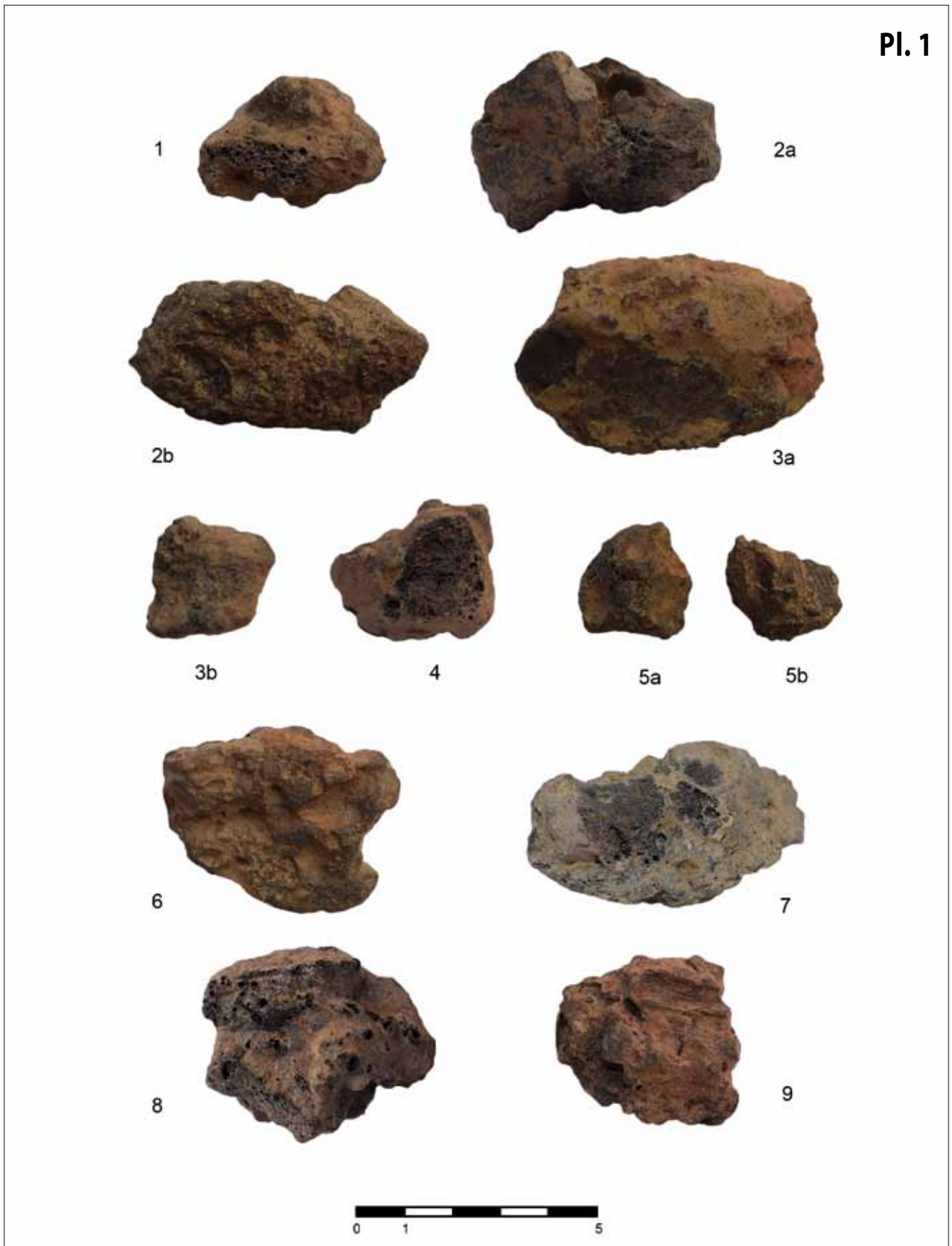
not carried out. But, how can we then explain the presented smelting finds associated with Roman period settlements in the Drava valley? The answer most probably lies in the decree issued by emperors Valentinian I. and Valens in 365 AD and confirmed by Valens in 370 or 373 AD, which allowed free local mining throughout the Empire with the condition of paying taxes and ceding the first purchase of metal for the state. A confirmation of this act can be found within the only excavated (Late)Antique smelting furnaces in the Drava Basin, unearthed at Virje – Sušine site which were dated at the turn of the 4th and 5th centuries (Sekelj Ivančan, Mušić 2014: 179, fn.8). Therefore, based on the currently available data we can assume that the mentioned decree marks the turning point i.e., the beginnings of bog iron ore extraction and smelting on the territory of the River Drava Basin during the Roman period, which continued for the following centuries. As for the question of whether this process already began during the Iron Age period, only future research will show.

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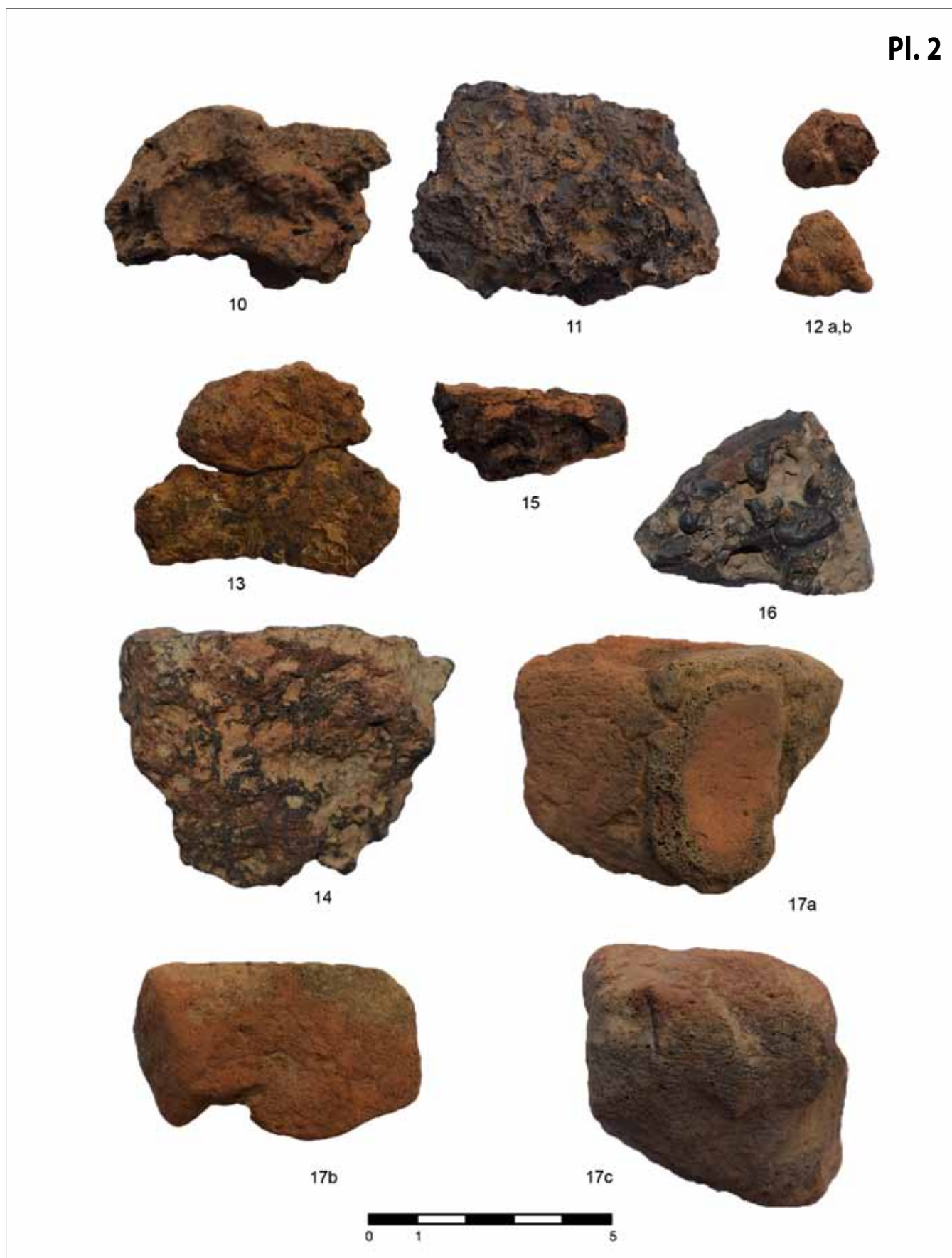
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Pl. 1



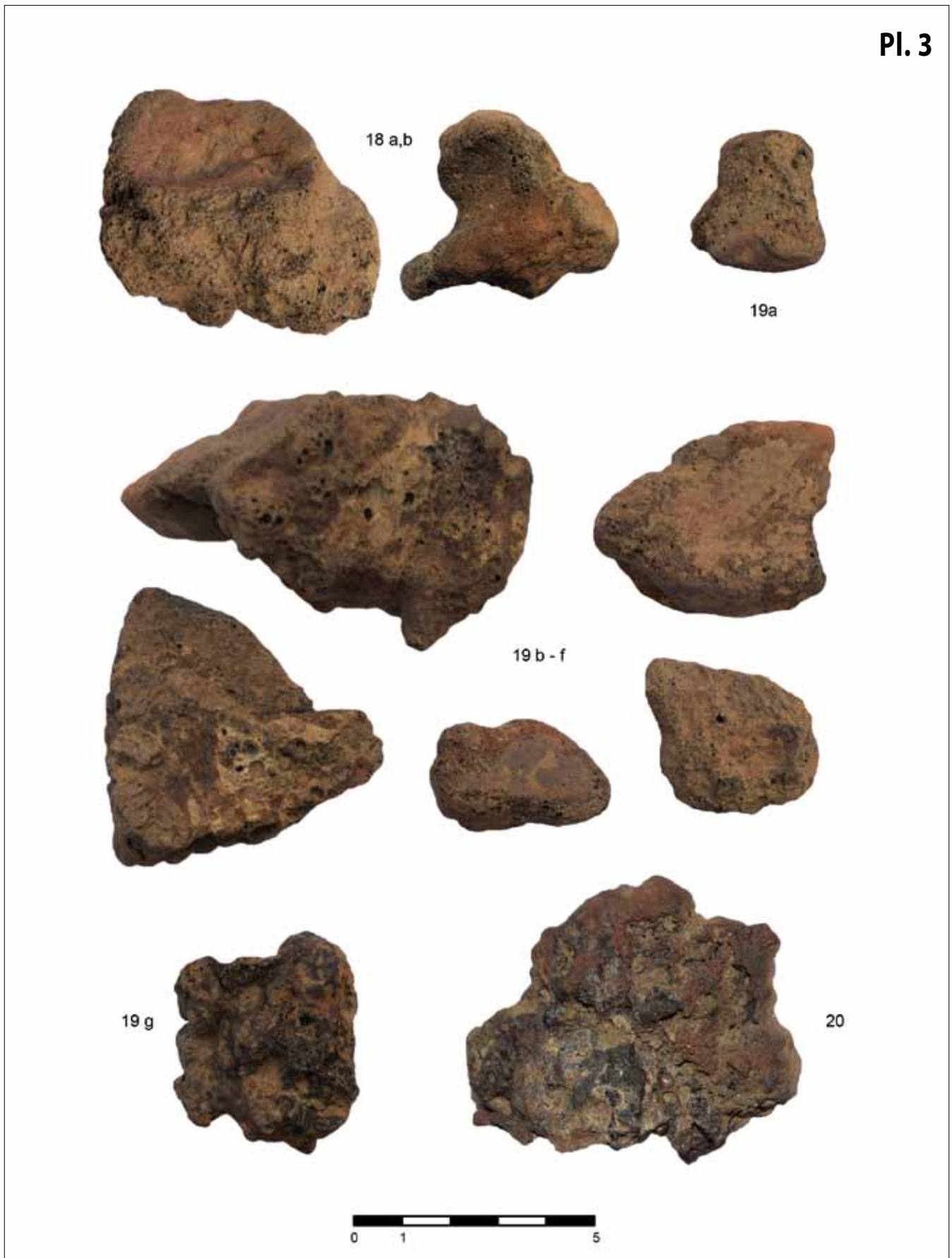
Pl. 1 1-9: Kunovec Breg - Kod poklonca

Pl. 2



Pl. 2 10: Delovi - Grede; 11: Draganovec; 12a,b: Novačka - Gradina; 13: Gola - Vlaško polje; 14. - 16: Vlaisav - Mulji; 17a-c: Vlaisav - Mulji IIA

Pl. 3



Pl. 3 18–19: Vlaislav - Mulji IIa; 20: Torčec - Međuriće 6

THE PRODUCTION OF *FERRUM NORICUM* IN HÜTTENBERG, CARINTHIA, AUSTRIA

Archaeological research on the production of ferrum Noricum - Noric steel - in Hüttenberg, Carinthia, Austria lasted from 2003 to 2010. Six furnaces, twelve smithing hearths, an ore roasting pit, the remains of a charcoal kiln, as well as beamslots and postholes of wooden buildings and stone foundations of houses were uncovered. According to the results of the excavations iron smelting started in the 1st century BC and lasted until the beginning of the 2nd half of the 4th century AD. The presence of buildings on the site as well as finds of pottery sherds, fragments of glass vessels and animal bones show that the workers and administrators lived on the site.

Key words: Roman iron production, ferrum Noricum, bloomery furnaces, smithing hearths, living conditions of the workers

INTRODUCTION

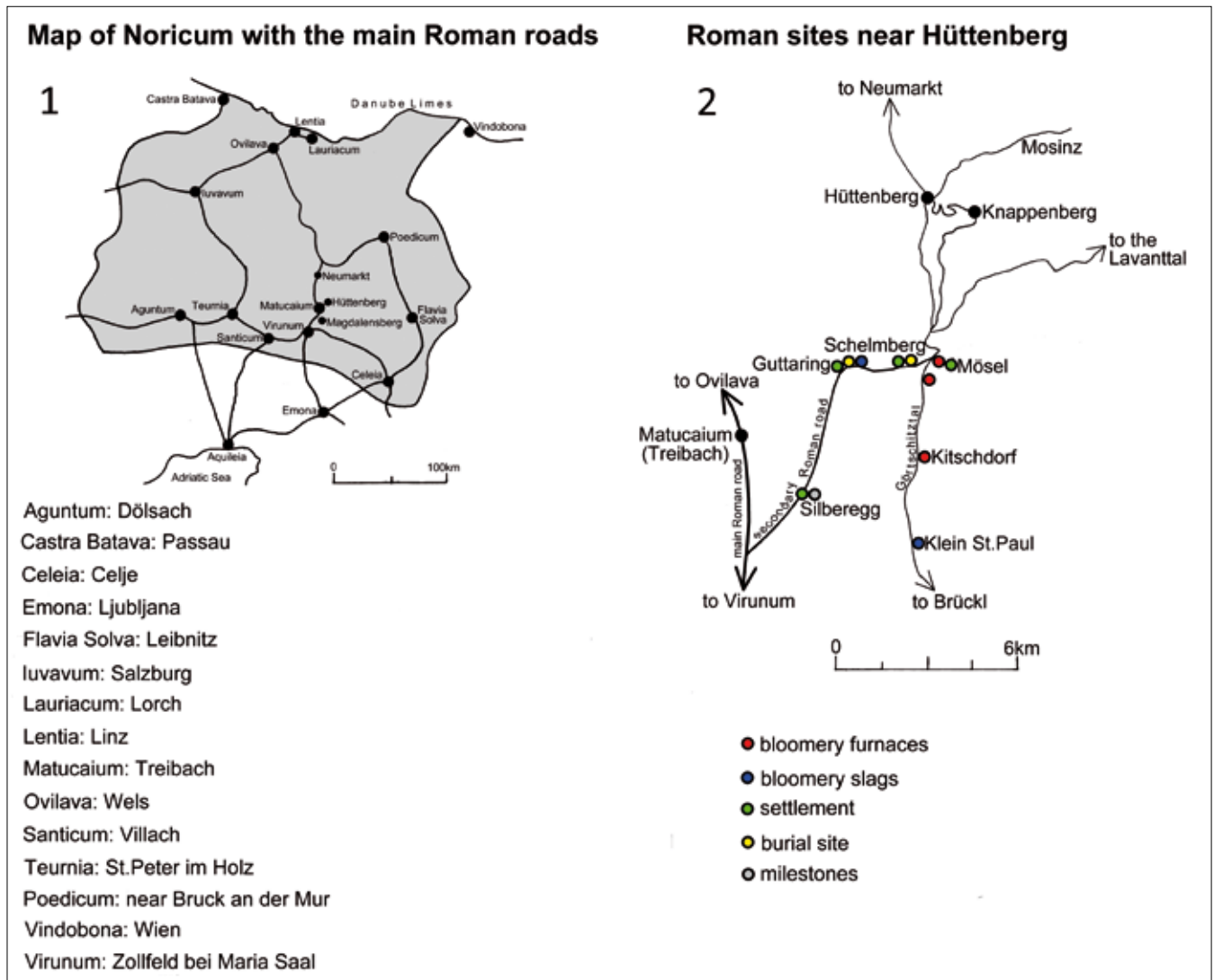
Noric steel, *ferrum Noricum*, is mentioned as high-quality steel in Latin and Greek literary sources since the end of the 1st century BC (Hofeneder 2017). Diplomatic and commercial connections between Noricum and Rome however date back to the 1st half of the 2nd century BC (Livius 39, 22, 45 and 54-55; 40, 34; 43, 5) and finally led to the foundation of a Roman trading post at Magdalensberg in the 1st half of the 1st century BC (Piccottini 1996). Excavations and survey conducted at Magdalensberg show that this trading post was connected to a Late La Tène period oppidum (Artner et al. 2008; Artner, Dolenz 2009; Dolenz 2009). The subsequent Romanization of the Noric people facilitated the peaceful annexation of Noricum by Rome in 15 BC and the Magdalensberg became the first administrative and commercial centre of the new province. Numerous iron bars, half-finished as well as finished iron objects found in the city on the Magdalensberg give evidence of trade with *ferrum Noricum* (Dolenz 1996; 1998).

In the middle of the 1st century AD, under the Emperor Claudius, the new capital Virunum was established in the plains at the foot of the Magdalensberg on the main north-south leading Roman road through Noricum, that continues across the Alps to Aquileia, the Roman trading port in the Northern Adriatic Sea, from where Noric steel was shipped all over the Roman world (Map 1: 1).

It has long been suspected that Hüttenberg with its rich manganiferous iron ores (siderite and limonite), that were mined until 1978, was the centre of production of this famous steel. The oxidized zone of the deposit reaches great depths. It was this ore that was smelted in antiquity. Limonite found at the Roman site Semlach/Eisner contains between 41 and 57 % iron and a little less than 2 % manganese (Prochaska 2008).

ROMAN SITES IN THE AREA AROUND HÜTTENBERG (MAP 1: 2)

The village of Hüttenberg with its *Erzberg* (ore mountain) is situated in the north-south running Görtschitztal. To the south of Hüttenberg a secondary Roman road led from the Görtschitztal to the southwest, joining the main road from Ovilava to Virunum in the vicinity of Matucaium, today's Treibach. At the end of the 19th century Roman settlements and burial sites, as well as two Roman milestones were discovered along this road.

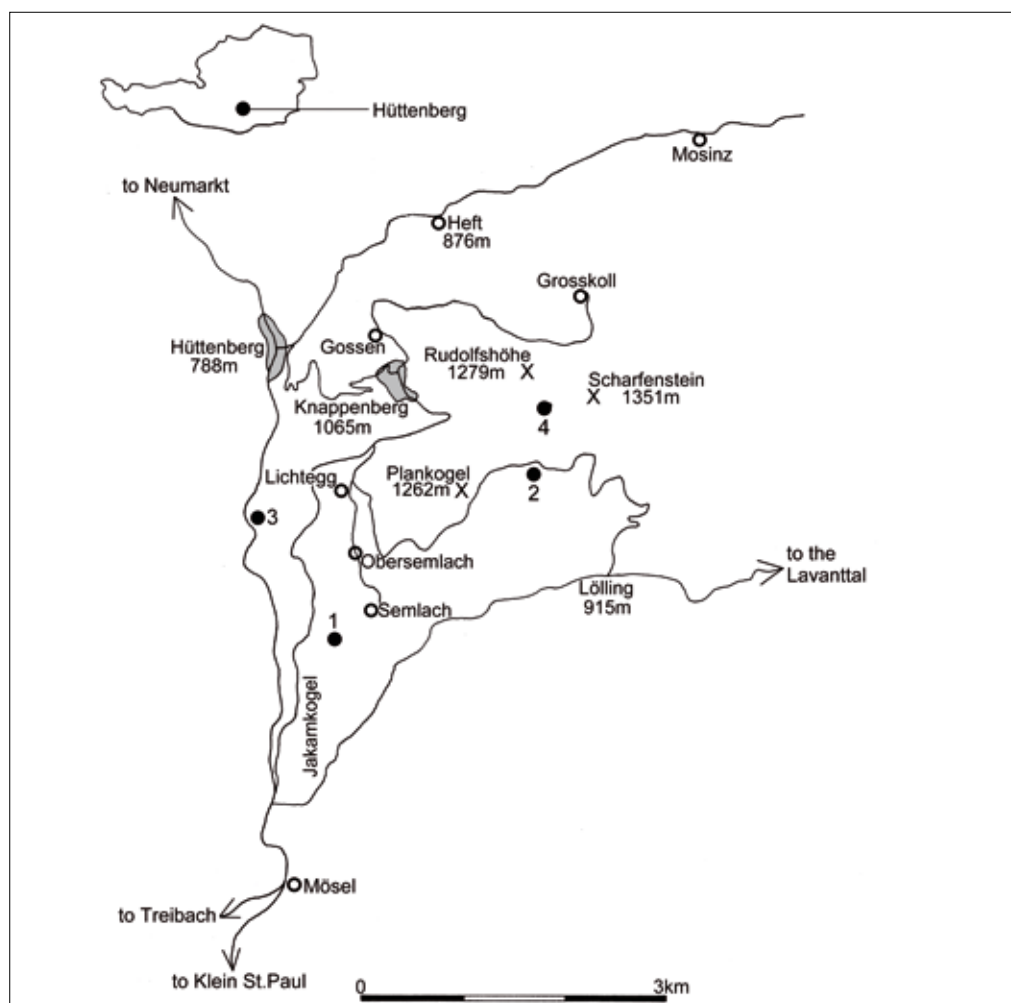


Map 1 Map of Noricum with the main Roman roads (1), Roman sites near Hüttenberg (2) (after: Glaser 2005)

At the junction of this secondary road with the Görttschitztal near Mösel remains of a Roman settlement were uncovered during rescue excavations in 1950 and 1973. During the construction of a pipeline in 1978 five furnaces were found near Mösel, three furnaces to the south of Mösel, and two more near Kitschdorf. Unfortunately, most of these furnaces were partially or wholly destroyed before the arrival of the archaeologists. The documented furnaces are big shaft furnaces similar to the ones found at the site Semlach/Eisner. In 1932 bloomery furnaces were supposedly discovered near Klein St. Paul (Glaser 2005).

IRON SMELTING SITES IN HÜTTENBERG (MAP 2)

During the construction of the railway in 1871 the remains of two bloomery furnaces of unknown date, but probably Roman, were found at Preisenhofgrund, also called site Mösel-Gitterbrücke (Map 2: site 3). The fact that only the part of the furnaces that was sunk into the ground was preserved led to their interpretation as bowl furnaces (Schmid 1932: 15-17, Fig. 8; Sperl 2003: 72). The drawing of a section through these features and their description however show that the furnaces resemble the ones found at the site Semlach/Eisner. They are large bloomery furnaces, sunk into the ground to a depth of 63 respectively 95 cm with a largest diameter of 158 respectively 126 cm. The freestanding shaft had collapsed and fallen into the sunken part of the furnaces.



Map 2 Map of Hüttenberg: 1. Semlach/Eisner, 2. Kreuztratte, 3. Preisenhofgrund, 4. old mine adit (map by: B. Cech)

In 1884, the skeletons of two miners, four coins of the 3rd century AD and pieces of Roman pottery were found during underground mining (Schmid 1932: 12).

In 1929 archaeological excavations at the site Kreuztratte (Map 2: site 2), also called site Lölling, uncovered features interpreted as a bloomery furnace of the Roman period although no dating finds were discovered at the site (Schmid 1932). This “furnace” sits on top of a slag deposit. It consists of dry stone walls, the inside of the shaft was not lined with clay and showed only slight discoloration from heat. Despite these rather unusual aspects for a bloomery furnace the interpretation of Schmid was taken for granted and this “furnace” was considered the characteristic type of furnace for the production of *ferrum Noricum* (Tylecote 1987: 156-157, 168; Straube 1996: 59-60). Unfortunately, the “furnace” itself was destroyed during the construction of a road, but archive research and a trench dug through the slag deposit in 2003 revealed the “furnace” to have been a lime kiln dating to the early modern period when farm houses were built at the Kreuztratte. The slag deposit contained pottery of the late 13th/early 14th century as well as numerous pieces of tuyères and channel slags typical for medieval slag deposits (Cech et al. 2004).

During field survey conducted at the Hüttenberger Erzberg in the course of the current project a small slag deposit was found in the old mining area near an old mine adit (Map 2: site 4). In addition to small pieces of tap slag, vitrified furnace lining, smithing slag and two small blooms were found at this site. Fragments of fibulae (Cech 2017b), Roman coins (Schindel 2017) and pottery (Steiner 2017a) allow the dating of this site to the 2nd/3rd century AD. In the near vicinity of the above mentioned mine adit ten very unusual mining tools, weighing between 2 and 3 kg, have also been found in the course of the survey (Fig. 1).

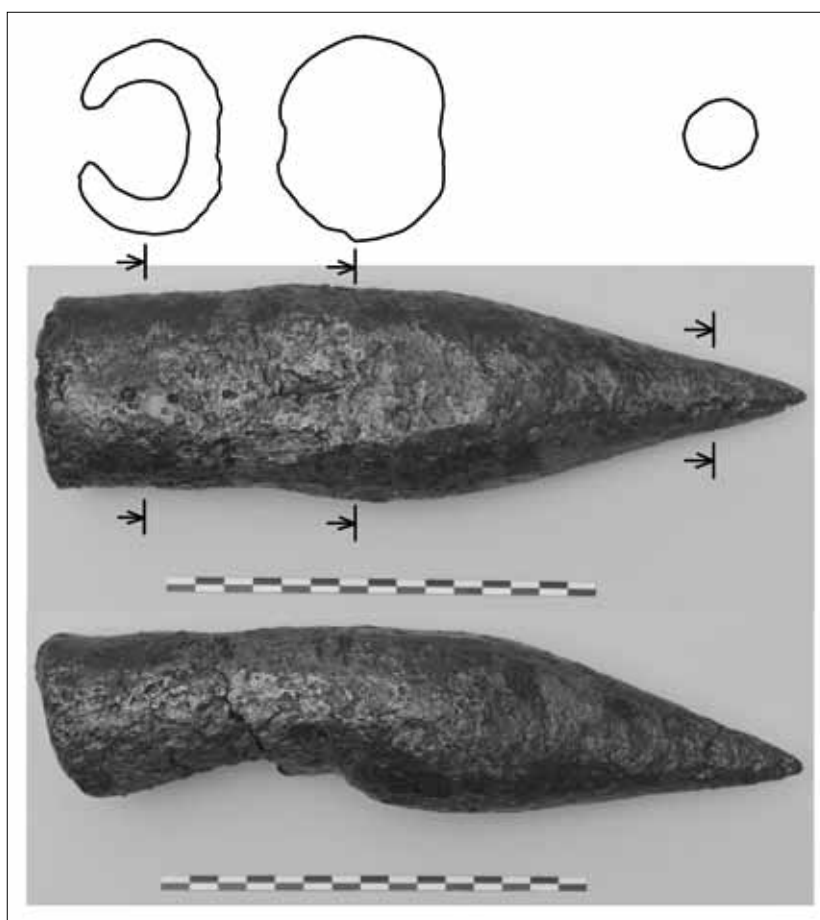


Fig. 1 Roman mining tool found near an old mine adit in the old mining district (photo by: A. Rausch, drawing by: S. von Osten)

These tools were most probably used like picks to mine the soft limonite of the oxidized zone of the ore deposit. The hafting, as well as other Roman finds in the vicinity suggest a dating of these tools to the Roman period. They were most probably made by the local smiths according to the specifications of the miners (Cech 2017b; Birch 2017a; Höcker 2017). Traces of a similar tool have been observed in the limonite of a late Iron Age mine at Piani d'Erna (Rota, Tizzoni 2006).

The most important site on the Hüttenberger Erzberg however is the site Semlach/Eisner (Map 2: 1), where systematic excavations took place from 2003 to 2010 (Cech 2008a; 2014; 2017a).

THE SITE SEMLACH/EISNER TOPOGRAPHY AND GEOMAGNETIC SURVEY

The central part of this site lies at an altitude of 957 to 962 m above sea level on gently sloping pasture. It is bound to the west by huge slag deposits, to the east it extends down the slopes of the Löllinggraben and to the south as far as the Jakamkogel Hill. A network of disused hollow ways to the west of the site lead to the ore deposits on the Hüttenberger Erzberg and down to the Jakamkogel.

Geomagnetic survey was carried out in four stages. Stage 1 aimed at finding sites by talking to the locals and researching and locating published sites. According to the results of this stage the site Semlach/Eisner was selected for detailed survey. Stage 2 consisted of the verification of the information gained in stage 1 with the help of geophysical search profiles using a very large grid. According to the results of stage 2 the central part of the site was located and a more detailed survey, using a grid of 2.5 by 2.5 m, was undertaken (stage 3). The results obtained in this phase formed the basis for stage 4; the detailed survey of areas destined for archaeological excavation with a grid of 1 by 1 m, respectively 0.5 to 0.5 m (Walach 2008; 2017).

Despite the fact that the presence of slags everywhere on the site made the interpretation of the results of geomagnetic survey very difficult, excellent results could be obtained. All furnaces excavated so far showed as distinctive anomalies on the isanomalic maps of the survey. Furnace 1 in trench 3 was dug solely according to the results of geomagnetics and is

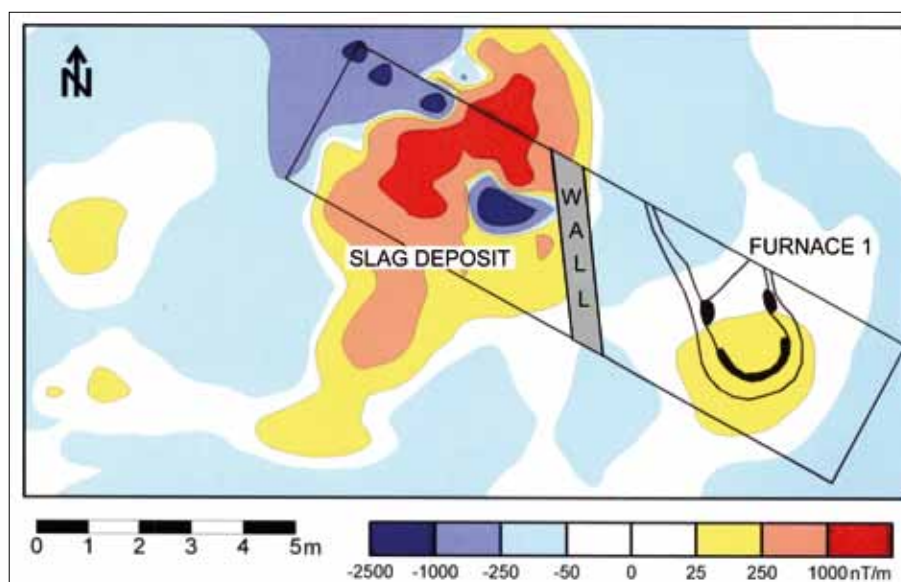


Fig. 2 Detailed geomagnetic survey of furnace 1: Isanomalic map (geomagnetics vertical gradient) with the results of the archaeological excavation; grid 0.5, x 0.5 m (isanomalic map: G. K. Walach)

an excellent example. Fig. 2 shows the results of the highly detailed survey of furnace 1 combined with the archaeological features. The interpretation of the anomalies correspond very well with the results of the archaeological excavation, which illustrates the importance of highly detailed survey for the selection of areas for excavation (Walach 2008).

ARCHAEOLOGICAL EXCAVATIONS AT THE SITE SEMLACH/EISNER CHRONOLOGY OF THE SITE

900 m² of the central part of the site have been excavated. The trenches 1, 2 and 5 to 14 lie adjacent to each other, trench 3 with furnace 1 lies to the north and trench 4 with artificial terracing of unknown purpose lies to the south of this (Map 3).

Potsherds suggest a beginning of the activity in the Late La Tène period (Artner 2008b; 2017b). So far no features belonging to this period could be uncovered.

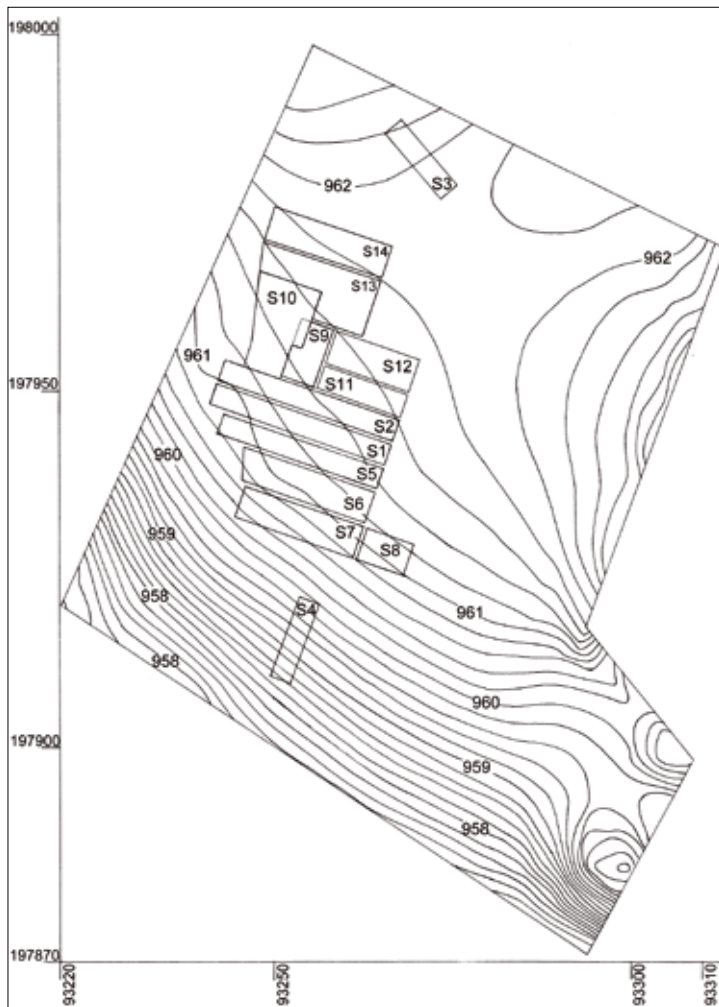
Map 4 gives an overview of the features uncovered in trenches 1, 2 and 5 to 14 and their chronology.

Timber construction phase 1

This phase is characterized by postholes, ditches and pits sunk into the subsoil. Five parallel beam-slots with postholes at their ends mark the ground plan of a timber construction of a dimension of 6 to 5 m (beam slot construction 1) (Fig. 3). Large pieces of slag found inside the postholes served as support for the post and are evidence for iron production during this earliest phase of occupation. Due to the general lack of dating finds this phase can only be roughly dated to the early Principate. After the wooden constructions had been abandoned a landslide originating in the hills to the north of the site occurred and covered nearly the whole of the excavated area. The reason why this landslide occurred was most probably due to deforestation followed by heavy rains. Numerous sherds of the Late Bronze Age were found in this material, but the site of the settlement is still unknown (Artner 2008a; 2017a). A small fragment of cast copper gives a tentative hint to Bronze Age copper smelting (Cech 2017c: 343). Two Roman coins found in the soil that formed right after the landslide and ceramics found in the material of the landslide allow a dating of this event to the time of around 100 AD (Steiner 2008; 2017b; Schindel 2017).

Timber construction phase 2

The features of this phase are postholes, ditches and pits sunk into the material of the landslide. Four parallel beam-slots mark the ground plan of a 4.5 to 4.5 large timber building (beam slot construction 2) could also be the remains of a similar construction. Six small smithing hearths (hearth 6 to 9, 11, 12) also belong to this phase. Soil formed after the



Map 3 Map of the central part of the site with excavated areas (2003–2010) (map by: B. Cech)



Fig. 3 Beam-slot construction 1 – view to the west (photo by: B. Cech)



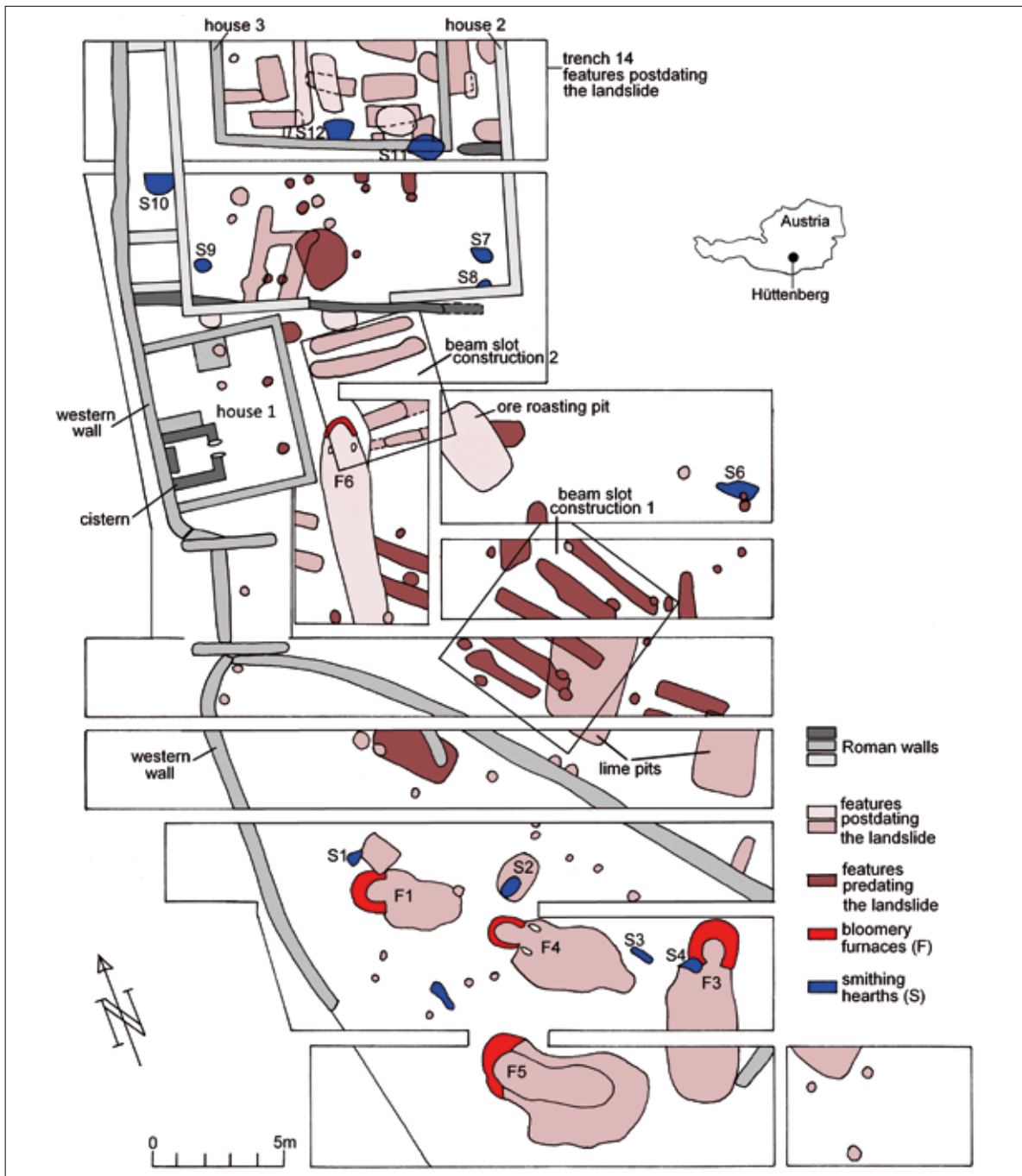
Fig. 4 The water cistern – view to the west (photo by: B. Cech)

wooden buildings were abandoned. Due to the lack of dating finds in this layer an exact dating of timber construction phase 2 is not possible, but it most likely dates to around the end of the 1st/beginning of the 2nd century AD.

Masonry construction phase 1

The constructions belonging to this phase are the northern western wall that was erected on top of an older slag deposit and a water cistern. The floor consists of waterproof mortar. It had a small opening flanked by stone slabs on its eastern side. Sediments had accumulated inside this opening (Fig. 4). The water came from a spring to the north of the site Semlach/Eisner and was led to the cistern by means of a wooden pipe. The oldest metallurgical installations (furnace 6 and an ore roasting pit) also belong to this phase.

Ceramics found in the slag under the northern western wall suggest that the wall was built during the 1st half of the 2nd century



Map 4 The central part of the excavation (trenches 1, 2 and 5 to 13): The archaeological features and their chronology (map by: B. Cech)

AD (Steiner 2017b). Two heaps of broken stones found in trench 13 are most probably rubble from the building of the wall. Smelting hearth 10 also belongs to this phase.

Masonry construction phase 2

This phase brought major changes in the spatial organisation and an increase in the smelting activity. Furnace 6 and the ore roasting pit were levelled with slag after they were given up. The cistern was filled up with rubble and the surrounding area was levelled with slag on top of which House 1 was built. The house was built in wattle and daub with a mortared floor, the cooking range was adjacent to the former cistern. The mortared floor soon became defective and had to be renewed. Now a layer of stones was put on top of the old floor before the mortar was poured in. During the course of this the cooking range was moved to the northern side of the house (Fig. 5). Ceramics found in the slag layer underneath



Fig. 5 House 1 after renewing the floor and moving the cooking range to the northern side of the house – view to the west (photo by: B. Cech)

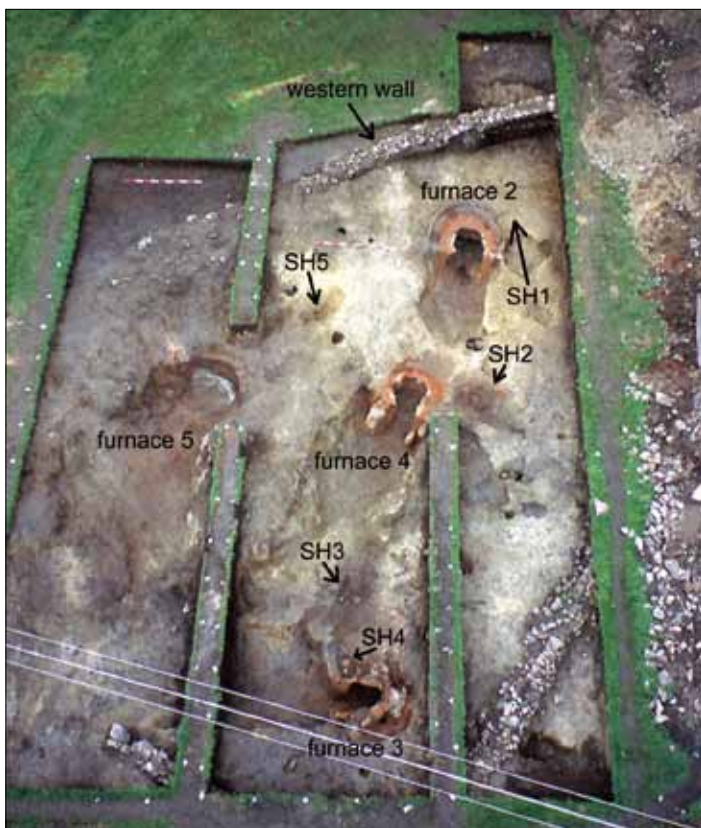


Fig. 6 The enclosed smelting area – view to the west (SH – smithing hearth) (photo by: B. Cech)

House 1 suggest that it was built in the 2nd half of the 2nd century AD (Steiner 2017b). House 3 which has been partially excavated also belongs to this phase. This house has dry-stone foundations, but there is no evidence on the construction of the walls and the covering of the floor. At the same time, the southern western wall was erected 4.5 m to the south of the northern western wall. Together with another wall it encloses a smelting area with four furnaces and five small smithing hearths (Fig. 6). The slags were deposited to the west of the western wall (Fig. 7). Two lime pits excavated in trench 1 and 2 belong to this phase of occupation. The smelting area and House 1 were abandoned around the middle of the 3rd century.

Masonry construction phase 3

After the abandonment of House 1, House 3 and the smelting area the gap between the northern and the western wall was closed. To the north of the excavated area House 2 was erected. It is 12 m wide and has an entrance of 3 m width. Ten metres of its length have already been excavated. According to the results of geophysical survey the entire length of House 2 is about 15 m. The size of the house as well, as its large entrance through which a wagon can pass, suggest that it was used as a storage hall (Fig. 8).

House 2 was built 1.8 m to the east of the northern western wall, the slag that had been deposited here was removed and the walls connected to each other by transversal walls. The space was then filled up with stones and loose mortar with smaller stones at the topmost layer. The reason for this elaborate construction was to ensure the stability of the house and the stones also served as drainage to prevent water from accumulating in the small space between the western wall and House 2.



Fig. 7 The slag deposit – view to the west (photo by: B. Cech)



Fig. 8 House 3 –view to the east (photo by: B. Cech)

The remains of a charcoal production mound excavated in trench 11 and 12 probably also belong to this phase of occupation. The smelting area to the south remained abandoned.

The end of the Roman occupation

So far the exact time when the Roman occupation of the site ended is still unknown. Dendrochronology of charcoal found inside furnace 1 (trench 3) dated it to the middle of the 4th century AD. After the Romans left, the last remaining walls collapsed. The only post-Roman evidence found so far is a shallow pit. The site remained free of buildings and was probably used only as pasture, as it is used today.

THE METALLURGICAL INSTALLATIONS

The ore roasting pit

The rectangular pit measures 3.6 by 2.2 metres and is sunk 70 cm into the ground (Fig. 9). The walls, as well as the bottom, show signs of having subjected to fire. The pit was filled with carbonated wood and at the bottom residues of roasted ore were found. It is not absolutely necessary to roast the ore from Hüttenberg, but roasting it before feeding it into the furnace gets rid of any humidity and thus facilitates the reduction in the furnace thereby saving fuel at the actual smelting process in the furnace. It also makes the ore brittle so that it is easier to break it into smaller pieces and getting rid of remains of bedrock.



Fig. 9 The ore roasting pit – view to the west (photo by: B. Cech)

The furnaces

The Semlach/Eisner furnaces are large shaft furnaces from which slag could be tapped during smelting. They were sunk into the ground to a depth of between 80 and 110 cm with a working pit for slag tapping and bloom extraction in front (Fig. 10). The freestanding shaft was not preserved. Their largest diameter varied between 80 and 124 cm and lay just below the inner openings of the blowholes defining the structures' combustion zones. Working pits in front of the furnaces were used for slag tapping and bloom extraction. The construction of the front of the furnaces is unknown as, in all cases, it was destroyed when the bloom was extracted following the final smelt. The fronts of furnaces 1, 4 and 6 were flanked by standing stones to provide structural strength and facilitate rebuilding after each smelt (Fig. 11). Furnace 3 consists of four consecutive furnaces built one inside the other. They are separated from each other by layers of vitrified furnace lining (Fig. 12). Furnace 5 and 6 consisted of two consecutive furnaces, again built one inside the other. The blowholes remained the same when the new furnace was erected inside the older one.

The furnace walls consisted of clay tempered with quartz, and were 30 to 40 cm thick. The surrounding subsoil and bedrock was discoloured by heating to a depth of up to 40 cm around the furnaces. The diameter of the furnace base varied between 80 and 115 cm. The base of furnace 1 was covered with stone slabs with a layer of very small slag fragments sealed beneath them as insulation (Fig. 13).



Fig. 10 Furnace 2 – view to the west (photo by: B. Cech)



Fig. 11 Furnace 4 – view to the west (photo by: B. Cech)

Furnace 6, the oldest furnace discovered at the site, is slightly different from the other five furnaces. Its freestanding shaft was built of sundried bricks (Fig. 14).

In all cases the inner surfaces of the furnaces is heavily vitrified and, in case of furnace 1, the vitrified clay had flowed downwards and covered part of the furnace base. In furnaces 2 to 6 the vitrification reaches to just below the inner openings of the blowholes (Fig. 15).



Fig. 12 Furnace 3 – view to the south (photo by: B. Cech)



Fig. 13 Furnace 1 – view to the south (photo by: B. Cech)

The preserved blowholes run from the ancient ground surface at an angle of 30° to 48° into the interiors of the furnaces, their inner openings being located between 40 and 60 cm above the bases of the furnaces. Each furnace had at least three but probably four blowholes originally, one being preserved in furnace 4, two in furnaces 1, 3, 5 and 6 and three in furnace 2. No



Fig. 14 Furnace 6 – view to the west (photo by: B. Cech)



Fig. 15 Detail of the inside of furnace 2. The vitrification of the furnace lining reaches just below the blow-holes – view to the west (photo by: B. Cech)

evidence of the use forced blast (bellows) in the form of tuyères was recovered though carbonised wood plugs were found inside the blowholes of furnaces 2, 3, 4 and 5 (Fig. 16). These are probably the result of the insertion of green wood into the blowholes to prevent the vitrified furnace lining from sealing their inner apertures at the end of the smelting process.



Fig. 16 Blow-hole of furnace 3 with traces of carbonised wood inside – view to the south (photo by: B. Cech)

The smithing hearths

All in all twelve small earthbound smithing hearths have been uncovered. They consist of shallow depressions lined with clay varying in size between 40 by 40 cm and 120 by 40 cm and often contain *in situ* smithing slags. The proximity of smithing hearths 1 to 5 to furnaces 2 to 5 suggests that they were used for bloom smithing (Fig. 17).



Fig. 17 Smithing hearth 2 – view to the east (photo by: B. Cech)



Fig. 18 Cone-shaped tap slag (photo by: N. Sautner)

THE METALLURGICAL WASTE

The tap slags from the site are very brittle and break easily into small pieces. However some larger slabs as well as cone-shaped fragments were recovered, that suggest the tapping opening was well above the surface of the working pit into which the slag flowed (Fig. 18). Other slag morphologies include dense, compact slabs of slag with flat surfaces.

The tap slags of the site Semlach/Eisner are iron silicate slags with a MnO - content of up to 10 mass-%. The manganese contained in the ore passes completely into the slag during reduction. The Al_2O_3 -, CaO-, MgO-, P_2O_5 -, TiO_2 -, and K_2O -content combined is less than 6 mass-%. The tap slags consist of around 45 surface-% olivine and 16-surface % wüstite. Most of the Mn^{2+} is bound to the mix-crystal of the olivine (Preßlinger 2008).

Seventeen pieces of unrefined iron have been recovered from the slag deposits and from inside the furnaces. Metallurgical analysis showed that they all have a high carbon content. They fell into three different categories dependent on carbon content: Hyper-eutectoid steel (carbon content: 1.4-1.6 %), white cast iron (carbon content 2.6-4.3 %) and grey cast iron (carbon content 2.5-3.5 %). Macroscopically they show a globular morphology with a plano-convex form. The microstructure of the hyper-eutectoid steel indicates quick cooling. The presence of grey and white cast iron however shows that some pieces cooled more slowly. This corresponds to the extraction of raw iron from the furnace, where conditions can rapidly change. It seems that these pieces of high carbon steel have been made unintentionally. The archaeological context in which these pieces were found shows that they were not retrieved in antiquity. As it is unlikely that the Roman smelters did not recognise these pieces as iron, they must have been intentionally discarded (Birch 2017b).

THE DAILY LIFE OF THE SMELTERS IN THE LIGHT OF THE FINDS

The finds recovered between 2006 and 2010 give an insight into to the daily life of the smelters living at the site. Tools give evidence of crafts, agriculture and transport. The presence of women is attested by fibulae exclusive to female dress and the bones of one or two newborn babies.

Most of the pottery is coarse household ware of local origin (pots of different sizes, jugs, beakers, bowls, plates and lids). The general lack of oil-lamps – only one fragment was found – is as remarkable as the scarcity of mortaria and amphorae. Terra Sigillata as well as fine ware is scarce. The predominance of coarse household pottery of local origin is to be expected in an industrial settlement as most of the population worked in the iron industry and probably could not afford fine tableware (Steiner 2008; 2017b; Radbauer 2017).

Glass finds are rare at this industrial settlement, as can be expected, as glass objects are more often associated with a luxurious lifestyle. Amongst the finds are fragments of high-quality beakers with facet-cut decorations, square and cylindrical bottles and an Aryballos, a bottle for perfumed bath oils (Tarcsey 2008; 2017).

Metal household items consist of knives and a scabbard fitting as well as hinges and clamps for chests and numerous nails. A bronze furniture fitting or door knocker in the shape of a lion's or panther's head was found inside House 1 (Cech 2008b; 2017c; 2017d).

A few carpenter's tools were also found at Semlach/Eisner. Woodworking is an integral part of mining and smelting industries (Cech 2017d). Wood is not only needed for props inside the mines and for building roofs, walls and floors of houses, but it is also needed mainly for roasting and smelting the ores and for bloom-smithing. Last but not least, wood is needed for cooking. The analysis of the charcoal from the late Roman charcoal production mound showed that mainly fast growing spruce wood was used for charcoal production, predominantly branch wood. Large trunks were used for props inside the mines and for building houses (Grabner 2017).

The stonemason's tools give evidence that the local stone of which the walls and the foundations of the houses were built was cut to the desired size and shape on site as attested by the two heaps of broken stones excavated in trench 13 (Cech 2017d).

The only leatherworking tool found so far is a double point for enlarging holes and was probably used to repair shoes, belts and the leather clothing of the smelters (Cech 2017d).

A spindle hook for guiding the thread during spinning and two loom-weights give evidence of spinning and weaving, traditional female crafts. These three objects are not only evidence of the presence of women but can also serve as evidence of sheep-breeding. Sheep were most probably mainly bred for milk and meat, but their wool was also utilized (Cech 2017e). The tools for leather and textile working are more reflective of craft production at a household scale than any commercial endeavour.

The only agricultural tool found so far is a fragment of a sickle that was probably used to cut grass for the draught animals (Cech 2017d). Grain farming seems unlikely because of the high altitude (around 1000 m above sea level) of the site.

A snaffle and a hub ring of a carriage wheel give evidence of transport, which is another integral part of mining and smelting industries (Cech 2017d). Ores and charcoal have to be transported to the smelting site and the iron produced has to be carried down into the valley. Food, as well as household implements and tools, have also to be brought up to the site.

A fibula of the type Aucissa, as well as three fibulae with a strong profile, a thistle fibula and a Norican-Pannonian double knob fibula, are personal ornamentation as integral part of clothing. The only piece of jewellery found so far is a spiralled finger ring made of silver (Cech 2017c).

Very few coins were found at the site. They were all found to the north of the enclosed smelting area, which is not surprising as it seems improbable that the smelters carried their purses during work. The small number of coin finds can be explained by the fact that the people living at the remote site did not have many opportunities to spend money, which made it unnecessary to carry a purse and limited the chance of coins being lost (Schindel 2017).

At Semlach/Eisner the presence of women is attested by the above mentioned loom weights and the spindle-hook as well as the fibulae attributed to female dress. The find of bones from one or two newborn babies give further evidence of the presence of women and might also hint at families living in the settlement. It is not unusual to find skeletons of newborn or very young children inside Roman settlements and cannot be seen as evidence of the killing of unwanted children. Children who died before teething were neither cremated nor buried in regular graveyards nor ritually mourned (Plin. Nat. 7, 17).

The most important source of evidence for the nutrition of the smelters are the animal bones found at the site. Bones of cattle, pigs and sheep and goats were found. These assemblages show that beef was the most common meat, followed by mutton. Bones of pigs are comparatively rare and pork played no great part in the diet of the smelters. Contrary to cattle, sheep and goats and pigs were bred solely for human consumption, which made pork an expensive meat. Chicken bones are very rare. Chicken were kept for their eggs and their meat was also more or less reserved for the upper classes. Bones of venison are extremely rare which shows that hunting played no part in supplying the community with meat. The bones of horses are from animals used for transport. Horseflesh was not eaten in Roman times, probably because of religious taboos (Böhm 2008; 2017).

SUMMARY

The research carried out at Semlach/Eisner shows that this was an important industrial complex, beginning at least in the 1st century BC and lasting until the second half of the 4th century AD. The stratigraphy gives evidence that the spatial organisation of the site changed a couple of times during its occupation. The material finds as well as the animal bones recovered illustrate the working and living conditions of the workers and administrators living on the site. Although the potsherds and small finds found at Semlach/Eisner are less numerous than on other Roman sites, they give some evidence of the life and the people who lived and worked at the site. Objects belonging to a higher standard of living are rather rare as most of the population were workers in the mining and smelting industry. The few objects that can be classified as moderately extravagant show that a number of individuals living at Semlach/Eisner wished to maintain a certain standard of living, even in a remote mining area. With an industry of this size, the presence of administrators and scribes can be assumed and it was probably these individuals who used the perfumed bath oils and fine table ware and had pork and chicken for their meals.

Personal ornaments and the bones of infants provide evidence of women and potentially families. Apart from woodworking, carpentry, charcoal making and stonemasonry, which are an integral part of mining and smelting operations as well as the building of the houses, no other crafts were practiced in a commercial sense.

Huge slag deposits show that iron was smelted here on a large scale over a considerable period of time. Bloom smithing was carried out in small earthbound smithing hearths in the vicinity of the furnaces. The size and construction of the six furnaces give evidence of the expertise of the smelters working here.

In conclusion, Semlach/Eisner consisted not only of metallurgical installations but also shows clear evidence of a settlement, whose finds provide valuable insights into the daily life on a Roman industrial complex.

ACKNOWLEDGEMENTS

The research was financed by the Austrian Science Found (2003 – 2005: project P16069-GP02; 2008 – 2010: project P20641-G02) and the European Union (2006 – 2007: project „Iron Route“, Alpine Space Interreg IIIB). The author thanks all her colleagues and students as well as the local population who were involved in the research in Hüttenberg and without whose enthusiastic cooperation it would have been impossible to realise this project.

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AN INSIGHT INTO CRAFT ACTIVITIES IN RURAL AREAS OF DALMATIA PROVINCE - FIRST DATA ON IRON WORKING AT THE ROMAN SETTLEMENT IN LOPAR (ISLAND OF RAB)

Within multidisciplinary research carried out at Podšilo bay in Lopar on the island of Rab (north-eastern Adriatic), on the bases of movable finds and, possibly, geophysical measurements, evidence of ironworking has been detected within a Roman rural site where ceramic building materials production was ascertained before. Preliminary analyses of several samples of slag, iron objects and nearby collected minerals support the presumption of metallurgical activities occurring at the site. An overview of regional and wider analogies allows to propose several scenarios of iron working setup, scale and organisation.

Key words: Roman rural sites, Roman Dalmatia, iron working, multi-crafting, pottery production

Research on the economy and craft industry of ancient province *Dalmatia* (eastern Adriatic and its hinterland) is still scanty and geographically sparse, until now favouring areas rich with monumental and epigraphic evidence, such as the ore-rich hinterland of today's Bosnia and Herzegovina (Škegro 1999: 17–138 and Durman 2002 for metals; see also: Suić 1981: 261; Glislsman 2005: 209; 2007; Sanader 2006: 154–155, 161; Kurilić 2008: 21–25), while activities of processing and production within coastal settlements, especially the ones active in the rural areas, have yet to be fully understood (e.g. Lipovac Vrkljan, Šiljeg 2012: 12). Therefore, more attention should be given to such sites and other parts of the province, by applying new approaches and methods, considering both direct, material evidence of crafts and processing activities (such as remains of infrastructure) and indirect evidence (such as moulds, wasters or the products themselves), while applying not only archaeological but also multidisciplinary methods. A similar approach has recently been attempted in regard to pottery and ceramics production within the coastal part of the province, yielding several new paradigms for the study of not only this craft, but also for better understanding of the development and economy of rural areas, their production activities and their chronology (see: Lipovac Vrkljan, Konestra 2018).

Within the *Archaeological topography of the island of Rab* project¹ a different set of multidisciplinary research activities has been carried out continuously since 2013, focusing on all aspects of archaeological heritage dating to all periods. Attention is being paid to human-environment relationship, in particular to the human impact on its environment that is visible in the various use of the landscape throughout time. Thus, within the aforementioned project not only movable finds and evidence of structures, but also other traces indicating economic activities and the exploitation of raw materials are being documented and studied. Among others, evidence of different diachronically disparate crafts has been evidenced including, for the Roman period, pottery/ceramics production and possible evidence for the processing of iron. It is the latter that will be tackled here in more depth, through archaeological and preliminary metallographic analysis of the evidence collected through reconnaissance and excavation at Podšilo bay in Lopar on the island of Rab.

¹ The project *Archaeological Topography of the Island of Rab* is led by A. Konestra and F. Welc, based on a collaboration between the Institute of archaeology in Zagreb and the Institute of archaeology of Cardinal Stefan Wyszyński University in Warsaw, with the participation of the Archaeology Museum in Zagreb; funding has been granted by the Ministry of culture of the Republic of Croatia, the local municipalities and Lopar Culture Centre, and the leading institutions.

THE SETTLEMENT AT PODŠILO BAY AND EVIDENCE FOR CRAFT ACTIVITIES

Podšilo bay is a secluded cove located on the NE part of Lopar peninsula, the northernmost part of the island of Rab (Fig. 1). When observing its geological structure, the island is composed of two anticlines and two synclines composed of Cretaceous carbonate rocks overlain uncomfortably by Eocene carbonates also known as the 'flysch' (Marjanac, Marjanac 1991; 2007). In Lopar the oldest geological stratigraphic unit constitutes Eocene clastics (Lopar Sandstones) (Marjanac, Marjanac 2007). The Lopar sandstones succession is built by sandstones and sandy marls (Marjanac, Marjanac 2007), which thus characterize substratum of Podšilo bay as well. The small, temporary stream Tićevo flows here from its source located westerly in its hinterland, through the bay into the sea.

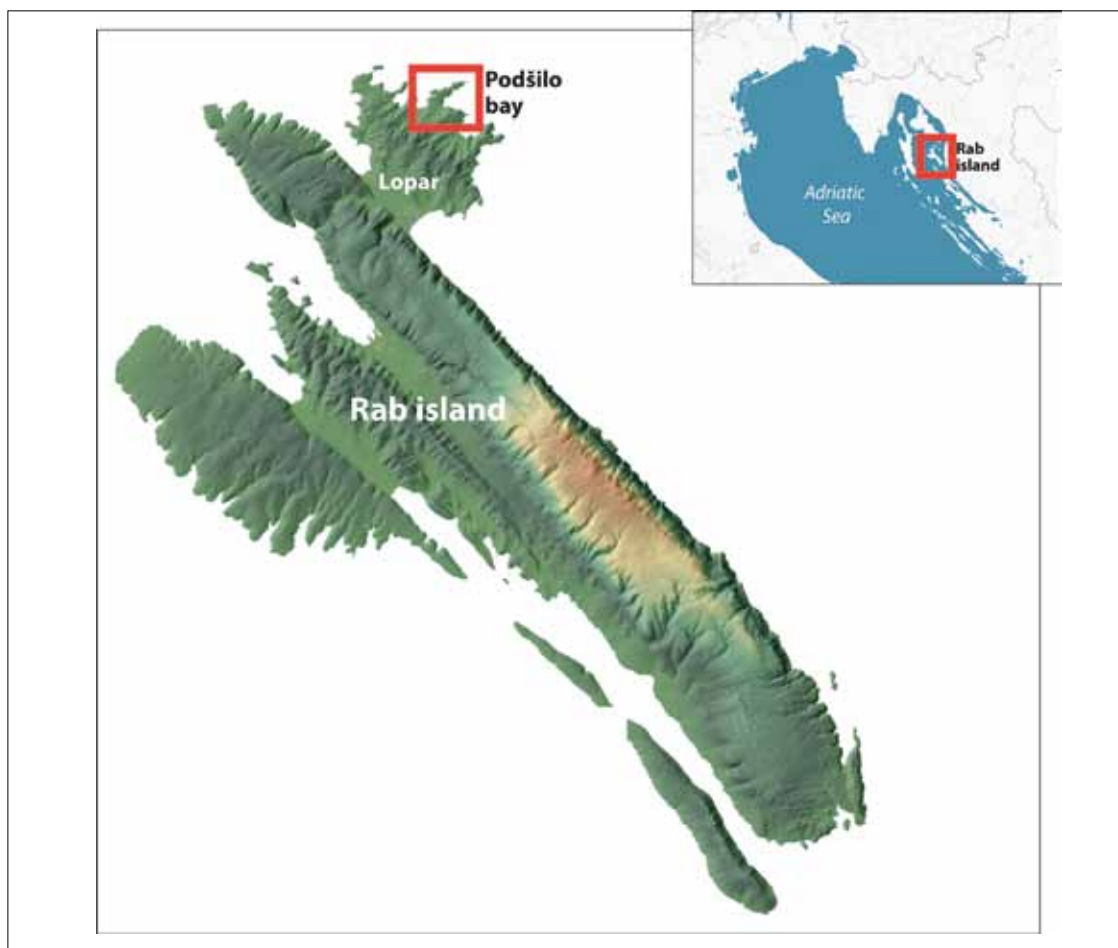


Fig. 1 Rab island with the location of Podšilo bay (basemap: DGU DEM; Google Maps/Snazzy Maps) (illustration: A. Konestra)

First archaeological research within Podšilo bay dates back to 2009 when a pottery kiln was excavated on its northern shores, just a few meters from the sea (Lipovac Vrkljan, Šiljeg 2010; 2012) (Fig. 2). Finds recovered from its infill and the surrounding area indicate it was most probably setup to produce ceramic building materials (tegulae and imbrices), while its highly eroded surroundings bare evidence suggesting the existence of other, mostly damaged kiln(s). Further research in the area, especially geophysical measurements conducted on a small flat plateau to the NW of the excavated kiln, proved this assumption (Welc 2018: 64–65), indicating the existence of a small, detached craft area (a workshop?) located at some distance from the residential part of the settlement evidenced within the bays hinterland.² In fact, as a result of systematic reconnaissance, multi-method geophysical measurements and trial trenching, a complex rural settlement comprising several buildings located on both slopes of the bay was detected (Fig. 2). Two of these structures were partially

² The local population calls the northern slope of the bay *Beli grad* (roughly translated as White city), probably due to the massive presence of allochthonous limestone blocks reused within the dry-stone terracing, clearance features and property fencing walls, whose original use was ascertained within the identified Roman structures (see: Lipovac Vrkljan, Šiljeg 2012: 21–22 with bibliography therein). Further microtoponymy provided by the local population includes the name *Podkućine* (roughly translated as Under the houses) for the area of the southern architectonic complex.

excavated through trial trenches at the sites Beli grad and Podkućine, yielding architectural remains and finds mostly datable to late Antiquity (Fig. 3), while ^{14}C dates suggest a timeframe of use spanning from the 3rd to the 6th c. AD (Welc et al. 2019; Konestra et al. 2020). Similarly, dates extracted from the excavated kiln place its use within the 3rd c. as well (Lipovac Vrkljan, Šiljeg 2012: 27).

Due to a strong erosion processes investing the whole Lopar area, and thus also Podšilo, surface archaeological material is usually found displaced either along the beds of periodical, storm associated flash floods or redeposited from higher ground, thus usually recovered below natural escarpments at the edges of terraces (Welc et al. 2017: 48, fig. 4). As standard surface finds' collection and documentation did not provide sufficiently precise location information, further mapping of all areas with hypothetically reconstructed erosion processes allowed the possible, more precise location of ancient architecture, always situated on flat terraces above the detected materials' concentrations (Konestra et al. 2019: 192–193, fig. 6). During these activities finds from such accumulations of eroded materials were collected, among which, especially along the bay's northern slope, lumps of ferrous materials were identified (Fig. 2). Similar lumps were also collected during excavations of Trench 1 at the Beli grad complex, along with several iron objects (mostly nails), while layers of ferrous (?) materials were identified in several areas near the shores of Tićevo stream. Furthermore, gradiometer survey of the area further north of the structures at Beli grad yielded interesting results as well. Two oval-shaped objects have been detected, with a diameter of about 2 m, which were characterized by a high value of the magnetic field strength (Fig. 4). The shape of the anomalies suggests either an elongated, possibly key-hole shaped or two smaller detached rounded structures, both allowing a possible association with blacksmithing furnaces (Munro 2020: 387). It remains to be seen what was the exact nature of these anomalies, as in a wider area around them no remains of structures or other features was detected either by gradiometer or GPR measurements.

All of the above sprung the need to analyse in more depth the collected evidence and the possibility of it being connected with some form of iron working, either smelting or smithing. Therefore, nine samples of materials deemed to be related to iron working or production were analysed at the Department of Conservation of the State Archaeological Museum in Warsaw, including samples deemed to be iron slag and iron-rich rocks collected from outcrops located near Tićevo stream (Pl. 1). The main aim of the research was to determine whether the samples are slags from the metallurgical process. In order to accomplish this task, the samples were visually inspected, cleaned of surface contamination, X-rayed, and macroscopically and microscopically examined. The results of these tests for each of the analysed samples are presented in the attached table (Tab. 1).

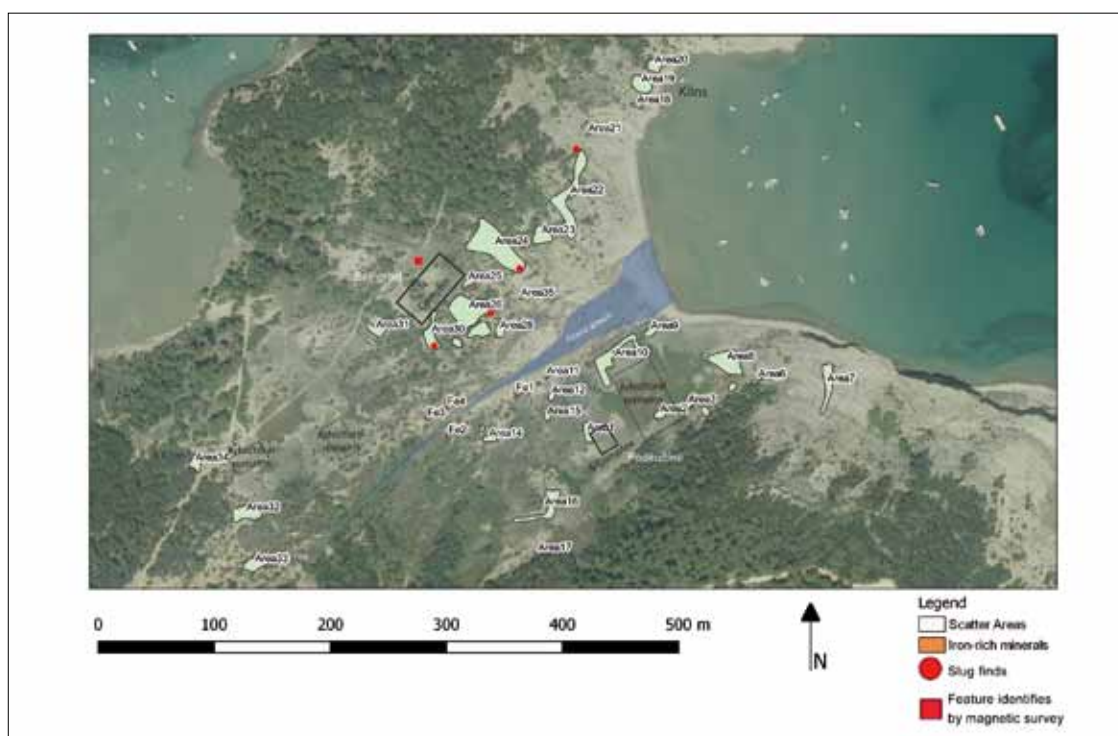


Fig. 2 Podšilo bay with locations of documented features (data collection and elaboration: R. Solecki, A. Dugonjić, F. Welc, A. Konestra; illustration: A. Konestra; basemap: DGU DOF)



Fig. 3 Results of excavations in the trial trenches in Podšilo bay: A - Podkućine Trench 1; B - Beli grad Trench 1 (photos and DOF: K. Rabięga)

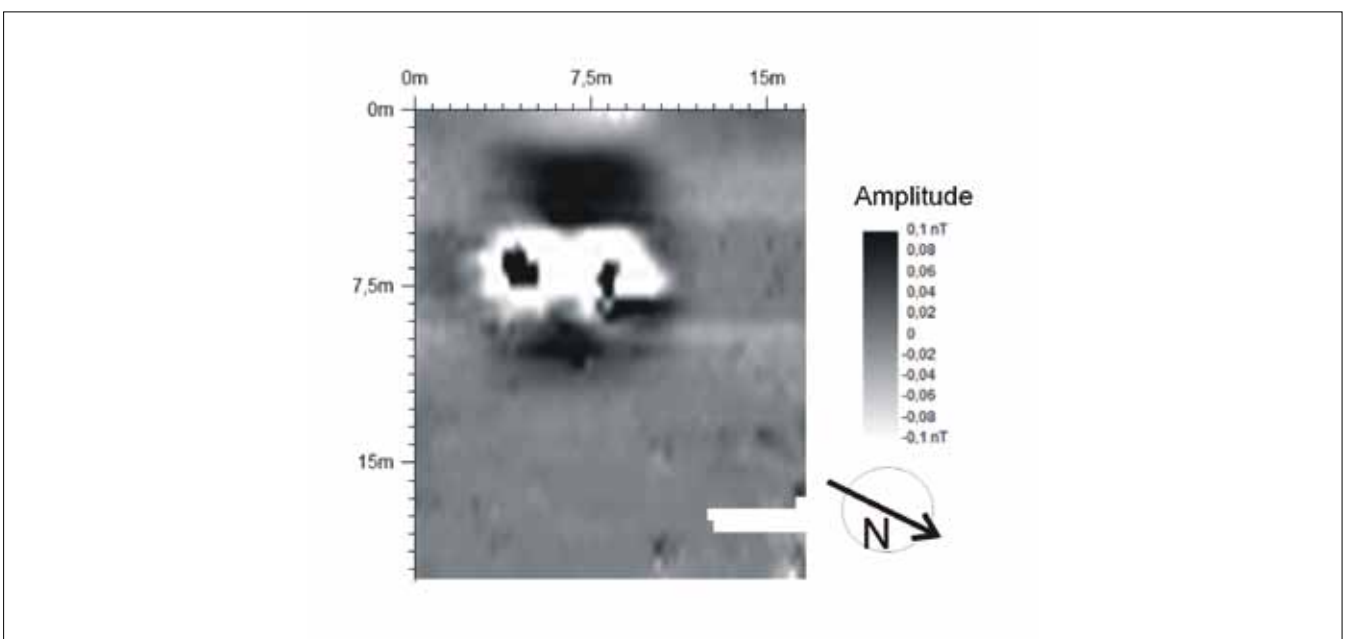


Fig. 4 Anomalies detected by magnetic survey on the northern slopes of Podšilo bay (measurements and elaboration: F. Welc)

Overall, the analyses conducted on samples from Podšilo bay confirmed without any doubt that this site was associated with metallurgical activity. The slag lumps (samples 3, 4, 7, 9) assuredly evidence that within the site some kind of an iron-working activity was carried out. The attainment of high temperatures, necessary for the metallurgical process, is evidenced by the significant degree of liquefaction of the slag forming a homogeneous, in some places porous slag mass (sample 7, 9). In some places, the microsections show outlines of Widmanstetten structures formed during the solidification of fayalite ($2\text{FeO} \cdot \text{SiO}_2$).

The irregular shape of the samples presented does not provide any basis for determining the iron reduction technique used at this site in the past, but might indicate smithing or recycling activities. They could have been formed both in earthen (cavernous) furnaces, as well as in the early stages of the process in vertical (shaft melting) furnace. There are no infiltration forms (icicles) typical of the smelting process, which could suggest the use of shaft furnaces or smithing.

Sample no. 4 is a porous lump of slag containing grains of sand. This conglomerate may have already formed after the ore reduction process, when the largely liquefied slag came into contact and mixed with sand in the immediate vicinity of the furnace (e.g., sandy soil?). If sand has entered the forming slag during the reduction process (i.e. inside the furnace, at high temperature), the silica (found in the form of grains) would have reacted with the iron oxides to form fayalite - the main component of the slag and grains.

Sample 2 is difficult to interpret. The shape (plate) and cross-section (Pl. 1) suggest that it may be both a form of slag cooling on a flat surface and a mineral with high iron content (ore). A conclusive explanation of this will be possible after analytical studies are performed, particularly phase analysis.

Among provided slag fragments, there were two samples of lumps consisting of clumped grains of mineral (silica) with a spherical shape (samples 1 and 6) (Pl. 1). The dimensions of the grains are close to each other (they are about 0.2 mm). These lumps were probably formed from carefully sieved river or sea sand. Their role in the metallurgical process at this site is unclear and could be clarified by further analytical studies.

Sample no. 5 is a clay. It has a relatively low content of impurities. This clay may have been used during the construction of the smelting furnace, e.g. in the form of bricks or as a furnace lining.

IRON WORKING AT PODŠILO - MULTI-CRAFTING, RECYCLING OR OBJECT'S REPAIR?

Production and processing of not only foodstuff has been ascertained within a number of rural settlements spanning the whole of the Roman world. In fact, rural, but maritime villas as well where most often seats of activities such as pottery production, lime manufacture and/or iron working (Marzano 2007: 63–67; 2018: 128; Giannichedda 2008: 202–203; for types of rural craft settings see: Peña 2017: 206–207). Moreover, some of the products of such activities were deemed to be a *fructus* of the estate, similar to wine, olive oil or other foodstuff (e.g. for pottery: Aubert 1994: 204–205; Pelliccioni 2010: 22–23; Tchernia 2016: 10–12; for iron working see: Pleiner 2006: 149–151). Crafts organization can thus be presumed (as intended in Peña 2017) and, at least judging by the evidence from other provinces, output from these activities could have been highly lucrative (e.g. iron working in Britain, see: Bray 2010), while in other instances it might have been produced for self-supply and local consumption (Giannichedda 2008: 202–203; Peña 2017: 212, 227–228).

While the results of the first analytical approach to the evidence of iron working at Podšilo do confirm metallurgical production going on at the site, they do not speak of its chronology, scale or organisation, thus allowing only to infer on the possible products. At this point it is also difficult to assess whether smithing or also smelting was going on at site, although more secure evidence for the latter is still lacking. Some data can, nevertheless, be obtained through the analysis of the other structures discovered within the bay, and their mutual relationships.

A fairly certain date for at least one phase of usage of the excavated pottery kiln places it within the 3rd c. AD, a time-frame recognised also in the material culture and absolute dates obtained from the samples collected in the trenches at Podkućine and Beli grad (Welc et al. 2019; Konestra et al. 2020). On the other hand, the complex's architecture, and especially construction techniques, might indicate a somewhat earlier setup, with other evidence pointing to life on the site lasting at least until the 6th c. AD (Konestra et al. 2020). The destination of the products from the pottery kiln(s), due to its relatively small dimension and products' features (e.g. lack of stamps), is assumed to be mostly for self-consumption on the site or in any case locally, but still opened to a debate (Lipovac Vrkljan, Konestra 2018: 23).³ If that is to be assumed, it is still unclear whether the setup of the kilns was related to a first construction phase or a renovation, as still no stamped tegulae (usually a common, chronologically indicative feature on similar sites) have been recovered, while some of the

3 Such an assumption might be further supported by the find of kilnworks in nearby Mahučina bay, located on the Sorinj peninsula closing from south Lopar Bay, and in front of another Roman rural site (Zidine) (Lipovac Vrkljan, Konestra 2018: 16).

Table 1 Results of preliminary metallographic analyses of samples from Podšilo bay (author: W. Weker)

Sample number	Tests performed	Observations	Test results
1	Cleaning, washing, x-ray examination, preparation of the microsection, microscopic examination.	The structure of the lumps is porous, brittle, heterogeneous, easily crumbling. No visible traces of high temperature impact. Visible dripstones forms of iron oxides. On two fragments there are forms of crystallized oxides – similar to that formed on plant fragments. There are also large lumps made of black Fe oxides (magnetite?).	Fragments of lumps not derived from the metallurgical process. These lumps may have formed in the vicinity of the metallurgical site as a result of a reaction of minerals with iron oxides.
2	Cleaning, washing, x-ray examination, preparation of the microsection, microscopic examination.	Compact, hard structure, no visible signs of re-melting, composed of black Fe oxides (magnetite?).	Mineral plate with high Fe content, needs further investigation (especially phase analysis).
3	Cleaning, washing, x-ray examination, preparation of the microsection, microscopic examination.	Porous lumps structure, melted, hard, composed of fayalite.	A slag lump formed in a metallurgical process (probably Fe smelting).
4	Cleaning, washing, x-ray examination, preparation of the microsection, examination.	Porous, hard, melted structure, composed of fayalite.	A slag lumps formed during a metallurgical process (probably Fe smelting).
5	Macroscopic examination, X-ray examination, sieve analysis, water rinsing.	The sample was completely dissolved in water. Sieve analysis allowed to separate 2 fractions from the clay sample: very small number of fractions with average size of 0.75 - 1.2 mm in diameter and slightly bigger fractions with diameter over 1.2 mm (small stones, plant remains, small clumps of Fe oxides). Properties typical for clay.	A sample of clay soil not directly related to the metallurgical process. This could be clay used in the construction of a furnace, for example.
6	Cleaning, washing, x-ray examination, preparation of the microsection, microscopic examination.	Porous structure of lumps, frangible, heterogeneous, easily crumbled. No visible signs of high temperature effects, composed of black Fe oxides (magnetite?).	A lump of mineral with high Fe content. Requires further study (phase analysis).
7	Cleaning, washing, x-ray examination, preparation of the microsection, microscopic examination.	Porous, lump structure. Melted. Hard, composed of fayalite.	A slag lump formed during a metallurgical process (probably Fe smelting).
8	Cleaning, washing, x-ray examination, preparation of the microsection, microscopic examination.	Visible outline of a longitudinal quadrilateral object.	A heavily corroded iron object.
9	Cleaning, washing, x-ray examination, preparation of the microsection, microscopic examination.	Porous structure, melted, hard, composed of fayalite.	A slag lump formed during a metallurgical process (probably Fe smelting).

recovered ceramic building materials are with high probability local products.⁴ Although pottery (see: Peña 2017: 214–216), but partly also architectonic ceramics production, are deemed to be a craft requiring both stable infrastructure, tools, a degree of specialisation and raw materials, instances of single kilns interpreted to have existed for limited time-spans are not a rare occurrence (e.g. Deltenre, Orlandi 2016).

One of the main questions that arises when scrutinising metalworking activities in the bay of Podšilo is its very location. It is still unclear if these activities could have been carried out within or in close proximity to what seems to be the main

⁴ A region-wide rebuilding within urban centres, proven by epigraphy at both *Rab* and mainland *Senia* (Lipovac Vrkljan et al. 2017: 328 with earlier bibliography; Zaninović 1981: 191), could also be proposed as a reason for a shortlived larger need for CBM.

residential area of the settlement/estate, since most of the slug has been collected within the eroded sediment in the northern slopes of the bay, which is in the vicinity and within the very structures at Beli grad (*villa?*). Possible pyrotechnical feature was also detected here by geophysics (see *supra*, Fig. 2, 4).

It is evident that the pottery kiln(s) were detached from the residential structures, probably in an attempt to separate a polluting and potentially dangerous craft from the living quarters of the site (e. g. Vennarucci et al. 2018: 594–595). A vicinity of an equally “undesirable” feature designed for metalworking seems therefore unlikely, especially if iron working is to be considered an organised and planned activity as CBM production seems to have been. This observation would speak, at least for the moment, against the possibility of multicrafting occurring simultaneously within the complex at Podšilo, and would indicate that reasons and modes of iron working setup might rather be sought elsewhere.

Possible explanations might be sought at sites boasting similar features, sites that comprise evidence of iron working within or in close proximity to a (former?) residential/productive unit of a rural settlement. On the eastern Adriatic examples are rare, mostly originating from nearby Istria (*X regio* of Italy) and pertaining to post-*villa* phases. The best evidence is perhaps that of Dragonera, in south-western Istria, where a smithy producing iron objects have been identified within the remains of an earlier *villa* (Starac 2010: 80–81). While the interpretation of the supposed smelting/smithing kiln is somewhat doubtful, in vicinity of this structure slugs and iron objects have been found, along with a heart located close to a base made of stone slabs (Starac 2010: 80–81; Koncani Uhač 2010: 244). Metallurgical activity at Dragonera has been dated in the 5th and apparently lasting until the 7th c. AD (Starac 2010: 113). Another similar, later setup of iron working within a rural *villa* was also found in the *ager* of *Pola*, at St. Cecilia near Guran, where within a space readapted from an earlier phase of the rural complex, layers of burnt soil, slug, pits and kilns/ovens/furnaces were established (Terrier, Jurković 2009; Marić et al. 2010: 338). As the associated movable finds have not yet been assessed, it is difficult to propose the exact function of these structures. Moreover, similar structures and metalwork activity traces have been discovered at St. Blek near Tar-Vabriga (in the *ager* of Parentium). This specific section of the site has been interpreted as a smithing workshop installed on the remains of a former food processing area (a kitchen?) (Konestra et al. 2021), but here again seemingly devoid of movable finds other than slag. The two latter examples do not present enough evidence for a secure dating of the iron working features, but those at St. Blek are certainly datable after the mid-Roman period. Lastly, in the hinterland of northern Liburnia (nowadays Lika region), a rural *villa* with a seemingly dedicated smithing/smelting area has recently been excavated at Lički Ribnik. The facility, dated to the 2nd-3rd c. AD phase of the complex, is located in a sector detached from the living quarters, close to a presumed kitchen (Ožanić Roguljić, Kolak 2018: 119–123). Finally, from the town of Rab, the discovery of a blacksmith's (?) heart and layers pertaining to the workshop within an area in close proximity to the (late Antique?) town walls (Jurković, Kranjec 2016) might indicate that new craft setup invested not only rural, but also the urban realm of the post-Roman eastern Adriatic, perhaps also as a recycling/recovery activity, as witnessed elsewhere (e.g. Tůmová, Cirelli 2019; Cirelli, Snyder 2021: 350–352; Murphy, Poblome 2021: 108–111).⁵

Further afield, similar situations are also well known from the Italian peninsula and beyond (Munro 2010; 2011; 2020; Castrorao Barba 2017; see also: Fleming 2012) indicating that, perhaps, iron working setup within rural complexes with the refunctionalisation of their spaces in late Antiquity is not such an isolated occurrence (Giannichedda 2008: 203). These structures, just as those pertaining to other productive activities are often connected to the recycling of materials from the very structures of the former *villa* (stone, glass, lead, iron etc.), especially when located within or at short distance from its residential quarters (Munro 2010: 227–229; 2011: 77; Bertoldi 2015; Deltenre, Orlandi 2016: 76). Such activities, to be seen as a stand-alone phase of post-*villa* occupation, indicate that recovering materials was a profitable endeavour certainly taken on by skilled craftsmen and not casual new inhabitants of the area, a practice that might be connected to a general trend of the late Antique economy (e.g. Marcone 2018; Giannichedda 2008), which at least in some areas sees a cessation of large scale extraction and production, but that was in fact carried out throughout antiquity (Giannichedda 2008: 192–193, 204; Munro 2010: 237–238; 2011: 77). Another instance of deconstruction of former architectural elements at Podšilo might be indicated by the column base found at Podkućine within a context of building abandonment (Konestra et al. 2018: 125). On the other hand, shaping and production of implements necessary for construction often occurred on-site during building phases, and it is precisely than that small-scale iron working might have been implemented, either during the first setup of the complex or during subsequent reconstruction (Munro 2011: 77–78, 85–86; 2020: 384). In the latter case repurposed and recycled materials from the previous building phases could have been used both onsite or off-site (Munro 2020: 385). To the first phase of construction on the site activities such as lime production might be linked, while it is still to be assessed

5 Evidence of iron smithing of earlier date are nevertheless known from several Roman towns (e.g. Quercia 2011: 206–208 for southern Italy), possibly including *Salona* (Ivčević 2019: 125–126 with earlier bibliography).

whether the allochthonous limestone used for construction (and with all probability lime production) was acquired in nearby areas (mainland Rab or nearby island of Goli and Grgur) by the construction team, estate workers or through trade.

Finally, another possibility might be pointed out, that is, the need of the estate to perform repairs to their tools and other iron implements, as small-scale finds of iron slug within *villa* assemblages might suggest (Pleiner 2006: 151; Kirigin et al. 2011), and as such part-time, small scale activity might have been located in closer vicinity to living/working quarters (e.g. Lički Ribnik, Ožanić, Kolak 2018: 119–123). If that was the case, a certain degree of crossover and shared knowledge between crafts, in this case pottery production and iron working, might be supposed (e.g. Dobres 2014: 201).

Being data still too scanty to draw definitive conclusions, the question as to whether Podišilo bay hosted a multi-crafting community (perhaps also engaged in other still archaeologically undetected crafts or productions) or CBM and iron production were connected to the erection, rebuilding or final demise of the architectural complex remains open. More information on the chronology of the latter activity will certainly aid a better understanding of crafts and production at this site, but possibly also island-wide, just as a better understanding of the architectonic complexes will allow to better define the activities conducted within each segment of the settlement.

ACKNOWLEDGMENTS

The analyses of iron and slag samples presented in this article were supported thanks to a grant from the Polish National Science Centre (Narodowe Centrum Nauki): *The fall, crisis or transformation? Correlation of the late antique settlement pattern changes with environment and climate fluctuations in the north-eastern Adriatic region based on results of geoarchaeological and palaeoclimatic research*, ID: 478202 NO. 2020/37/B/HS3/02458.

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Pl. 1

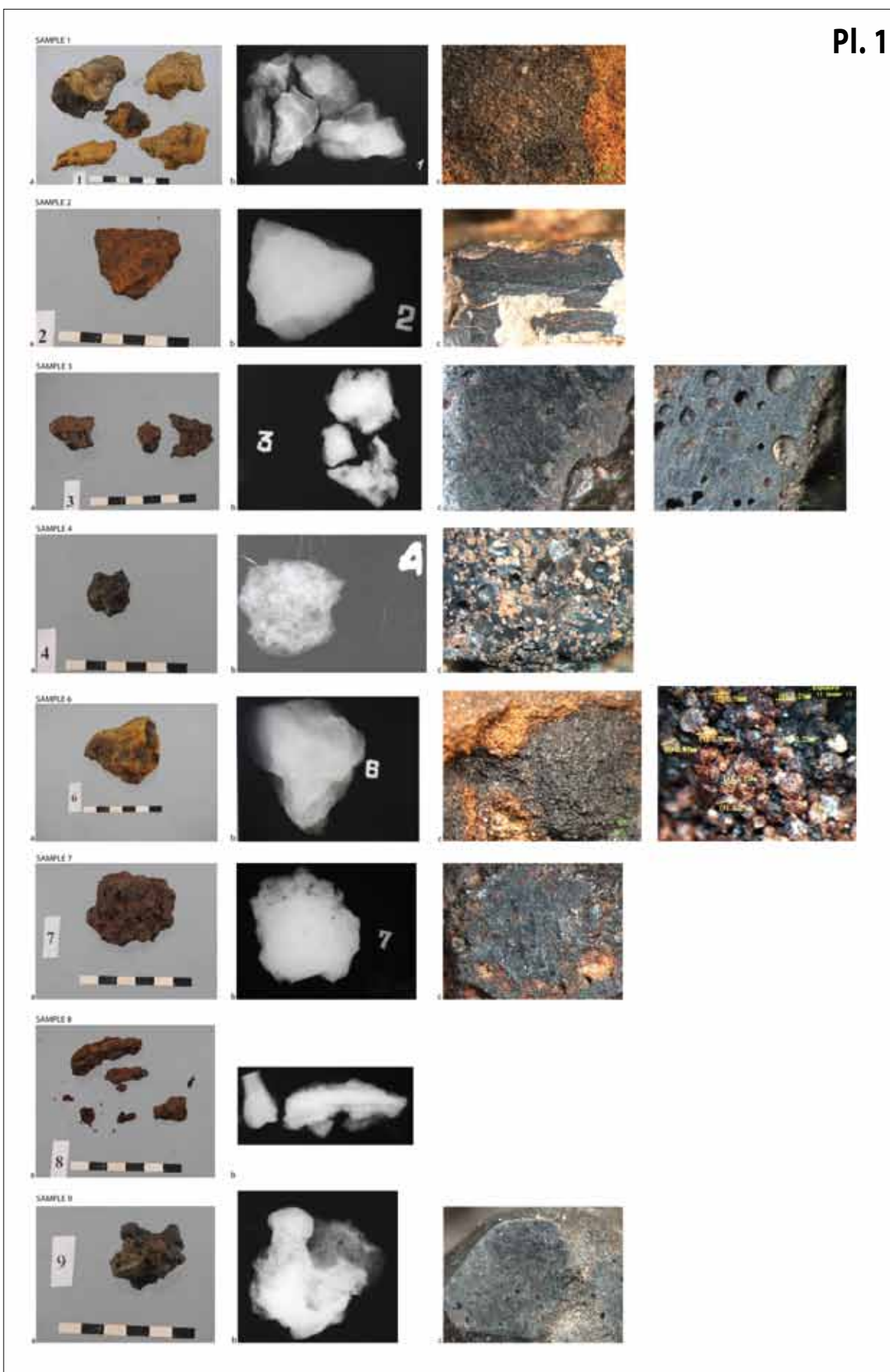


Plate 1 Samples images: a - macroscopic image; b - X-ray image; c - microscopic image (photos and images: W. Weker)

PRŽANJ IN LJUBLJANA – A METALLURGICAL SITE WITH TRADITION?

The lowland settlement of Pržanj near Ljubljana was excavated in 2004 and ¹⁴C-dated between the 5th and 12th centuries. The site is marked by intensive metallurgical activity, making it unique from the other contemporary settlements in Slovenia.

This paper presents the results of the mineralogical and chemical analyses of twenty two (22) iron slag, ore, and furnace lining samples from Pržanj and suggests a preliminary interpretation of the results.

An optical emission spectrometer with an inductively coupled ICP-OES plasma was used for chemical analysis and X-ray powder diffraction XRD for phase analysis. Additionally, we used the Rietveld method to determine the proportion of the crystalline phase.

The mineral phase analysis showed that the site, in which very high temperatures were reached, was undoubtedly used for iron smelting. Ore analysis showed that they exploited goethite, and the slag analysis showed that two different ore smelting processes were practised. Lime was added to one, but not to the other. In some samples, we observed that the added ore was unroasted. Also, in all samples that were apparently exposed to very high temperatures (above 1000 ° C), the mineral fayalite (2FeO.SiO₂) is found, which supports the assumption that quartz (SiO₂) was used as a flux.

Key words: archaeometallurgy, Late Antique slag, Early Medieval slag, Pržanj near Ljubljana archaeological site (Slovenia), fayalite iron slag, bloomer, iron smelting, iron ore

INTRODUCTION¹

The lowland settlement of Pržanj near Ljubljana was investigated in 2004 (Turk, Svetličič 2006). It is ¹⁴C-dated between the 5th and 12th centuries, with the most dates between the 7th and 10th centuries. This site is characterised by intensive metallurgical activity, which is reflected in the more than 230 kg of slag discovered. The Pržanj site is the first, and so far only, to offer insight into the iron metallurgical practices of the early Middle Ages in modern day Slovenian. In addition, given the ¹⁴C- dates and material, we presume that the metallurgical site may have been in use as early as Late Antiquity.

The purpose of this paper is to present the preliminary results of metallurgical analyses of 22 slag and ore samples from the site. We hope that with the results, we will be closer to answering questions such as: can we identify different metallurgical processes and knowledge over a long period of occupation at the settlement? Moreover, was this activity continuous, or did it change between Late Antiquity and the early Middle Ages?

SETTLEMENT PRŽANJ NEAR LJUBLJANA²

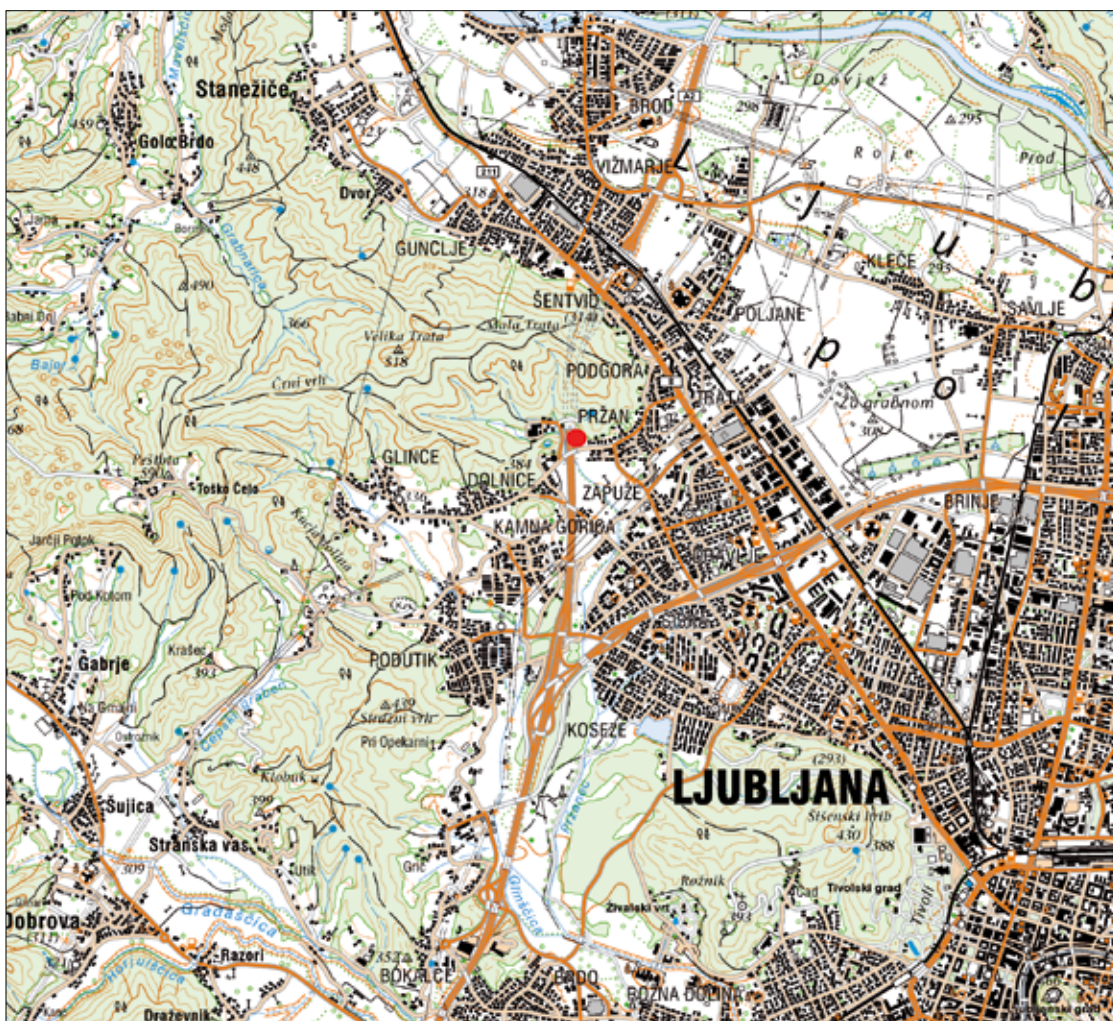
Once located on a meadow at the southern foot of the Gradišče hill above Šentvid near Ljubljana (Fig. 1, Map 1), where the southern entrance to the Šentvid tunnel is today, a settlement was discovered during the excavation of a 3,200 m² area. It was bordered on the north and east by the Pržanec stream, with part of the settlement on the other side of the stream. On the south and west sides, the borders of the settlement are not clear. In part of the site, a hollow was filled with a grey clay layer, which indicates that it was swamped for a long period of time, but as the groundwater level dropped, it was covered by vegetation (Verbič 2004).

1 The contribution presents the results of the research (co) financed from the national budget pursuant to the contract between the Slovenian Research Agency and the National Museum of Slovenia (research programme P6-0283).

2 Data summarized after the report (Turk, Svetličič 2006) and after the publication (Hrovatin, Turk 2008), where data on the first four ¹⁴C-dates are also presented.



Fig. 1 Panoramic view of the Pržanj site. View to the north (photo: I. M. Hrovatin)



Map 1 Map with the location of the Pržanj site (red dot) (source: Geodetska uprava Republike Slovenije, National Topographic Map at 1:50 000 Scale, access 4.1.2020)

The highest concentration of both archaeological features and artefacts were found in the central and eastern part of the site, almost along the Pržanec stream itself (Fig. 2).

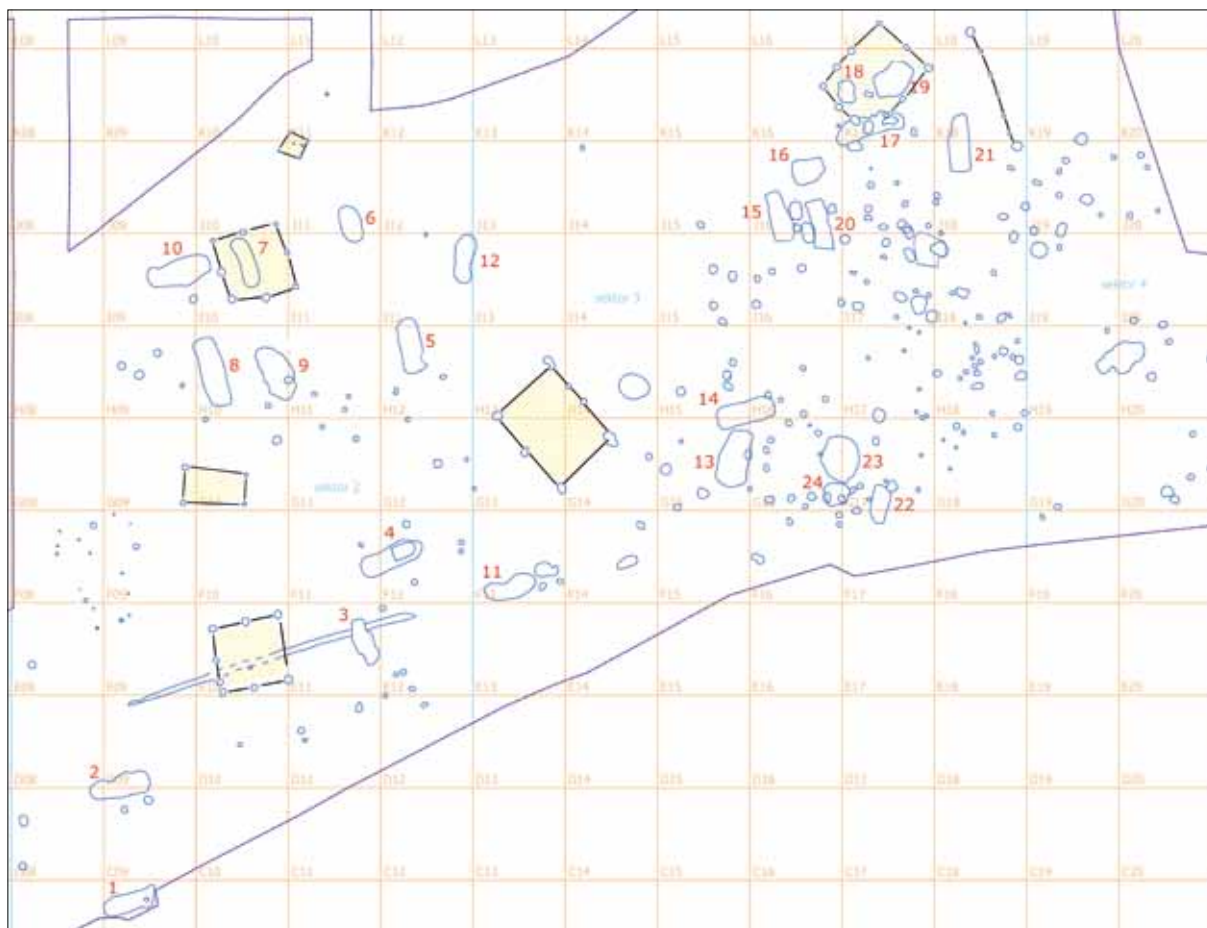


Fig. 2 Plan of the Pržanj site. View to the north. 24 larger pits (marked with red numbers), 5 buildings (marked with a yellow hatch), and many smaller pits and postholes were discovered

An essential feature of the site were the pits of predominantly oval or rectangular oblong shapes (Fig. 3). Of the 24 bigger pits, 19 belonged to this group. The remaining five pits had an irregular or round ground plan. In addition to these, slightly smaller pits with an almost completely round shape appeared in the eastern part of the research area.



Fig. 3 View of the pit no. 17. View to the east. Three slag samples were analysed from this pit. A total of 13.2 kg of slag was discovered in this pit (photo: I. M. Hrovatin)

The pits were filled with a dark layer containing charcoal, and numerous stones,³ which sometimes formed an apparently deliberately built paving along the walls and along the bottom, and sometimes lay in disorder over the whole surface of the pit. In addition to the stones, there were many artefacts recovered - fragments of pottery, individual pieces of Roman and early Medieval glass, iron slag, and large amounts of burnt clay, which clearly indicates traces of fire in or near the pits (Fig. 4).



Fig. 4 Selected pottery (in the back), a larger piece of slag from layer SE 67 (middle front) and part of the furnace lining with slag (left) (photo: T. Lauko)

In many cases, the bigger pits were accompanied by individual postholes, which could be remains of auxiliary roof structures, like canopies. In some cases, they formed groups of parallel or rectangular lines. This is indicative of floor plans of buildings, presumably houses (Fig. 2). The building in the south-western part of the site was the most well defined with seven postholes for the pillars of the roof, and next to it a partially preserved building identified by five postholes.

Most of the postholes in the eastern part of the site were seemingly disordered and therefore not possible to determine which were contemporary. The group of seven postholes that formed a straight line along the stream bed on the eastern edge of the site was among exceptions. Given that those postholes lay in the deepest layer of the settlement, they may be understood as a remnant of the terracing of the terrain along the bank of the stream.

No preserved clay kiln that could be undoubtedly defined as a smelting furnace was discovered at the site. But charcoal, burnt stones, and large quantities of iron slag, including several on burnt clay, show that some of the pits were probably used in the smelting process. It is also possible that smelting furnaces existed but were completely destroyed and parts of them were used to fill in the pits. Smelting activity is also indicated by the choice of the location in the immediate vicinity of the Pržanec stream, with a wooded hinterland that provides wood for furnaces, and the settlement also lay on a clay layer that would enable the construction of clay smelting furnaces.

Ten charcoal samples from seven larger pits, two postholes, and one smaller round pit were ¹⁴C-dated. The earliest date has a range between 420 and 610 (Hrovatin, Turk 2008: 145), and the others range between 535 and 1169. According to these dates, the settlement existed somewhere between the 5th and 12th centuries. As the analysis of the entire material has not yet been completed, we do not yet know exactly whether the settlement existed continuously throughout the entire period or was used only occasionally or in certain periods.

So far, only material from pit no. 17 has been analysed in detail (Hrovatin, Turk 2008: 146–148). The majority of the finds are pottery, dated in the period between the 8th and 10th centuries, but with characteristics connected with a Late Antique tradition (Hrovatin, Turk 2008: 147).

Two glass beads from the site were also evaluated and analysed by the combined method of proton-induced X-rays and gamma rays (PIXE, PIGE) (Knific, Šmit 2018: 379, 389). These beads belong to the group of “mosaic beads with an eye”, dated to ca. 800, and perhaps even earlier. They have come in large quantities from the East to the markets throughout Europe (Knific 2008: 36). The analysis showed that they were made of halophytic glass, which was in use in this area from the second half of the 8th century onwards (Šmit et al. 2009; Šmit et al. 2012; Knific, Šmit 2018: 378–381). Unusually, the charcoal from the pit with one of the beads was dated between 535–678 (with a probability of 81.1%), which is more than

3 Lithologically, these are mainly shales, mudstones and quartz sandstones, but also quartz conglomerate occurs (Verbič 2004). Some of the stones were burnt and some exposed to the heat for long time since they looked severely damaged and weathered.

a hundred years older than the generally accepted dating for mosaic beads (Knific 2008: 36).

All of this evidence suggests that Pržanj is the only site of its kind in Slovenia. It is a lowland settlement with intensive metallurgical activity, which operated both in Late Antiquity and in the early Middle Ages. The nearest parallels to Pržanj are in Podravina in Croatia and were researched in the last thirty years (Valent et al. 2017).

METHOD

In 2020 we analysed 22 samples of slag and ore from Pržanj, some of which come from pits that are radiocarbon-dated. We ground slag samples in a ball mill to obtain a fine powder suitable for chemical and phase analysis. An optical emission spectrometer with an inductively coupled ICP-OES plasma was used for chemical analysis to obtain the chemical composition (not including oxygen) (Agilent 720). Table 1 presents the chemical composition of the samples converted to oxides according to XRD phase analysis.

For phase analysis we used X-ray powder diffraction XRD, an X-ray diffraction device (XRD, Panalytical XPert Pro PW3040 / 60) (Burja et al. 2014; Burja et al. 2015). Additionally, we used the Rietveld method to determine the proportion of the crystalline phase.

Table 1 Chemical compositions of slag converted to oxides. The first column contains sample designations and - in some cases - indicative dates, according to ¹⁴C dates of charcoal samples from the same pits

Sample ID / dating	MgO	MnO	V ₂ O ₃	TiO ₂	CaO	K ₂ O	Al ₂ O ₃	P	SiO ₂	FeO
ORE	0,00	0,17	0,00	0,00	0,31	0,00	0,00	0,14	0,00	99,38
053 FURNACE LINING	1,62	0,15	0,00	1,90	0,22	3,87	6,07	0,18	77,07	8,91
619 PIT 21	0,42	0,11	0,00	0,58	0,30	1,35	2,12	0,21	29,95	64,96
532 PIT 20	1,73	0,32	0,00	0,68	0,98	1,25	1,96	0,20	31,47	61,40
485 PIT 17 5 (7 th -8 th cent.)	2,27	0,36	0,11	0,70	1,31	1,75	2,74	0,24	30,54	59,98
485 PIT 17 3 (7 th -8 th cent.)	0,64	0,16	0,00	0,38	2,67	2,84	4,44	0,11	77,43	11,32
481 PIT 16	2,02	0,29	0,11	0,82	0,93	1,36	2,13	0,17	30,49	61,68
395 PIT 14 (end of 10 th -12 th cent.)	0,97	1,95	0,18	0,96	1,69	0,86	1,35	0,18	17,27	74,59
224 PIT 4 (7 th -8 th cent.)	4,46	0,42	0,55	0,50	2,54	1,66	2,61	0,24	28,85	58,16
053 SLAG	1,35	0,23	0,00	0,55	0,91	1,35	2,12	0,17	28,90	64,42
167 PIT 1	7,28	0,91	1,17	1,45	2,92	2,93	4,58	0,44	57,22	21,09
161 PIT 9 (3/3 of 8 th -end of 10 th cent.)	0,09	0,23	0,00	0,47	1,18	1,34	9,04	0,17	18,83	68,65
140 PIT 4 (7 th -8 th cent.)	2,02	0,10	0,00	0,29	1,43	1,79	11,07	0,18	18,54	64,58
421 PIT 13 (3/3 of 8 th -beginning of 11 th cent.)	0,11	0,68	0,14	0,36	1,33	0,98	8,56	0,19	15,49	72,15
487 PIT 18	0,07	0,15	0,00	0,28	0,73	1,07	8,19	0,12	26,70	62,69
145 PIT 5	0,07	0,35	0,00	0,60	0,79	1,33	15,75	0,19	22,81	58,11
485 PIT 17 (7 th -8 th cent.)	0,08	0,03	0,00	0,31	0,33	0,95	6,53	0,11	16,60	75,07
221 PIT 4 (7 th -8 th cent.)	2,01	0,12	0,15	0,36	0,53	0,97	12,43	0,22	22,44	60,77
489 PIT 19	1,15	0,24	0,00	0,57	2,26	1,94	3,05	0,13	28,55	62,11
551 PIT 19	0,77	0,19	0,00	0,75	4,66	2,05	3,22	0,10	27,78	60,48
433 PIT 15	1,49	0,36	0,00	1,00	3,08	2,45	3,84	0,17	37,49	50,12
158 PIT 8 (3/3 of 8 th -beginning of 11 th cent.)	0,91	2,10	0,19	1,05	2,85	0,92	1,44	0,23	17,42	72,88

RESULTS INTERPRETATION

Chemical analysis showed that all samples contained some iron, while three contained more than 50% FeO.⁴

From the XRD analyses (Tab. 2) we see that the samples have different mineral phases, most of the phases - wüstite, goethite, fayalite, hercynite, hematite and magnetite - contain iron. Of these, four samples⁵ already contain partially reduced iron oxides of the FeO type in the form of wüstite or fayalite. This strongly suggests that these are residues from a metallurgical smelting site, as high temperatures are required for their formation.

The sample from SE 619 (pit 21) is also interesting because it is probably the product of the reaction of ore with the furnace or flux, and iron oxides are also in the form of goethite and a small proportion in the form of magnetite. This occurs during the heating of the goethite, which can only happen in the furnace when it is stocked with unroasted ore. Therefore, we conclude that in this case the ore was not previously roasted. Roasted ore is no longer in the form of goethite, but magnetite. The same can be said for samples 487 (pit 18) and 485 (pit 17), except that they also have added lime.

Table 2 Preliminary interpretation of the phase analysis. Samples containing lime are marked in yellow and lime-free in green. The first column contains sample designations and - in some cases - indicative dates, according to ¹⁴C dates of charcoal samples from the same pits

Sample ID / dating	wuestite	goetithe	fayalite	hercynite	rutile	quartz	lime	hematite	magnetite
ORE		100							
053 FURNACE LINING					5	80		5	10
619 PIT 21		55		1		44			4
532 PIT 20	3		73	14		1			
485 PIT 17 5 (7 th -8 th cent.)	21		66	11		2			
485 PIT 17 3 (7 th -8 th cent.)	21		67	12					
481 PIT 16	25		57	12		6			
395 PIT 14 (end of 10 th -12 th cent.)	39		34	25		1			
224 PIT 4 (7 th -8 th cent.)	32		63	12		3			
053 SLAG	10		73	14	2				
167 PIT 1	32		49	7		8	4		
161 PIT 9 (3/3 of 8 th -end of 10 th cent.)	11		72	9			3		5
140 PIT 4 (7 th -8 th cent.)	33		39			11	3		15
421 PIT 13 (3/3 of 8 th -beginning of 11 th cent.)	23		57	16		1	3		
487 PIT 18		43				33	11		12
145 PIT 5	11		39	25		7	2		
485 PIT 17 (7 th -8 th cent.)		43				33	1		12
221 PIT 4 (7 th -8 th cent.)	19		49			22	2		8
489 PIT 19	26		68			4	1		
551 PIT 19	31		42			6	22		
433 PIT 15	14		70	8		5	3		
158 PIT 8 (3/3 of 8 th -beginning of 11 th cent.)	34		33	29		1	3		

⁴ It should be noted that in order to simplify the display, we considered for all iron that it is in the form of FeO, although in reality it is in several forms.

⁵ Samples: slag from layer SE 053, residue of furnace from layer SE 053, sample of ore and sample from SE 619 (pit 21), which is quartic ore.

We have identified two different iron extraction processes. In the first case, **lime** was added to the furnace as a flux, but not in the second case (Tab. 2). The increased lime content in the slag may be the result of several factors, such as ore and ash on the furnace lining, as well as the deliberate addition of CaO-rich materials such as various limestones or bones as a flux to lower the melting temperature (Kramar et al. 2015: 716). A very high content of lime was also present in all six samples of slag from the Late Antique layers in the settlement of Castra (today's Ajdovščina). The authors attribute this to the use of local siderite ore, but because the lime content can be up to 16%, they do not exclude intentional addition of CaO-rich materials to lower the melting point (Kramar et al. 2015: 717). In Pržanj, some samples contained lime and some did not. This indicates that either this is not due to a specific ore or two different sources of ore have been used. It is more likely that in some smelts, CaO-rich materials were added, while in others they were not.

These two processes are clearly not temporally exclusive or limited, as slag with or without lime can occur in the same pit (for example in pits 4 and 17, Tab. 2), as well as in pits dated to Late Antiquity (pit 4) or later, in early Medieval pits (Tab. 2).

It is possible that the processes are tied solely to the knowledge and experience of the individual metallurgist. Indirectly, however, we can assume that if there were several active metallurgists in the settlement, they did not all have the same knowledge.

In addition, the question arises as to whether different metallurgical processes have been used for different qualities of iron, and thus for different objects. This cannot be answered at this time. An analysis of iron objects, however, would certainly help.

The majority of samples contains fayalite ($2\text{FeO}\cdot\text{SiO}_2$) together with quartz (SiO_2), suggesting that quartz could have been added as a flux. At high temperatures the quartz binds with iron oxides to form fayalite. Due to its low melting point of 1205°C , fayalite enables better melting of slag (Jackson et al. 1993).

Wüstite (FeO) is probably present in the samples due to partial reduction of ore, and hercynite ($\text{FeO}\cdot\text{Al}_2\text{O}_3$) is most likely a result to the reaction of ore with furnace lining.

Goethite is an iron ore ($\text{FeO}(\text{OH})$) that does not yet have additional bound water as limonite ($\text{FeO}(\text{OH})\cdot n\text{H}_2\text{O}$). The presence of goethite does not mean that they did not use local ore – called “bobovec”, as goethite and limonite are related minerals and can be present in the same ore.

It certainly raises the question of whether they may have exploited the so-called “bog” iron ore. Mineralogically, bog iron consists of goethite, quartz, and variable amounts of aluminosilicates. The typical geochemical composition for bog iron ores in general are iron (Fe_2O_3) and silicon (SiO_2) as the main components of various bog iron phases (Brenko, Borojević Šoštarić 2020: 20). Mineralogical and chemical composition of samples from Pržanj site may support this possibility (Tab. 1, 2) and also, that the site lies at a location where the hilly area flows into the lowland part at the edge of the Ljubljana Marshes.⁶ Also, the thick clay layers discovered at the site indicate that the micro location was swampy for a long time. This issue could definitively be resolved by sampling and analysis of sediments in the wider vicinity of the site.

Recent geological research in Podravina, Croatia has shown that both Late Antique and Early Medieval metallurgists exploited “bog” iron ore, which is formed there due to favourable natural conditions: swampy terrain, groundwater fluctuations, special bacteria (Sekelj Ivančan, Marković 2017; Brenko, Borojević Šoštarić 2020: 20).

CONCLUSION

Archaeometallurgical analyses of these and additional samples are still ongoing, as well as analyses of ceramics and glass have not yet been completed, so we present here more of a preliminary observation than conclusions.

- The analysis of the mineral phases showed that it was certainly a metallurgical smelting site, where very high temperatures were reached.
- Ore analysis showed that they exploited goethite, which, along with limonite, could be found in a local ore, but also opens a possibility that they exploited bog iron ore.
- In the analysis of slag, two different ore smelting processes are indicated. Lime was added to one, not to the other.
- In three of the samples we can say that the added ore was unroasted. This is true for both types of samples, with lime and without lime.
- In all samples that were apparently exposed to very high temperatures (above 1000°C), the mineral fayalite is found together with quartz (SiO_2), which supports the assumption that quartz was used as a flux.

⁶ Geologist Ivan Rakovec reported about iron found on the eastern edges of Ljubljana Marshes (Rakovec 1955: 28) and about an ore, presumably bog ore (in Slovene *jezerski železovec*) in the area called Vič (south-western part of Ljubljana, also on the edge of Ljubljana Marshes) (Rakovec 1955: 58).

In our future work we will analyse the samples with an electron and an optical microscope (SEM and LOM). In electron microscopy, we will use micro-chemical analysis using an X-ray energy dispersion spectrometer (EDS) and determine the crystal structure of microstructural phases by analysing diffraction patterns of backscattered electrons (EBSD). With this technique we will also be able to elaborate on the cooling rate of slag and the temperature of formation.

We hope to better understand the metallurgical knowledge of the early Middle Ages through slag analysis. Together with the ongoing analyses of glass and ceramic material, we hope to better understand other aspects of life in this settlement as well as other social processes, such as the transfer of technological knowledge among different population groups.

Translation to English: Daša Pavlovič, Ana Mihelić
Proofreading: Kevin Garstki

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AN IRON PROCESSING WORKSHOP AT CARANSEBEȘ (17TH CENTURY)

Some places for iron processing were discovered here, during the excavations from 2017 and 2018. They are differently dated, starting at least from the 14th century and continuing until after the area was integrated in the Habsburg Empire.

The historical information regarding the iron processing in Caransebeș is quite poor. We know that, during the 16th century, the iron was brought from Bocșa region, known for its rich iron resources.

The excavated area is situated west of the inner fortification, near the medieval road that crossed the town from north to south.

Fragments of melted iron and iron slag, scattered or grouped, apparently without any connection between them, were discovered from the beginning in the Cass. 2/2017. Here they were mixed with fragments of broken bricks, stones, small fragments of mortar and charcoal. Most likely, based on the stratigraphy, this feature functioned during the 17th century, being contemporary with the street paved with stone immediately after the middle of the 16th century. Unfortunately, only a small portion on the western side of the cassette and a stone on the southern one were preserved from its elevation.

Other two groups of melted iron were identified in the northern side of S. 2/2018, coming probably from two different installations, but very close chronologically. Nails, most likely to be melted, together with iron fragments were discovered in both furnaces/hearths. Unfortunately, now we cannot know how it was looking its elevation, because the area was completely rearranged later, and partially covered with a layer of clay, with variable thicknesses between 20 and 30 cm, depending on the structures below. The total amount of iron discovered in S. 2/2018 raises to 3.500 kilograms, to which can be added 328 grams of nail fragments, most likely collected with the purpose to be melted, 318 grams of melted iron fragments and 220 grams of scattered nails.

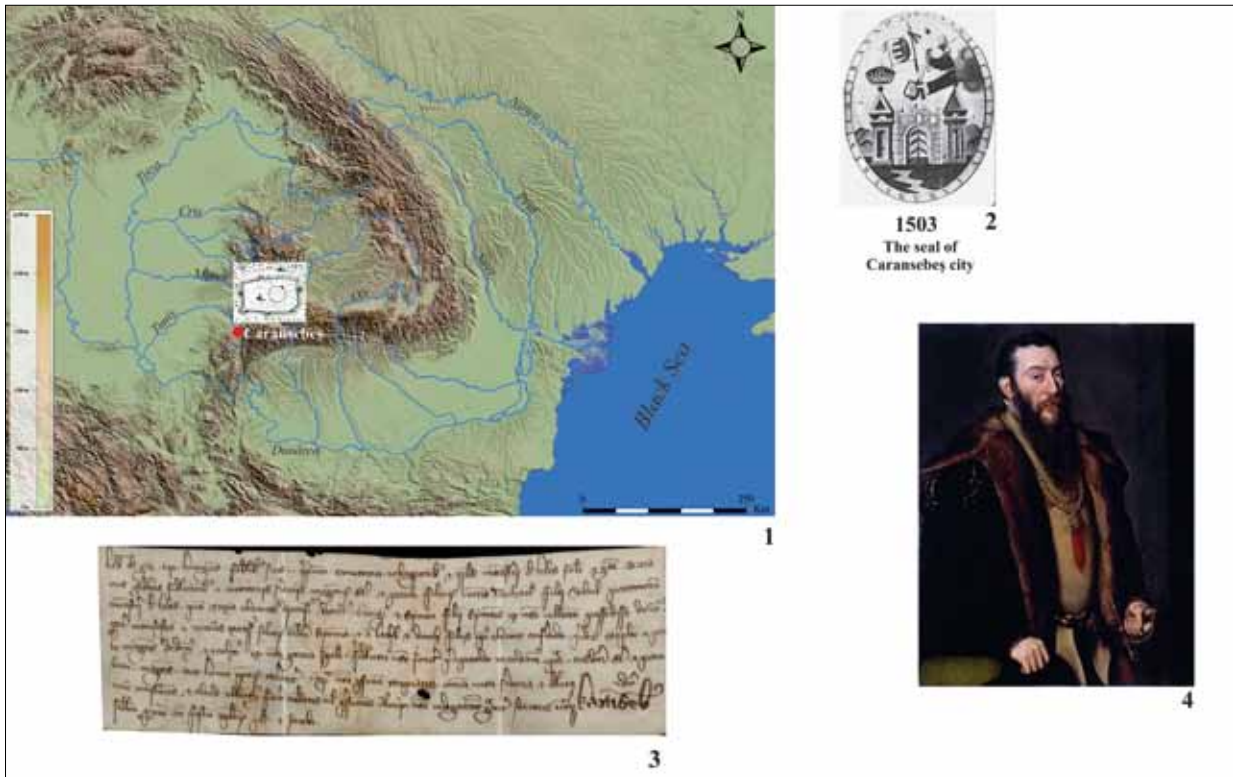
If we look at the surface observed on the profiles of sections and cassettes, the dimensions of the workshop were most likely quite large, about 12/8 m.

Key words: town, workshop, iron, pavement, coin, fireplace

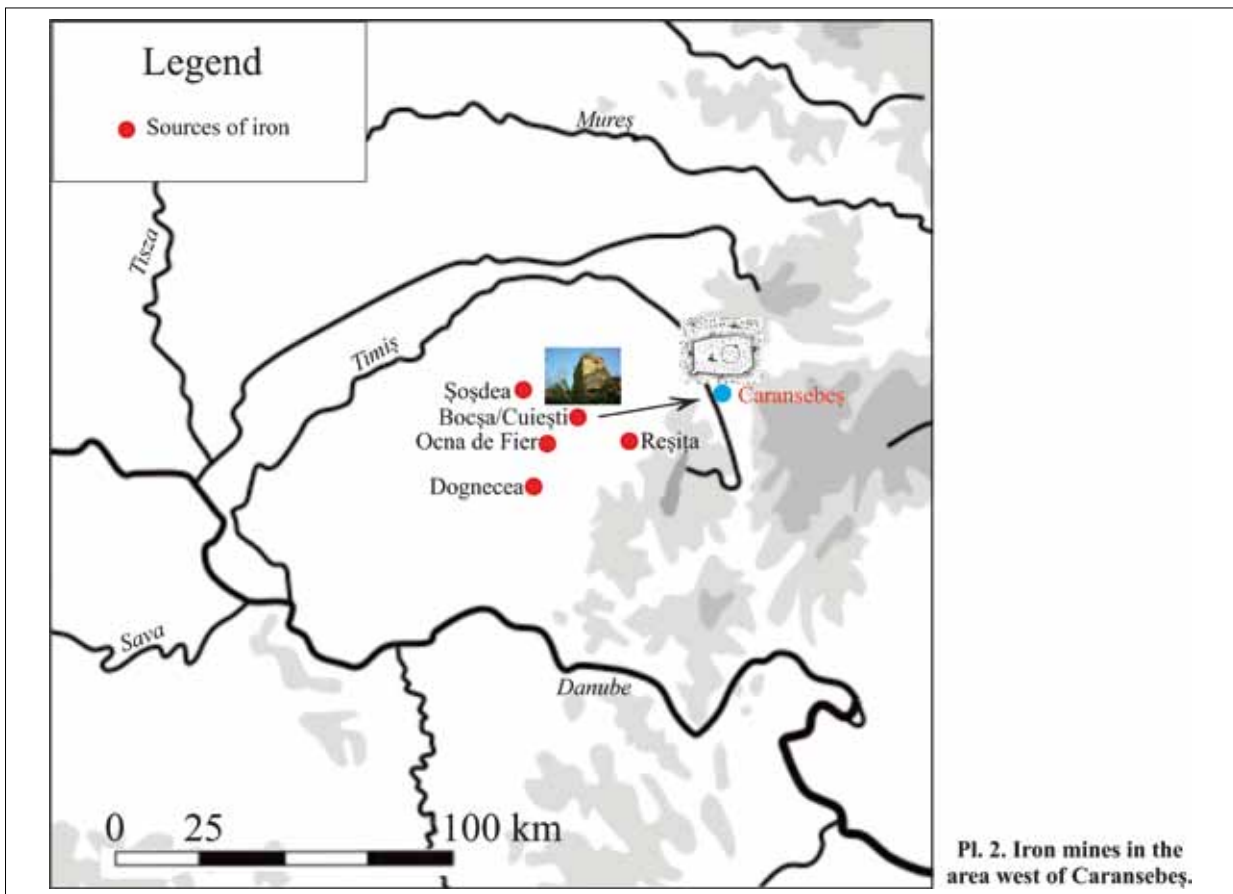
The medieval small town of Caransebeș (Sebeș; Pl. 1: 1) was attested for the first time during the reign of the king Ladislaus the Fourth "the Cuman" (1272–1290) (DIR, C, veacul C, XIII, II (1251–1300), doc. 359: 316) (Pl. 1: 3). Over time, its name had been changed, becoming Caransebeș, and in 1503 the town had its own seal (Groza 1993: 90, Fig. 1) (Pl. 1: 2).

Because of the imminent attack of the Ottoman Empire, immediately after the middle of the 16th century, the town attested in documents was fortified again, by an architect sent from Sibiu by the imperial general Giovanni Battista Castaldo (Călători străini despre Țările Române, Maria Holban, Maria Matilda Alexandrescu-Dersca Bulgaru, Paul Cernovodeanu (eds.), Vol. 2, București, 1970: 317) (Pl. 1: 4). At that time, the area between the River Mureș, Tisza, Danube and Southern Carpathians was systematically destroyed, for two years, by the Ottoman armies under the leadership of Pasha Mehmed Sokollu (Clot 1997: 198).

As a border town, with a significant defensive role, Caransebeș also needed blacksmithing workshops for the necessities of the garrison and of the local population, too. At the same time, the city was located near an important trade road that connected the southern Danubian area with Transylvania and the Hungarian Kingdom.

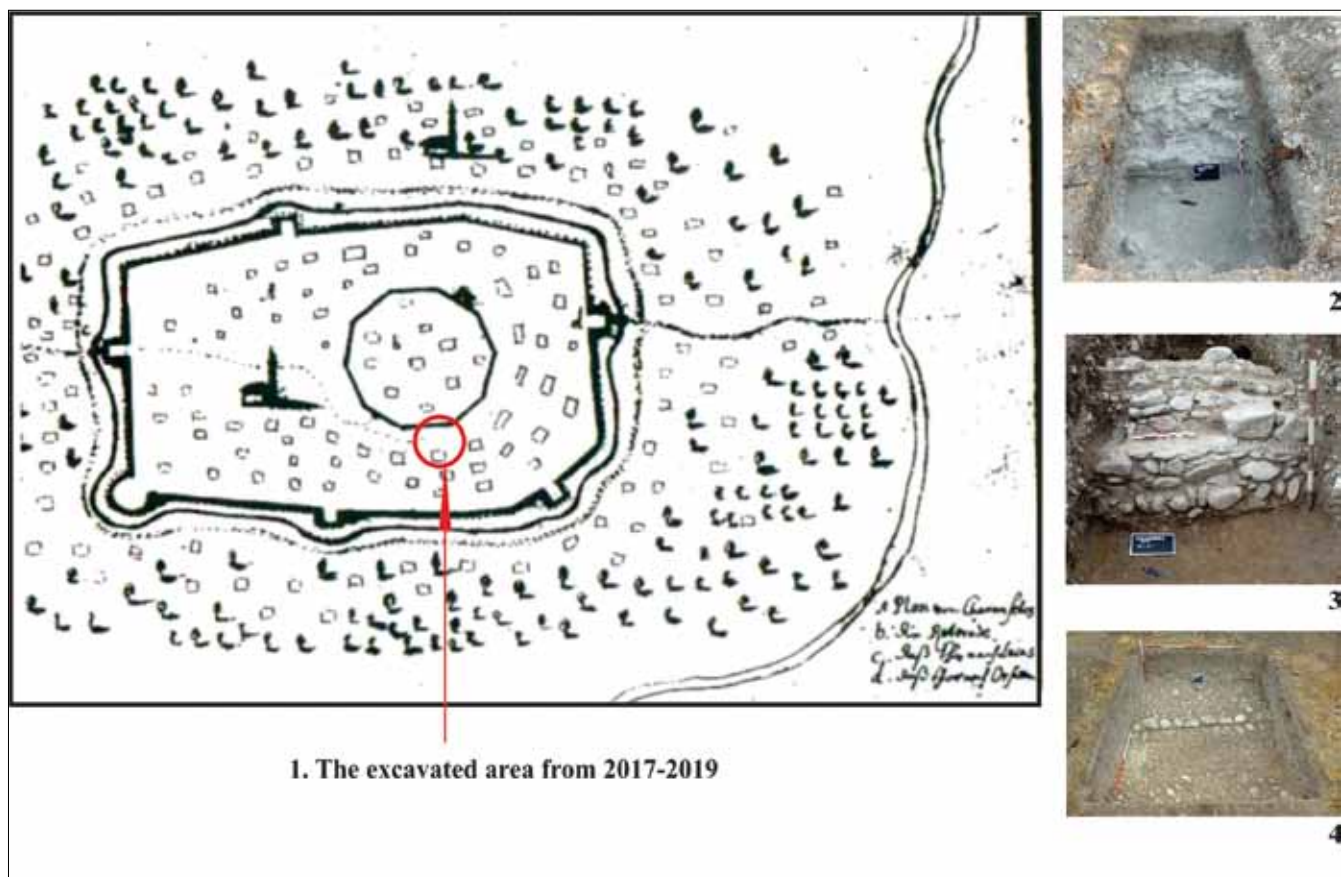


Pl. 1 1. Caransebeș town (made by: Mihai Florea); 2. The town's seal from the year 1503 (after: Groza 1993); 3. The first document about the town Sebeș (Caransebeș); 4. Giovanni Batista Castaldo, portret by Antonio Moro (https://it.wikipedia.org/wiki/Giambattista_Castaldo)



Pl. 2 Iron mines in the area west of Caransebeș (drawing: S. Oța)

Pl. 2. Iron mines in the area west of Caransebeș.



Pl. 3 1. The map of Caransebeș town from 17th century (after: Groza 1993); 2. Cass. 1/2017, wall fragment; 3. S. 1/2017, wall fragment from the little fortification; 4. Cass. 1/2019, sidewalk (photo by: S. Oța)

The historical information regarding the iron processing in Caransebeș is quite poor. Although the region is poor in metals, these were brought from the western neighbouring areas, most probably the Bârzava River basin or Dognecea Mountains, where mines were attested since the Middle Ages (DRH, C, XI (1356–1360): 85; Achim 1993: 59; Țeicu 1998: 260–261, 267), later used during the Ottoman period (Koch-Tufiș 2005: 368, 369). The region between the present-day cities of Moldova Nouă and Bocșa, and even further north, to Șoșdea, is known to be rich especially in iron ores, exploited since Antiquity (Stoicovici 1983; 1985; Țeicu 1987: 323, 325, 338, 343; 2003: 349, 350, 351; Țeicu, Lazarovici 1996: 102–106; Oța, Oța 2009: 196). We know that, during the 16th century, the iron was brought from Bocșa region, known for its rich iron resources (Țeicu 1996: 24). Bocșa was situated on the middle course of the Bârzava River, north-northwest of Reșița and west of Caransebeș (Pl. 2). It is quite difficult to say whether these acquisitions continued from the same centre or not in the following century, especially since we do not have yet metallographic analyses.

During 2017 and 2019, our archaeological research was concentrated in the central part of the fortified town (Oța et al. 2018b; 2019; 2020) (Pl. 3: 1), west of the small fortress inside (Pl. 3: 2, 3) and on and near the medieval road (Pl. 3: 4). Some places for iron processing were discovered here, during the excavations from 2017 (Pl. 4: 1, 2) and 2018 (Pl. 4: 3). They are differently dated, starting at least from the 14th century and continuing until after the area was integrated in the Habsburg Empire (Feneșan 1997). This article will focus only on those dated during the 16th and 17th centuries.

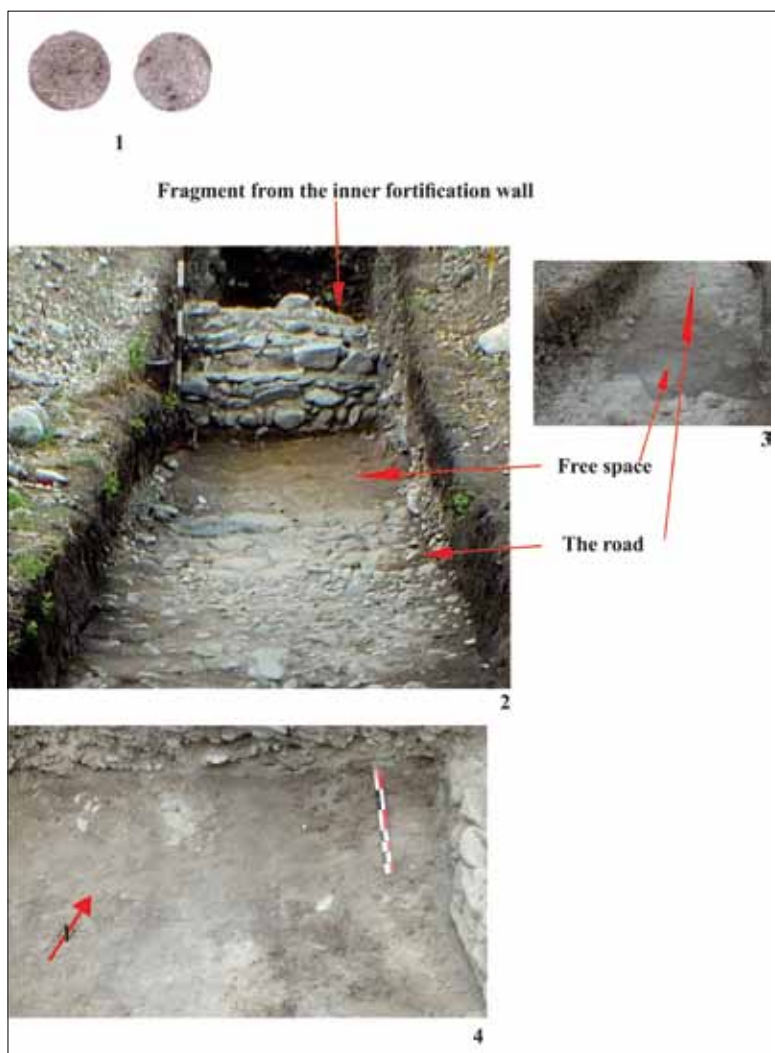
From the very beginning, we have to say that the research of this area is a partial one, and will continue in the next years.

The excavated area is situated west of the inner fortification (Pl. 3: 1), near the medieval road that crossed the town from north to south. During the 16th and 17th centuries, the houses were ranged to the pavement or the sidewalk near the street, to the west. A coin, issued by Gabriel Bethlen (1613–1629)¹ (Pl. 5: 1) found on the medieval pavement (Pl. 3: 4) prove that the street was used at that time. There was no sidewalk between the inner fortification and the road (Pl. 5: 2, 3), but only a few meters of compacted earth (Pl. 5: 4).

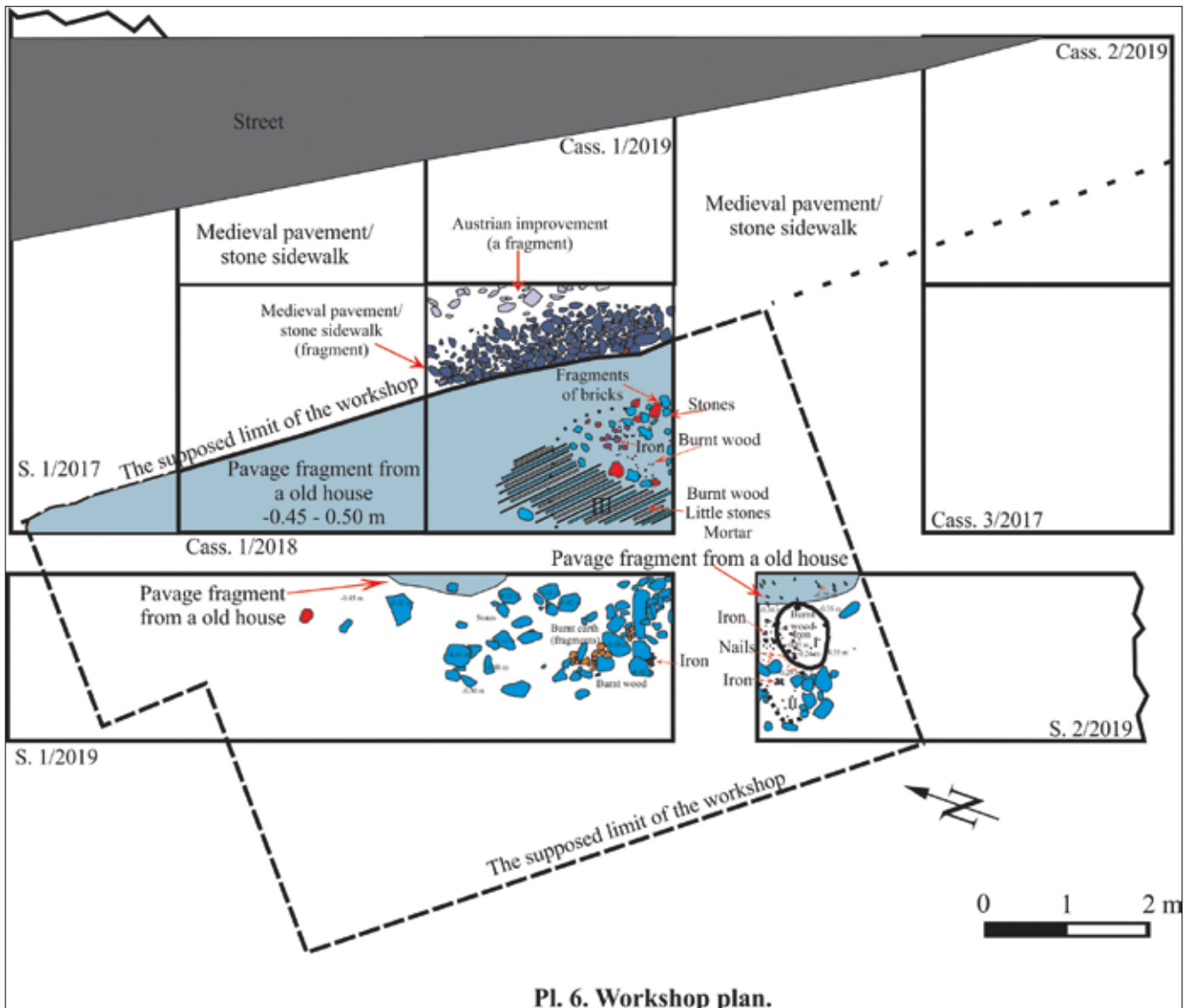
1 The Banate of Lugoj-Caransebeș was occupied by Ottoman Empire, in the first phase between the years 1658-1688 (Feneșan Cr. 1977: 223-238).



Pl. 4 1–2. Cass. 2/2017. Fragment of fireplace with iron bits inside; 3. S. 2/2018. Fireplaces with scoria/dross iron; 4. S. 1/2018. Fragment of fireplace with iron bits inside (photo by: S. Oța)



Pl. 5 1. Coin, issued by Gabriel Bethlen (1613–1629); 2, 3. Part of the road in front of the inner fortification; 4. The free space with fireplaces, bird bones and pottery fragments (photo by: S. Oța)



Pl. 6. Workshop plan.

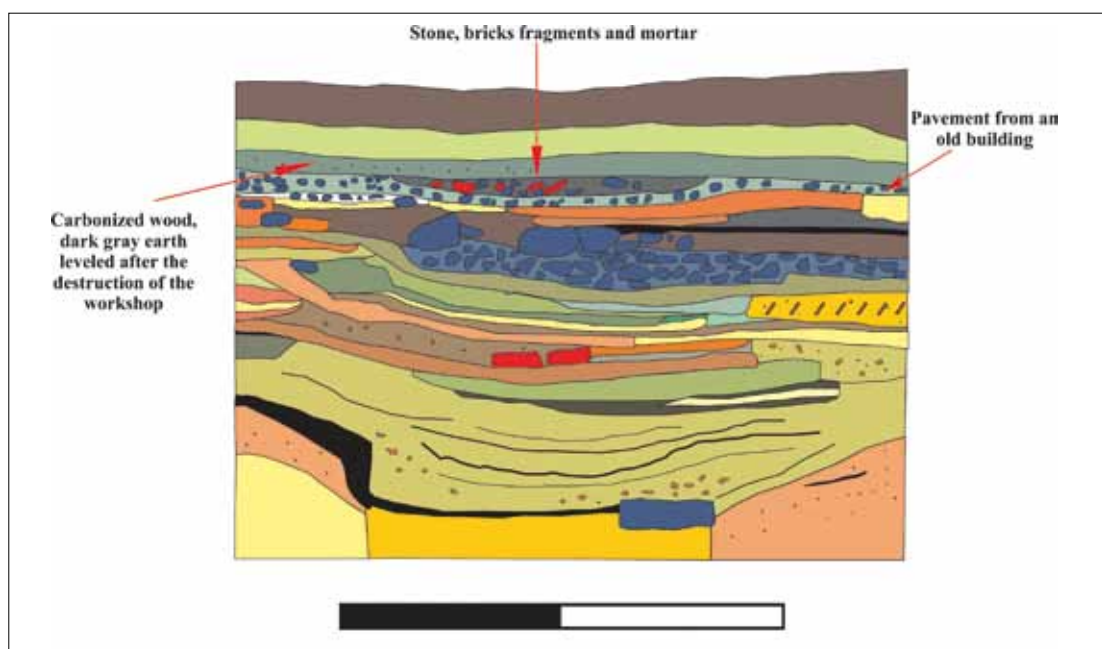
Pl. 6 Workshop plan (drawing: S. Oța)

The coming of the Austrians (1688)² after the Ottomans abandoned the area (Feneşan 1977: 239–243), then the return of the Turks (1689), and finally of the Austrians radically changed the aspect of the fortified town. The Austrians destroyed the old Ottoman buildings or the oldest ones, and began rebuilding others until 1696 when they left the city (attested both by documents and by an Austrian coin found in the construction level of a building). Most likely these buildings were destroyed by the Ottomans, and then, after the return of the Austrians, in 1718, the fortification was demolished and its area rearranged (Groza 1993: 94–95; Oța et al. 2018a; Oța 2019).

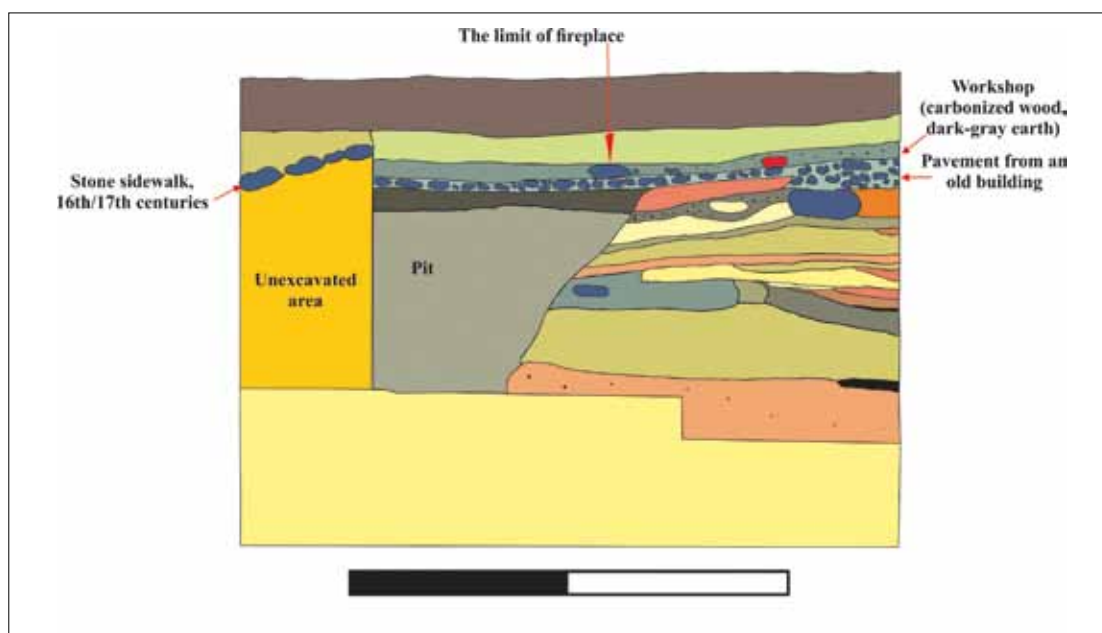
Fragments of melted iron and iron slag, scattered or grouped, apparently without any connection between them, were discovered from the beginning. Initially, they appeared between 0.28 and 0.40 m depth, in the cassette 2/2017, to the southwest (Pl. 4: 1, 2). Here they were mixed with fragments of broken bricks, stones, small fragments of mortar and charcoal. Most likely, based on the stratigraphy, this feature functioned during the 17th century, being contemporary with the street paved with stone immediately after the middle of the 16th century.

The fragment of the researched furnace or hearth was built on a pavement made of small stones (Pl. 6, 7, 8, 9). Unfortunately, only a small portion on the western side of the cassette and a stone on the southern one were preserved from its elevation.

² Some of these transformations were also observed as a result of the archaeological research between 2017 and 2019.

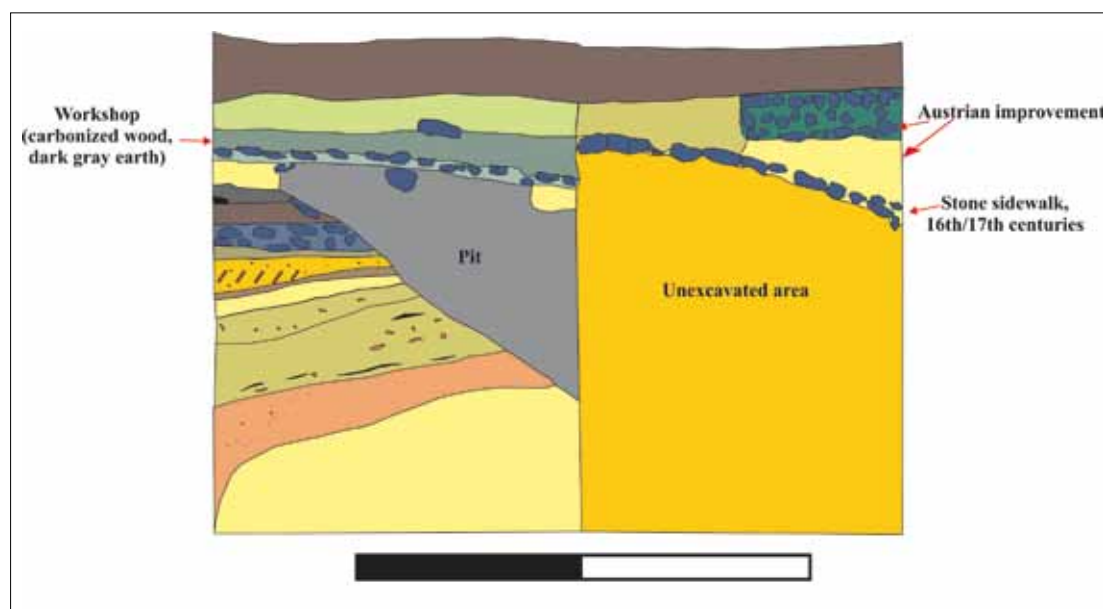


Pl. 7 Cass. 2/2017. The western profile (drawing: S. Oța)



Pl. 8 Cass. 2/2017. The southern profile (drawing: S. Oța)

The fact that the hearth or the furnace was only partially registered in Cass. 2/2017, Cass. 1/2018 and S. 1–2/2018, could be a clue that, initially, the blacksmith's installation was arranged on the floor of a destroyed house, probably before the middle of the 16th century, when we suppose that the street was paved with river stone. On the eastern profile of the cassette 2/2017 one can clearly see that the house pavement is earlier than the street, being observed up to its western limit, but a few centimeters below it. In this cassette, the observable dimensions of the installation were 1.40/1.40 m (Pl. 4: 1, 2). Fragments of melted iron were discovered here. The level of gray soil scattered over the entire excavated area in Cass. 2/2017 can be explained by the destruction of the furnace for melting or processing iron (Pl. 13). After its destruction,



Pl. 9 Cass. 2/2017. The northern profile (drawing: S. Oța)

the content of the furnace was scattered around, near the sidewalk. This is the reason why the same soil type as inside the furnace was observed on the profile. The large heap of stones in the southern end of S. 1/2018, to the east, most likely comes from the structure of the destroyed furnace (Pl. 4: 4; Pl. 6).

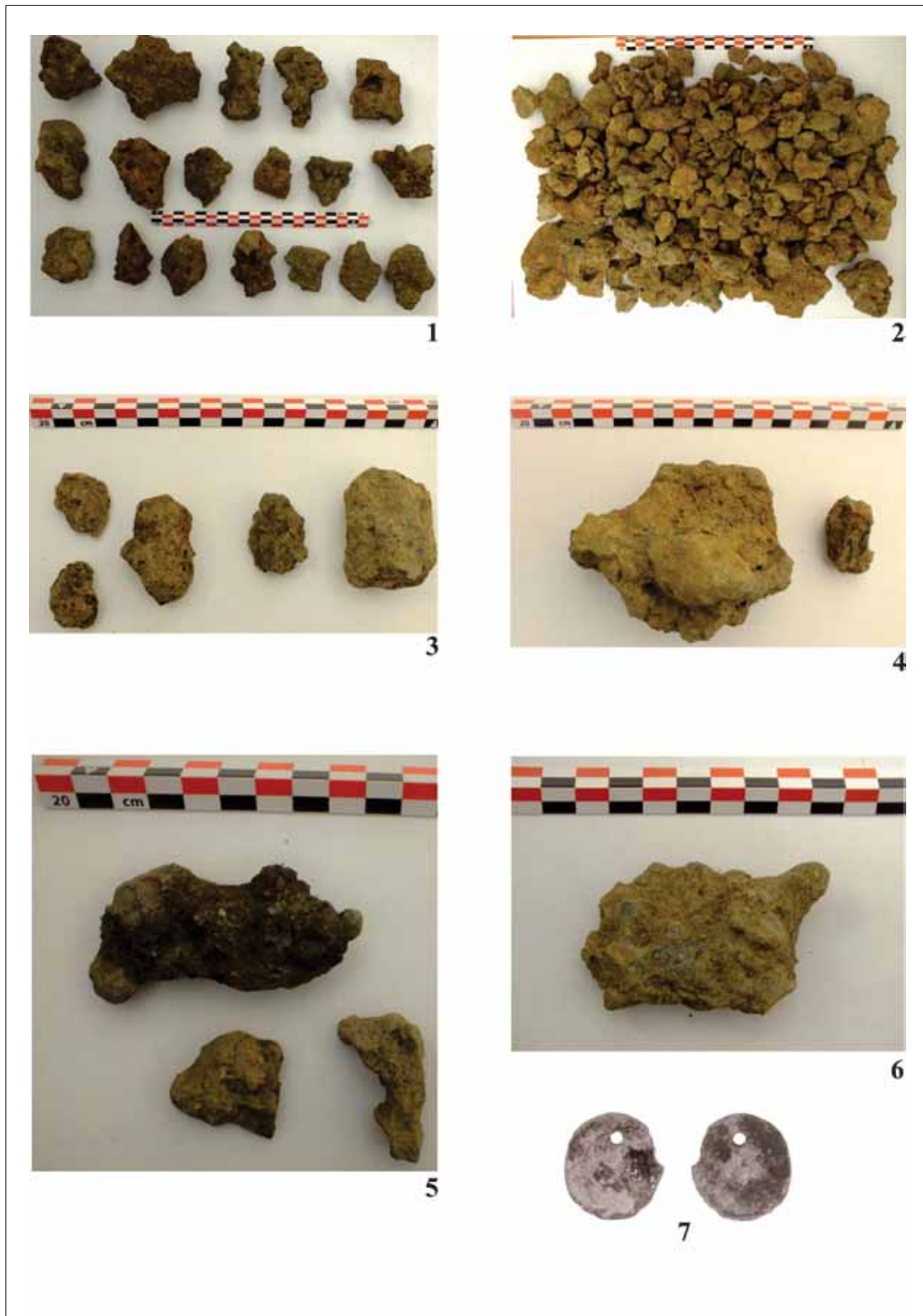
Other two groups of melted iron were identified in the northern side of S. 2/2018, coming probably from two different installations, but very close chronologically (Pl. 4: 3). The oldest one, to the east, is of relative small dimensions, 60/70 cm. A few stones were kept on its western side. The other installation has an elongated shape, rounded at the corners and its dimensions are 1.10/0.45 m. A fragment of a possible stone cupola, observed near the northern profile, was preserved. A few stones were kept on the edge, to the south and west. Nails, most likely to be melted, together with iron fragments (Pl. 10: 1–6) were discovered in both furnaces/hearths (Pl. 11, 12). A coin issued during the reign of the emperor Maximilian II of Habsburg (1563–1576) was found nearby (Pl. 10: 7). The fact that the coin is perforated allows two assumptions: either the coin came, by chance, from a destroyed grave, from the cemetery of the small fortress, situated nearby, or it was brought here on purpose, to be perforated and then deposited in a grave.

Most probably, this iron processing installation functioned during the 17th century, but we cannot exclude the possibility to begin even in the 16th century, after the abandonment of the earlier building. Unfortunately, now we cannot know how it was looking its elevation, because the area was completely rearranged later, and partially covered with a layer of clay, with variable thicknesses between 20 and 30 cm, depending on the structures below. The rearrangement of the area is contemporary with the arrival of the Austrian imperial army in Caransebeș, in 1688. The chronological succession of the installations must be the following: the oldest one was that discovered in S. 1/2018, in the center of the square, the next one was probably that situated nearby, and the last most probably the installation found in cassette 2/2017.

If we look at the surface observed on the profiles of sections and cassettes, the dimensions of the workshop were most likely quite large, about 12/8 m (Pl. 6). The iron processing installations, with different places in the planimetry of the structure, were situated in its southern and south-eastern half. We cannot exclude the possibility of one or two rooms, for living, situated in the opposite side.

The total amount of iron discovered in S. 2/2018 raises to 3.500 kilograms, to which can be added 328 grams of nail fragments, most likely collected with the purpose to be melted, 318 grams of melted iron fragments and 220 grams of scattered nails.

Most likely, common use iron objects were produced here, such as nails, spikes, probably horseshoes. However, no tools used for this activity, as anvils, chisels, hammers or pliers were found. The objects found in this area consist of usual household tools. Having a relative small surface, used for different purposes, such as houses, workshops, and markets etc.,



Pl. 10 1–2. S. 2/2018, North. Iron fragments and scoria/dross; 3–6. S. 2/2018. Iron bits and scoria/dross from workshop; 7. Coin issued during the reign of the emperor Maximilian II of Habsburg (1563–1576) (photo by: S. Oța)



Pl. 11 1–5. S. 2/2018. Iron nails found inside the workshop (photo by: S. Oța)



1



2



3



4

PI. 12 1. S. 2/2018, North. Iron sheet and iron nails (completely or partially preserved); 2. Horse shoe, fragment; 3. Iron clamp from the workshop; 4. Iron item found inside the workshop (photo by: S. Oța)



Pl. 13 1–6. Cass. 2/2017. Items and nails from the workshop (photo by: S. Oța)

probably the town was relatively well cleaned after each abandonment of houses or workshops, either due to their old character or to the destructions caused by military conflicts or fires, and the new buildings were constructed not in nearby areas, but on the same surface as the old ones.

In the territory from today Romania, others blacksmith workshops were discovered in Moldavia (Bilavschi 2016: 76–87), at Suceava (two from 14th – 15th centuries) (Matei et al. 1962: 756), Baia (one from 15th century) (Neamțu et al. 1980: 51–53; 1984: 62, 64; Bătrâna et al. 2017), Roman (from 15th – 16th centuries and from 16th – 17th centuries) (Hânceanu 2017) and Aldești-2 (Ursachi 1968: 141–142, 144–145). Their dimensions are smaller. Most were set on fire, and the vast majority of the inventory remained on place, except for the blacksmith's tools (most of them were set on fire but the majority of the inventory remained *in situ*, except for blacksmith tools). Unfortunately, most of these workshops are still unpublished. The one found at Baia, for instance, served as workshop and house at the same time, while those from Roman were only workshops.

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TECHNICAL EXAMINATION AND CONSERVATION OF THE EARLY MEDIEVAL SWORD FROM BOJNA-BREKINJOVA KOSA

The article discusses the early medieval sword discovered accidentally in 2011 during the exploitation of the quarry at Bojna–Brekinjova Kosa in Sisak-Moslavina County (Croatia). Subsequent rescue archaeological excavations of the site resulted in the discovery of an early medieval graveyard from the pre-Romanesque period with finds of major importance for early medieval Croatian history. During and after the conservation-restoration treatment of the sword, additional technical investigations were carried out to gain a better understanding of the artefact, to reconstruct the manufacturing techniques and to trace potential source(s) of iron used to make the sword. According to the metallographic examination, the blade was pattern-welded and presumably constructed from nine rods, of which only four were pattern-welded composites, while the osmium isotope analysis suggests that iron used in the manufacture of the sword could have come from deposits in Swabian Jura, southwestern Germany or Lorraine in eastern France.

Key words: Bojna–Brekinjova Kosa, sword, conservation-restoration, metallography, osmium isotope analysis

INTRODUCTION AND FIND CONTEXT

Bojna–Brekinjova Kosa is a stratified archaeological site situated in the western part of the Banija region, not far from the town of Glina in Sisak-Moslavina County. The first archaeological field survey of the site was carried out in 2010 by archaeologists Lazo and Zoran Čučković from Karlovac City Museum (Čučković, Čučković 2011: 297), which resulted in the discovery of an Early Iron Age hillfort. Due to possible damage to the site caused by the exploitation of a modern quarry, two campaigns of rescue archaeological excavations were organized under the supervision of archaeologist Vinko Madiraca. While the first campaign in 2011 produced some early medieval pits and pottery, it was the second campaign in 2015 that resulted in the discovery of the sacred or sepulchral walled structure together with burials containing rich grave goods, some of which rank among the most impressive early medieval grave finds discovered thus far in Croatia (see: Madiraca et al. 2017: 145–215 for a detailed description of the site and finds). The most notable finds include gilded silver riding spurs with buckles, fittings and strap-ends, a Constantin V Copronymus gold coin, silver necklaces, a pendant with clear quartz embedded in gold, and silver belt fittings. Due to the exceptional significance of the site, the Croatian Conservation Institute launched systematic archaeological excavations in 2016, work that continues to this day.

The Carolingian sword discussed in this paper was discovered accidentally in 2011 during the exploitation of a quarry at Bojna–Brekinjova Kosa by one of the workers, who eventually brought it to the local Sisak City Museum (Fig. 1). Although the circumstances of the discovery are unclear, it is reasonable to assume that the sword originates from a grave probably destroyed during work in the quarry.



Fig. 1 The sword before conservation-restoration treatment (photo: D. Doračić)

METHODS USED FOR CONSERVATION-RESTORATION AND EXAMINATION OF THE SWORD

Conservation-restoration treatment consisted of standard and well-known methods aimed at preserving the physical and historical integrity of the sword.¹ The process started with routine preliminary investigations, which included microscopic inspection, investigative cleaning² and radiography (Fig. 2).³ Stabilization, i.e., the removal of the chloride ions present in the sword, was carried out using standard alkaline sulphite desalination treatment (see: North, Pearson 1975: 1–14), while the original surface⁴ was revealed by means of a micro-sandblasting machine and other mechanical tools. The final stages of the conservation-restoration process involved impregnation, gap filling, surface protection and retouching.

For metallographic examination,⁵ a sample from one side of the blade was taken c. 415 mm from the lower guard. The specimen was embedded in epoxy resin, polished and etched with 3%-Nital (HNO_3 solution in ethanol) to reveal its metallographic structure and with Oberhoffer's reagent to reveal phosphorus-rich zones. Grain size was determined according to the ASTM E112-124 standard, while the microhardness was measured according to the Vickers method with 0.2 kg load. The Jernkontoret scale was used for the assessment of the content of slag inclusions, which were also characterized by means of scanning electron microscopy coupled with an energy dispersive spectrometer (SEM-EDS). The instrument was operated at 20 kV accelerating voltage using a silicon drift detector with a thin Si_3N_4 window. Detector resolution was 129 eV measured at MnKa. Detection limits for most elements measured were 0.1 wt%. Since it was not possible to perform the reliable quantitative analysis of the statistically representative number of inclusions per zone (Dillmann, Héritier 2007: 1816), only qualitative and semi-quantitative analyses have been conducted.

The laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) method was used to analyze metal matrix of the sword employing a Thermo ICAPO ICP spectrometer coupled with the Resonetics laser system (ArF, 193 nm).

Osmium isotope analysis was used to trace the origin of iron utilized in the manufacture of the sword. The determination of the concentration of osmium as well as the measurement of the osmium isotopic composition (Os IC) were carried out on a modified Finnigan-MAT 261 thermal ionization mass spectrometer according to the method specially developed and described by Brauns (see: Brauns 2001).⁶

Finally, the basic typological determination of the sword was made using Jan Petersen's classification based on hilt designs (Petersen 1919), while the blade of the sword was compared to Alfred Geibig's typology (Geibig 1991).

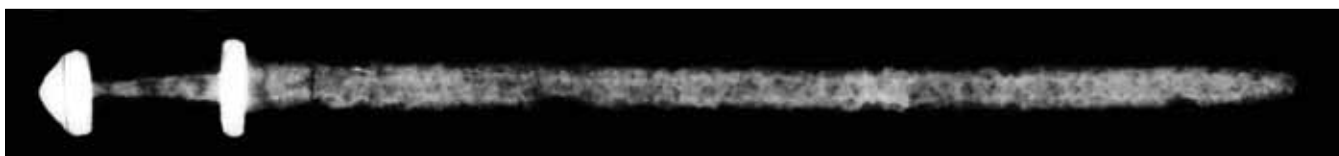


Fig. 2 Radiograph of the sword with a clearly visible line between the cutting edges and the core of the blade (made by: J. Barbić, M. Rastović)

- 1 Conservation-restoration of the sword and SEM-EDS analyses of slag inclusions were carried out by D. Doračić at the Archaeological Museum in Zagreb.
- 2 Investigative cleaning refers to the partial cleaning of an object to locate and reveal the original surface (see e.g., Cronyn 1990: 6–7, 63–67, 172–4, etc.).
- 3 Radiographs were made by M. Rastović and J. Barbić at the Zavod za zavarivanje i toplinsku tehnologiju d.o.o. in Zagreb.
- 4 The limit of the original surface and its informative potential and importance is explained e.g., in Bertholon 2007: 31–36 and Cronyn 1990: 8, 64, 184, 190–191.
- 5 Metallographic examination was conducted by J. Hošek at the Institute of Archaeology, Czech Academy of Sciences, Prague.
- 6 LA-ICP-MS and osmium isotope analysis were carried out by M. Brauns at Curt-Engelhorn Zentrum Archäometrie in Mannheim.

SWORD DESCRIPTION AND TYPOLOGICAL DETERMINATION

The sword from Bojna has a double-edged blade with an undecorated hilt consisting of a triangular pommel and an upper and lower guard.⁷ The overall length of the sword is 895 mm, while the blade itself is 730 mm long and 5 mm thick. The width of the blade just below the lower guard is 53 mm, while most of the blade is between 40 and 45 mm wide, indicating that a significant part of the cutting edges had been lost due to frequent sharpening and corrosion. Narrowing is only visible close to the point. The sword weighs 900 g and the balance point is situated c. 175 mm below the lower guard. Shallow and indistinct fullers on both sides are approximately 20 mm wide and visible only in short portions of the blade. Radiography of the sword revealed traces of pattern-welded decoration resembling a herringbone pattern with a ZS-twist filling most of the middle portion of the blade (Fig. 3a).

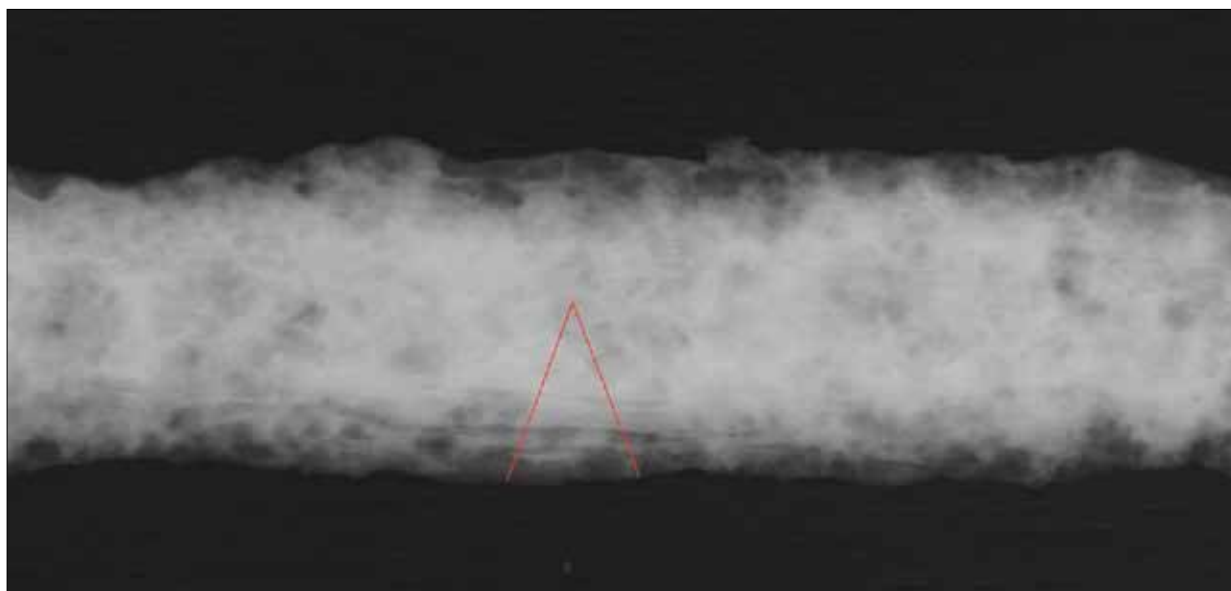


Fig. 3a Detail of the radiograph showing traces of pattern-welding and sampling area (made by: J. Barbić, M. Rastović)

The overall length of the hilt is 165 mm while the grip itself is 99 mm long. Traces of a wooden grip (or the wooden core of a grip) were discovered below the upper guard, while remnants of the wooden scabbard were identified just below the lower guard. All traces of wood are preserved in the form of pseudomorphs.⁸ The triangular iron pommel (63 mm long, 22 mm high, 17 mm wide) is firmly attached to the upper guard (70 mm long, 20 mm high, 19 mm wide), while the lower guard is somewhat larger – 80 mm long, 22 high and 22 mm wide. The tang of the sword runs all of the way through both of the guards as well as the pommel and narrows towards the upper guard (from 2.5 to 1.5 mm). The joints are tight and regular and were most likely also fastened with wooden shims (Figs. 3b, 3c).

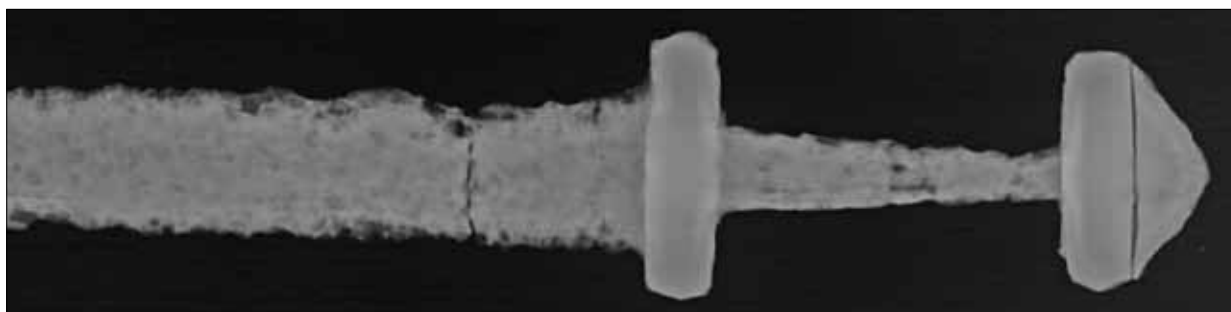


Fig. 3b Detail of the radiograph showing the construction of the hilt (made by: J. Barbić, M. Rastović)

7 Nomenclature of sword parts can be found in e.g., Pierce 2002 or Košta, Hošek 2014: 57–59.

8 The term “pseudomorph” refers here to wood impregnated with corrosion products (Cronyn 1990: 183).



Fig. 3c Traces of mineralized wooden grip preserved on the tang (photo: D. Doračić)

According to Jan Petersen's typology, the sword from Bojna could be classified as an undecorated variant of type H,⁹ although some features like the absence of rivets for securing the pommel to the upper guard and the lack of decoration are instead characteristic of type B from which it derives (Jones 2002: 17).¹⁰ As stated by Petersen, type H swords appear from the very beginning of the 9th century to the middle of the 10th century (Petersen 1919). On the other hand, Geibig's typology was used for the determination of the blade. Considering the dimensions and shape of the blade (minimal tapering with a short tip), pattern-welding decoration and shallow and indistinct fullers, the blade could be categorized as type 1, which ceased to exist by the end of 8th century (Geibig 1991: 83–90, 150–154). Consequently, the sword from Bojna might have been manufactured at the end of the 8th or at the very beginning of the 9th century. However, it's worth noting that swords, especially their blades, could have had a fairly long "working" life and were handed down from generation to generation (Oakeshott 2002: 1), i.e., it is not improbable that the blade was manufactured even earlier with perhaps a different hilt, while the existing hilt was added later in accordance with new trends.

METALLOGRAPHIC EXAMINATION AND SLAG INCLUSION CHARACTERIZATION

Metallographic examination of the sample taken from one side of the blade revealed ten main areas with specific metallographic structures and different proportions of carbon and/or phosphorus (Fig. 4). A pearlitic-ferritic structure with a carbon content of 0.5%, grain-size ASTM 10 and hardness of 207 ± 19 HV0.2 appears in Area I (Fig. 5a). A similar structure is seen in Area II (0.35 - 0.2% C; ASTM 9 10; 170 ± 16 HV0.2) (Fig. 5a). The structure of ferrite and pearlite in Area III has less than 0.2% C, grain-size ASTM 8, and hardness of 125 ± 8 HV0.2 (Fig. 5b). The structure in Area IV has a carbon content of about 0.3 percent, grain-size ASTM 10, hardness of 187 ± 19 , and consists of ferrite and pearlite. The structure in Area VI is ferrite with traces of pearlite; size of grains varies between ASTM 6 and 8, hardness is c. 160 HV0.2 (Fig. 5b). In Area V, there is a gradual changeover from the microstructure documented in Area IV to that documented in Area VI. The structure in area VII is pearlite with ferrite (0.4% C; ASTM 9; 205 ± 12 HV0.2), while Area VIII is ferrite. Area IX consists of ferrite and pearlite (c. 0.35% C; ASTM 8-9; 192 ± 4 HV0.2), and Area X consists of ferrite with some pearlite, which is distributed on the boundaries of the ferritic grains (c. 0.25% C; 252 ± 12 HV0.2) (Fig. 6). When etched with Oberhoffer's reagent, welds in the form of "white lines" are visible between areas III (cutting edge) and IV (core), areas IV–VI (core) and VII–VIII (one surface panel), and areas IV–VI (core) and IX (the other surface panel). In addition, Area X has, compared to the other areas, an increased phosphorus content (Fig. 6).

While the metal matrix contains both coarse and fine slag inclusions, most of the matrix is relatively pure (the overall slag content corresponds to a level of 2 to 3 on the Jernkontoret scale). As reported by Schwab et al., slag inclusions originate from different stages of manufacture such as smelting, refining and forging (Schwab et al. 2006: 439). Three main

⁹ A brief and comprehensive overview of hilt and blade classifications, including chronology, is given in Jones 2002: 15–24.

¹⁰ See also Petersen 1919, *The Norwegian Viking Swords*, translated by Kristin Noer, <http://www.vikingsword.com/petersen/pts089h.html> (17 August 2021).

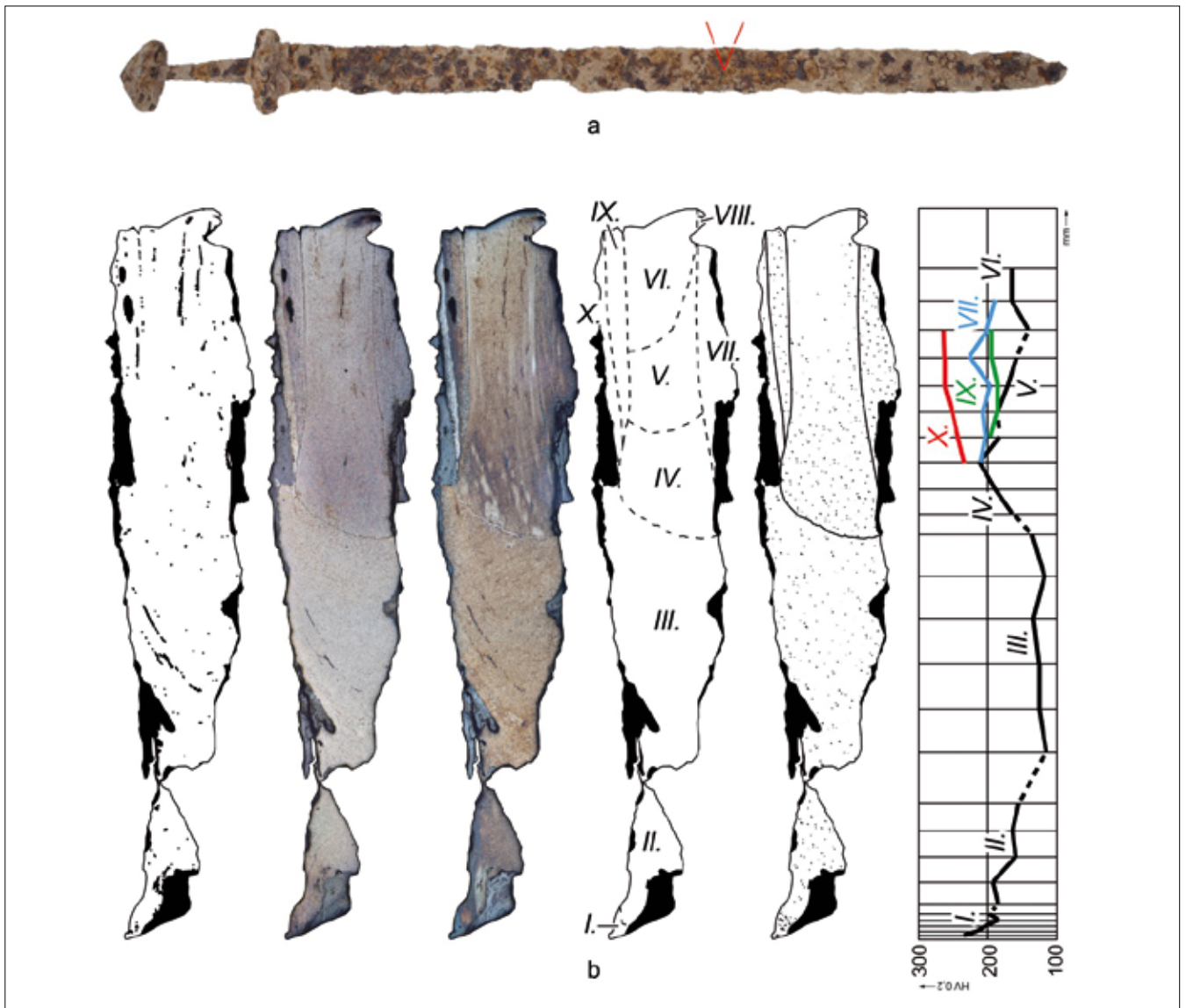


Fig. 4 The sword and the sampling method utilized (above); schematic drawings of the blade sample (from the left: unetched state, after nital etching [photomicrograph], after Oberhoffer etching [photomicrograph], layout of described areas, main welds and distribution of carbon in the sample; variation of hardness in the sample) (drawings and microphotos: J. Hošek)

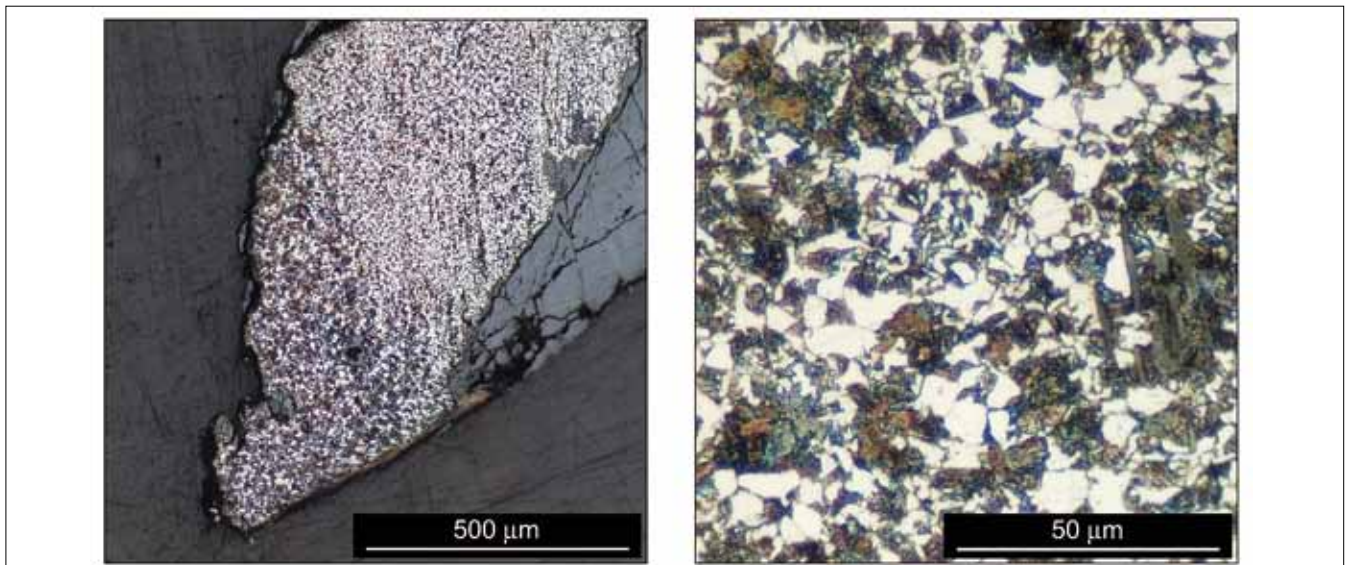


Fig. 5a Photomicrographs of the cutting edge showing pearlitic-ferritic structure of Area I and II (left) and Area I (right); etched with Nital (made by: J. Hošek)

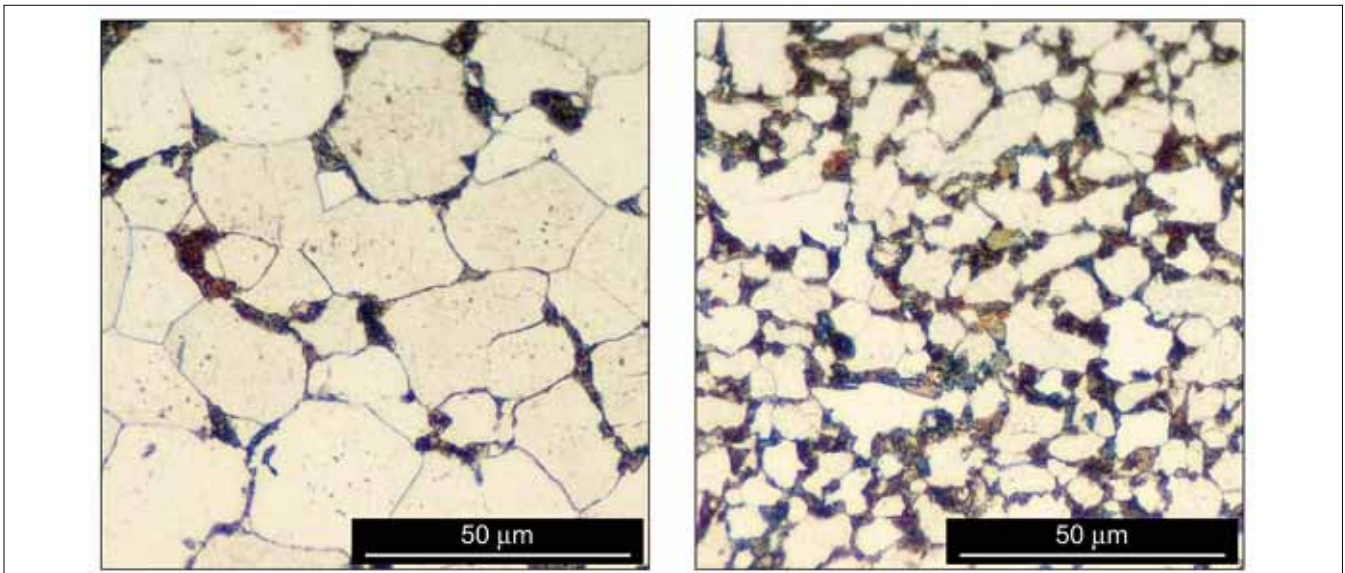


Fig. 5b Photomicrographs of the Areas III (left) and IV (right) showing ferritic-pearlitic microstructure; etched with Nital (made by: J. Hošek)

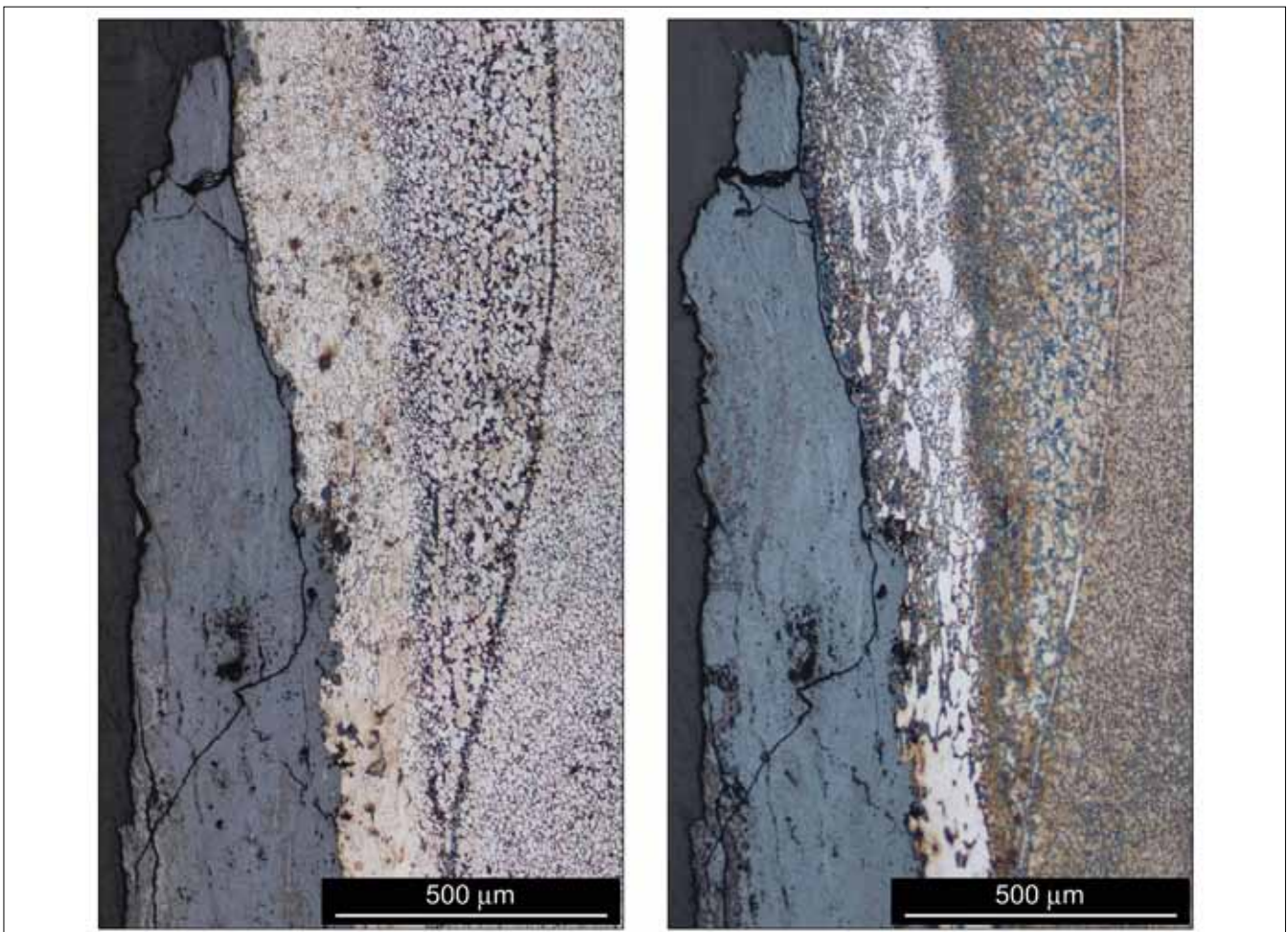


Fig. 6 Photomicrographs of Areas X, IX and IV showing pattern-welded surface panels; etched with Nital (left) and Oberhoffer's reagent (right) (made by: J. Hošek)

types of inclusions could be distinguished in the specimen: one phased (either almost pure wüstite or glass), two phased (fayalite or wüstite in glassy matrix) and three phased fayalite-wüstite-glass composite.¹¹ Most inclusions are elongated

11 For the basic composition and morphology of slag inclusions in bloomery iron see e.g., Hedges, Salter 1979; Buchwald, Wivel 1998; Starley 1999; Buchwald 2005.

and relatively small¹² (5–80 microns long), indicating intensive forging above the softening point of the slag, i.e., 800–900 °C (Hedges, Salter 1979: 164), or more likely between 1000 and 1100 °C (Buchwald 2005: 64). The forging probably continued at lower temperatures (600–800 °C) as evidenced by broken slag inclusions and fragmented fayalite laths inside slag inclusions (Buchwald 2005: 123) (Figs. 8a, 8b, 8c).

The chain of fine slag inclusions originating from forge-welding are also distributed along the welding lines. Forge-welding of the bars or rods of which the sword is composed was most likely carried out at temperatures above white heat,¹³ typically around 1250 °C (Rostoker, Dvorak 1990:159). The absence of Neumann bands and slip lines within the microstructure suggests that there had been no cold forging at room temperatures. Also, no traces of quench-hardening were discovered in the microstructure of the sample, so the blade was probably allowed to cool slowly after the final hot forging operation (see e.g., Continuous Cooling Transformation diagram for steel with 0.4% carbon in Buchwald 2005: 157).

According to the obtained data, the middle portion of the blade consists of pattern-welded surface panels welded onto a core of heterogeneous material varying between iron and steel. At the time, it was a standard construction, as fully pattern-welded blades, i.e., those lacking a middle non-pattern-welded inter-piece, are not typical for Carolingian swords.¹⁴ Towards the cutting edges, iron rods were forge-welded to the middle portion and, most likely, additional welded-on rods of steel finally formed the cutting edges themselves (the presumed method of construction is shown in Fig. 7). A few swords with analogically constructed blades are known from Nechvalín–Homole, grave 36, and Opolany–Kanín, grave 54 (both from the territory of today's Czech Republic; see: Hošek et al. 2019: 184, 199), Machów, pow. Tarnobrzeg (from the territory of today's Poland; see: Rauhut et al. 1968) and Kirimäe (from the territory of today's Estonia; see: Anteins 1968).

As demonstrated by Thiele et al. (2014b), pattern-welding doesn't have any positive effect on the mechanical properties of long blades of swords and should be regarded generally as a decorative technique. Its decorative effect was based on the fact that phosphoric iron (containing as a rule at least 0.4% P) etches differently compared to phosphorus-free iron and steel; the appearance of etched phosphoric iron then depends on the etchant employed (see, e.g., Thiele et al. 2014a; Thiele 2018). It seems that the blade was not quench-hardened in the place of sampling (and most likely was not quenched at all).

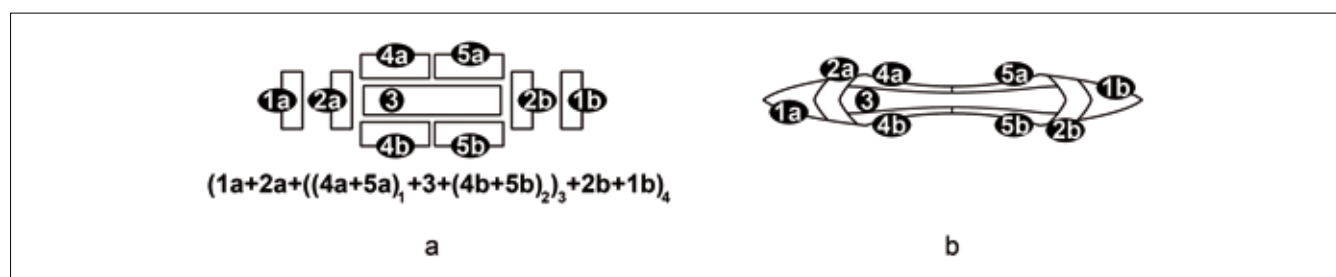


Fig. 7 The blade manufacturing scheme: assumed assembly and welding of the initial billet (left); typical appearance of the finished blade in cross-section (right) (drawing: J. Hošek)

THE QUESTION OF PROVENANCE

It is widely assumed that Carolingian swords discovered in Croatian territory originate from Frankish workshops along the Rhine River (Vinski 1985: 64–65; Belošević 2007: 410; Bilogrivić 2019: 114). However, no attempts have been made thus far to trace the origin of iron used in the manufacture of the swords. To date, several methods for determining the provenance of iron have been proposed. Some are based on a comparison of major and trace element concentrations of metal and slag inclusions with that of ore (see e.g., Hedges, Salter 1979; Buchwald, Wivel 1998; Coustures et al. 2003; Blakelock et al. 2009; Leroy et al. 2012; Héritier et al. 2016), while others are based on a correlation of isotope signatures of the iron object and ore (see e.g., Degryse et al. 2007; Brauns et al. 2013; Milot et al. 2016). Nevertheless, both the chemical and isotopic signatures of the ore deposits tend to overlap due to the similar genesis of many iron ores (Dillmann et al. 2017: 109). In order to trace the origin of iron used for the manufacture of the sword from Bojna, osmium isotope analysis was chosen due to the fact

12 Rostoker and Dvorak used the terms “large and small inclusions,” demonstrating that large inclusions are more closely related to the smelting process, while the composition of small inclusions could be significantly altered during forging operations (Rostoker, Dvorak 1990: 154–159).

13 On forging colors and temperatures, see: Buchwald 2005: 132.

14 The construction methods of Carolingian swords are well described in Košta, Hošek 2014: 271–296 based on a detailed investigation of Mikulčice swords.



Fig. 8a Typical small elongated two-phase slag inclusion with fragmented fayalite laths (light grey) in glassy matrix (dark grey) (SEM-BSE photo: D. Doračić)

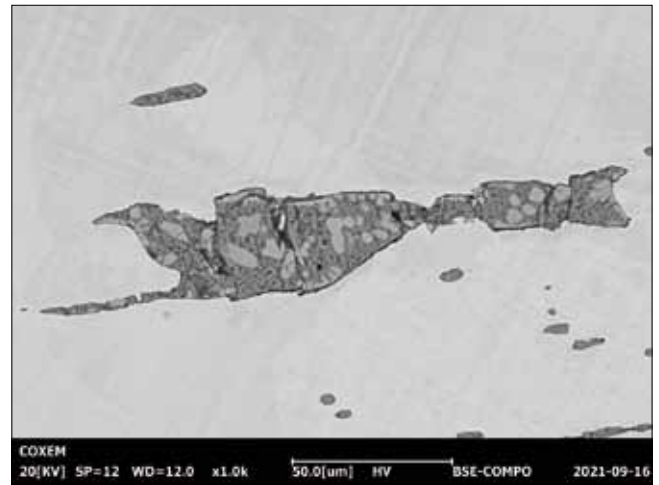


Fig. 8b Typical coarse three-phase slag inclusion with wüstite (light grey), fayalite (middle grey) in glass matrix (dark grey) (SEM-BSE photo: D. Doračić)

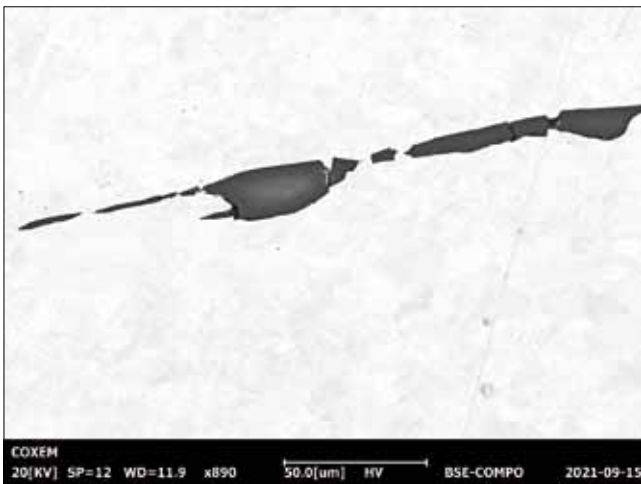


Fig. 8c Typical one-phase glassy slag inclusion (SEM-BSE photo: D. Doračić)

that osmium is a highly siderophile and immobile element whose isotopic composition remains unchanged from iron ore to final product, making it a rather reliable tracer for the provenance of archaeological iron (Brauns et al. 2013: 848; 2020: 2/16). Among seven osmium naturally occurring isotopes, ^{187}Os (daughter isotope of ^{187}Re) has proven to be the most useful for determining iron provenance and is usually expressed as the $^{187}\text{Os}/^{188}\text{Os}$ ratio.

The Os analysis of the sword showed that the metal matrix of the blade contains 1129 ppt of osmium and that the $^{187}\text{Os}/^{188}\text{Os}$ ratio is 0.6596 (Fig. 9). The comparison of acquired Os data with an already existing database shows good agreement with the iron ores from the Swabian Jura in southwestern Germany. However, as shown by Dillmann et al., there is an overlap of Os isotopic signatures of ores

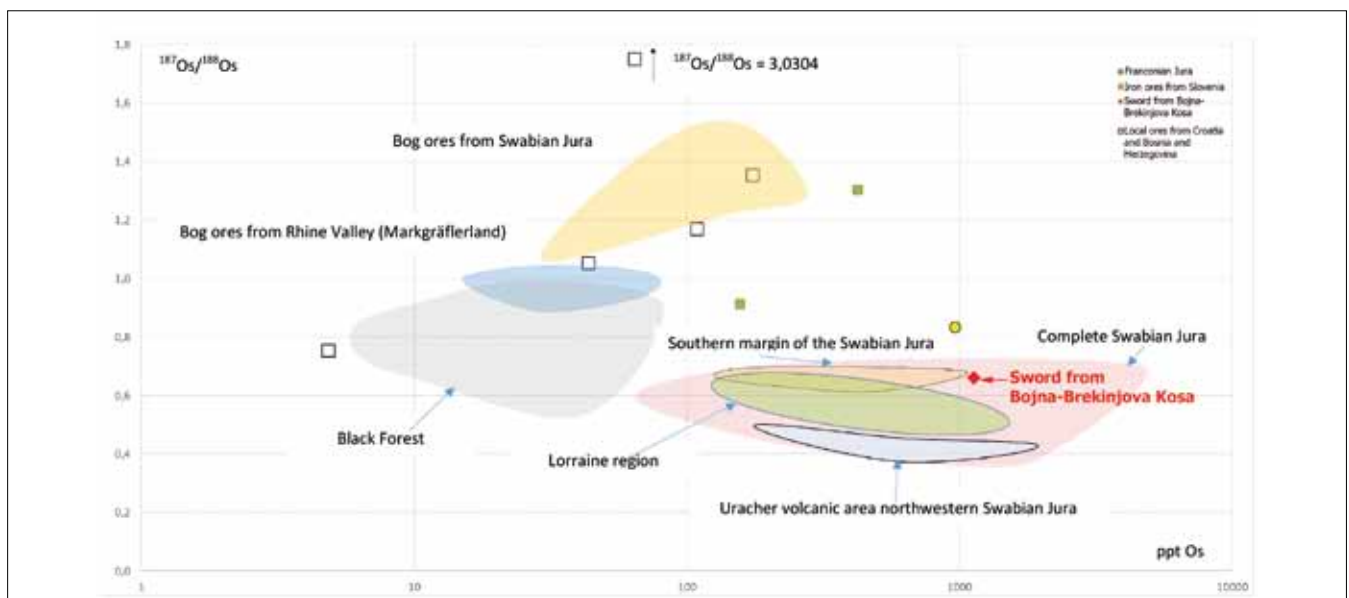


Fig. 9 Os isotopic signatures of the most common iron ores found in southern Germany and eastern France (sword from Bojna is colored red, squares depict local ore deposits) (drawing: M. Brauns)

from the Swabian Jura with the ores from the Lorraine region in eastern France (Dillmann et al. 2017: 114–115). Therefore, at this point, both deposits could have been a potential source of iron used to make the sword. The comparison with the Os isotopic signatures of local iron (hematite/limonite) ore deposits obtained from Trgovska Gora, Petrova Gora, Rude and Virje in Croatia¹⁵ as well as Ljubija in Bosnia and Herzegovina and Stara Fužina in Slovenia showed clear incompatibility. Therefore, as previously assumed, local production can definitely be ruled out.

As described by Buchwald, the ancient method of producing a wrought iron object consisted of four stages: ore roasting, ore reduction (smelting, bloom production), bloom refining (production of iron bars for trading purposes) and the manufacturing stage (final shaping, forge welding, assembling, etc.).¹⁶ Considering the obtained data, one clue might be that the first two stages and possibly the third one (production of the billets) took place in the Swabian Jura area or perhaps the Lorraine region, while the final sword manufacture stage was performed in one of the Frankish workshops along the Rhine River (possibly situated in neighboring Strateburgum). Considering the aforementioned possible long “working” life, the sword could have been manufactured in the fourth or even third quarter of the 8th century and subsequently imported to the territory of early medieval Croatia at the beginning of the 9th century either as a gift, trade or war booty (Fig. 10).

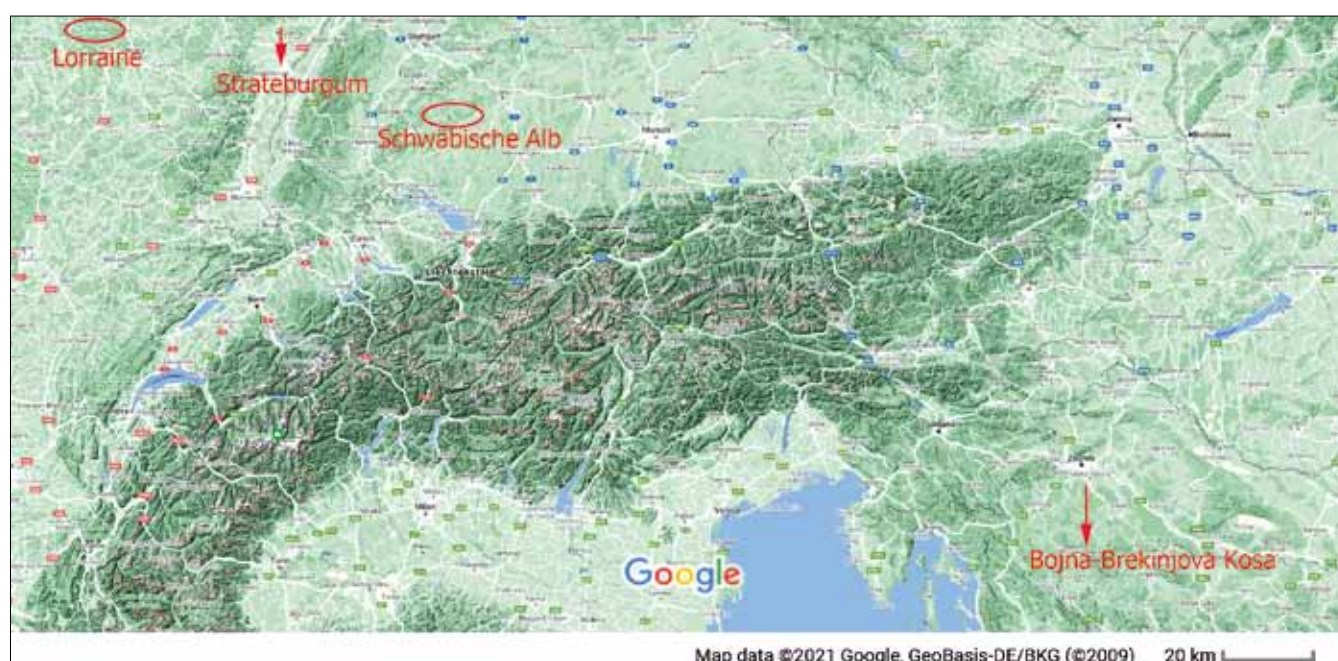


Fig. 10 Map showing the locations of Bojna–Brekinjova Kosa (finding place), Lorraine and Swabian Jura (possible sources of iron ore used in the production of the blade) and the medieval town of Strateburgum (place of hypothetical Frankish workshop) (Google, marked by: D. Doračić)

CONCLUSION

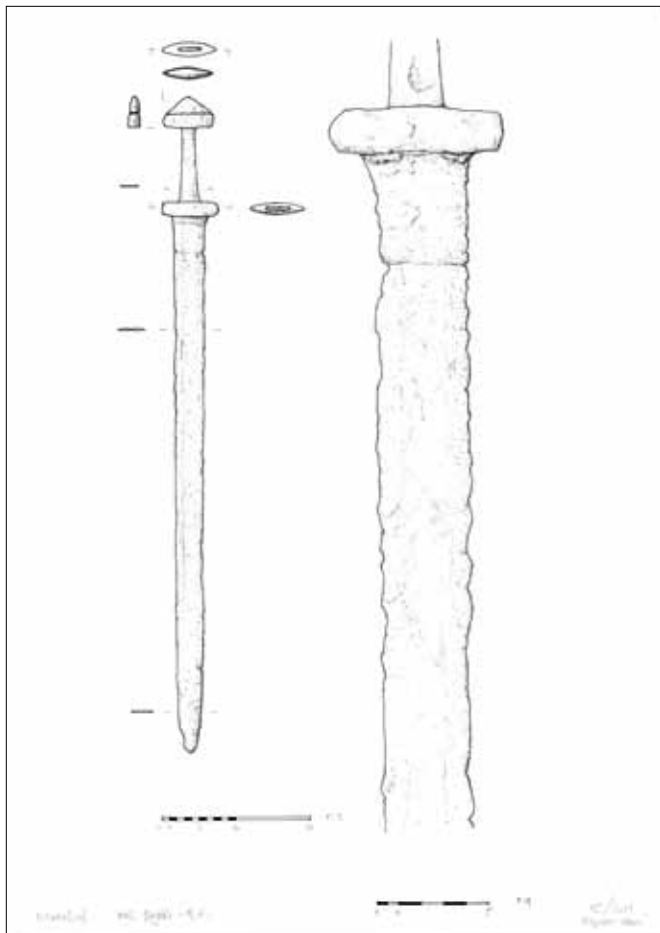
Based on the results of the technological examination, it is possible to conclude that the blade of the sword from Bojna–Brekinjova Kosa was provided on both sides with a surface pattern-welded panel made up of two composite rods (each consisting of layers of steel and phosphoric iron alternating with each other) twisted in the ZS direction to form a herringbone pattern. The cutting edges of steel are not directly attached to the middle portion, but there is iron (presumably a rod of iron on each side) in between. A blade construction of this type seems to be rare, as only a few analogies have been documented to date across Europe. Bars or billets employed to make the blade were produced possibly in the Swabian Jura area in southwestern Germany or the Lorraine region in eastern France. However, it should be noted that in the case of osmium isotope analysis, only a negative result is certain, so a possible future agreement with another deposit cannot be ruled out (Dillmann et al. 2017: 109). Consequently, the results of the provenance analysis should be regarded more as an indication rather than a straightforward fact and further research is definitely required for a better determination (Figs. 11, 12).

15 Unpublished data from the Bojna–Brekinjova Kosa conservation–restoration project.

16 A description of the bloomery process is given in e.g., Buchwald 2005: 90–100; Craddock 1995: 241–250, etc.



Fig. 11 The sword after conservation-restoration treatment (photo: Lj. Gamulin)



ACKNOWLEDGEMENTS

The authors wish to acknowledge Miljenka Galić for her excellent drawings of the sword, Andrea Čobić from the Department of Geology, Faculty of Science for obtaining the samples of local iron ore deposits, David Gaul for the language corrections, Josip Barbić and Milan Rastović from the Welding Institute in Zagreb for making X-ray photos and Tajana Pleše and Ljubo Gamulin from the Croatian Conservation Institute for their kind permission to reprint the photo of the sword after conservation treatment.

Fig. 12 The sword from Bojna–Brekinjova Kosa Site (drawing: M. Galić)

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THE TRANSFER OF IRONWORKING TECHNOLOGIES IN SLOVENIAN TERRITORY BETWEEN THE 14TH AND 16TH CENTURIES

In the mid-14th century, significant progress in ironworking was made in Slovenian territory in which foreign ironworking masters and entrepreneurs were of crucial importance. They predominantly originated from the area of northern Italy, which was one of the most technologically developed ironworking centres in Europe at the time, where water power was used to power ironworking facilities as early as in the 13th century. Around the mid-14th century this technology was transferred to Slovenian territory. It was first implemented in the Selca and Canal Valleys, where ironworking masters bearing Italian names were documented in the written sources. Around 1400, masters of Italian origin were also attested in the developing ironworking centre Bela Peč (Fusine in Valromana).

During the first half of the 16th century, blast furnace technology was introduced in the Slovenian territory. Ironworking masters from northern Italy again played a crucial role in the implementation of this technology. The master craftsmen were followed by many entrepreneurs of Italian origin, who invested the required capital to develop mines and ironworking facilities. However, Italian masters were not equally represented in the Carniolan and Carinthian ironworking centres. While their presence was very significant in the Canal and Selca Valleys it was much weaker in other major ironworking centres, especially in Carinthia. It seems that the Italian influence spread only to the southern part of this province. The territory of northern Italy also played an important role as the biggest export market for the products of Carniolan and Carinthian ironworks.

Key words: ironworking, technological improvements, late Middle Ages, Slovenian territory, migration

INTRODUCTION

Metallurgy in the Slovenian territory¹ has a rich history spanning thousands of years. Today, it continues to be one of the most important economic sectors in the Republic of Slovenia. In previous millennia, metallurgy saw the introduction of several technological innovations that usually signalled great breakthroughs in the mining and processing of metals. The two most important innovations for the development of the ironworking industry in the pre-industrial era were the use of water power for ironworking facilities and the indirect process of iron production in blast furnaces. Master ironworkers from northern Italy played the key role in the transfer of both new technologies to the Slovenian territory.

The methodology applied to the research of these processes has significant drawbacks arising from the specific nature of the researched subject. Written sources only rarely provide information that is sufficiently exact for the researcher to be able to determine with accuracy whether the new technology had been used in a given area or not. Even harder to verify are the method and the direction of the acquisition of the new technology. Was the new technology the result of developments in the local knowledge, or was it transferred from other technologically more advanced environments? If the new technology was transferred from other environments, from where was it transferred, and how is this to be verified? Given the limited accuracy of the sources, in this case, the best way would be to derive conclusions based on the

¹ In this paper, the term Slovenian territory is used to denote the territory of the present-day Republic of Slovenia and the neighbouring regions where Slovenian minorities are still present. Historically, this is the province of Carniola with parts of Gorizia, Carinthia, Styria, and Hungary (Prekmurje and Porabje Region).

analysis of names found in sources; this, however, could prove to be a double-edged sword, because a name alone does not communicate a person's exact origin but is only the approximation of it. Moreover, names are not always adequate sources for the determination of an individual's ethnic and linguistic identity. As will be pointed out below, some of the following results, particularly those associated with the Late Middle Ages, should therefore be treated with some caution.

INTRODUCTION OF WATER POWER TO EUROPEAN IRON INDUSTRY

For centuries, ironworkers used human or animal power as their predominant source of power to manufacture and process iron. Once they began using water power to power bellows, this increased the amount of air pumped by bellows into bloomery furnaces, consequently raising the temperature in furnaces, which in turn became larger and thus delivered more iron in a single smelting process. Water power was also applied to trip hammers used for forging lumps of iron, which, because of more efficient furnaces, had become increasingly larger (Sprandel 1968: 221; Gimpel 1993: 66–67).

Experts researching the beginnings and spread of the use of water power in the European iron industry are not unanimous in their conclusions. Some advocate the use of water power as early as in the Early Middle Ages. This claim, however, should be treated with great caution, as references are very sporadic, and the use of water power cannot be confirmed with a high degree of certainty. The mere fact that an ironworks was located on a river does not make it certain that it had harnessed water power; this applies, in particular, to the period before the 14th century. The interpretation that places the beginning of the use of water power in the European iron industry into the 13th century thus seems to be the most accurate, although one cannot discard entirely the possibility that this technology had appeared before the 13th century and then took some time before it was widely adopted (Johannsen 1953: 91–93; Sprandel 1968: 221–226; Gimpel 1993: 13–14; Pleiner 2000: 282–283).

According to German medievalist Rolf Sprandel, the oldest known and unambiguous reference to the use of water power in iron industry dates back to the beginning of the 13th century in what is now the province of Halland in southern Sweden, where the Danish Cistercian monastery Sorø operated an ironworking facility. The second oldest reference originates in northern Italy and states that in 1226 two water-powered ironworks operated in Semogo, a place in the commune of Bormio. Two early references to the use of water power, dating back to 1251 and 1294, originated in the Alpine valleys north of Bergamo. Concerning the early use of water power in the iron industry of the northern Apennine Peninsula, a source from 1179 referring to the alleged use of water power in the Ardesio Valley north of Bergamo should also be mentioned (Sprandel 1968: 221–226, 372–373). Thus, it was during the 13th century that northern Italy emerged as one of the most important and technologically most advanced centres of the iron industry in Europe.

Other unambiguous references to the use of water power mostly relate to the mid- and late-13th century and are geographically scattered across Europe: Schwäbisch Gmünd in Baden-Württemberg, Jędrzejów in the south of Poland, Domašov u Šternberka in Moravia, and Escoussens and Villeneuve-sur-Yonne in southern and central France. In the first half of the 14th century, the use of water-propelled wheels in the iron industry spread throughout Europe. The first indisputable references to the use of water power in the iron industry in a given area do not automatically mean, however, that water power was used by all ironworking plants in this area soon after that. Several decades may have passed from the first implementation of this new technology to its general and widespread use (Sprandel 1968: 222–224, 362, 373) (Fig. 1).



Fig. 1 A detail of a mid-16th-century woodcut showing the use of a water-powered hammer to process iron (Georg Agricola, *De re Metallica*, © archive.org)

IRON INDUSTRY IN THE SLOVENIAN TERRITORY AND THE INTRODUCTION OF WATER POWER

In the Eastern Alps area, the advances in ironworking technology took place during the 13th century, specifically in Erzberg in Upper Styria and Hüttenberg in Carinthia. In Styria, in particular, the technological advances are well documented in written sources, which indicate an increase in the mass of lumps of iron (blooms) by 2.5 times between 1227 and 1262. The developments in the central Carinthian iron-producing region are somewhat less clear; we may, however, assume, that the increase in production took place before 1266, when Hüttenberg is mentioned in written sources for the first time (Pirchegger 1937: 14–15, 43). Although the sources do not directly reveal the actual cause of technological advances in this region, it is likely the use of water power that led to the increase in production and thus raised the economic importance of both ironworking centres. The German historian Karl Dinklage assumes that the ironworks of the Hüttenberg area began using water power between 1230 and 1250 (Dinklage 1953: 129; Mitterauer 1974: 243–245). The Czech archaeometallurgist Radomír Pleiner also recognises the Alps region and its vicinity as one of the centres of early use of water-powered bellows for iron ore smelting, particularly in the light of a large number of favourable river currents available there. He assumes that the new technology in this area spread during the 13th century or shortly thereafter but also admits that many details of this development remain obscure (Pleiner 2000: 138–139, 282–283).

While the new technology spread relatively quickly in the surrounding regions, it takes approximately another century before sources are able to demonstrate its use in Carniola and its immediate vicinity. The first references to ironworking activities in the Slovenian territory date back to 1291 when a source refers to four *praeznich* on the estate of the Freising Diocese in the Upper Sava Valley (the location of the current Mojstrana), who were most probably feudal iron smelters and were obligated to pay their landlord an annual due of 80 lumps of iron (*80 ferra*) (Blaznik 1963: 130, 166). Based on the limited information and the type of source available (a rent-roll) it is not possible to establish whether they were already using water power. However, in the absence of later sources and because of the relatively early reference, it seems more likely that these ironworking masters were not yet using water power for their ironworks.

Despite the geographical proximity and connections between these provinces, it was not from Erzberg or Hüttenberg that the waterpower technology was transferred to Carniola and the Canal Valley, which at the time was part of Carinthia, but rather from northern Italy. The first known works that probably used water power and were set up by an ironworker from the northern Italian area started operating in the territory in question before 1348, when one Francis (*Francisiche*) was granted permission by the official (*pflieger*) of the local Bamberg Diocese Seigniorship to set up a trip hammer in the forge in Laglesie San Leopoldo (Lipalja vas/Leopoldskirchen) in the Canal Valley, followed by the permission in late 1353 or in the early days of 1354 to set up a second trip hammer (Dinklage 1953: 111; Wiessner 1968: 141).

In the following decades, the Canal Valley developed into an important ironworking centre for the processing of Hüttenberg iron, which was delivered there by merchants from Villach. Of the blacksmiths working there, a significant share was represented by masters from northern Italy. In 1399, there is a reference to a blacksmith Bartolomeo, who worked as a foreman in two forges in Malborghetto (Naborjet/Malborgeth), both of which were owned by one *Cuncz Lill, Vogel genannt*. In the same year, a forge on the Slizza River (Gailitz/Ziljica) near Tarvisio (*smytten gelegen an der Geilücz*) was owned by *Seraphin, Anthoni* and *Lasar* (Koller-Neumann 1982: 129, 142) (Fig. 2).

At around the same time as in the Canal Valley, the first references to the use of water power in Carniola appear, specifically in the Selca Valley. Once again, the central role in the establishment of an ironworking centre was held by master ironworkers from northern Italy, whose names (e.g., Giacomo, Bartolomeo, Silvester, Monfiodin)² can be found in the first document of 1354 with which the local landowner, Albert II, the Bishop of Freising, conferred on these master ironworkers the right to ironworking in the five forges they had already set up in the area. Although there is no direct reference in the document concerning water power, its use can be assumed with a considerable degree of certainty because four years later, there is a mention of two forges and a sawmill operated by one master ironworker in the vicinity of a water stream. One of the forges and the sawmill were located on the Selška Sora River and the second forge on the Dašnica Stream. The remaining three forges most probably operated on the Selška Sora River (BayHStA, HL 4, Hochstift Freising, fasz. 135, 1379 4/29; CKSL, 1354 6/9, 1358 10/16). Over the following decades, the Selca Valley became one of the largest ironworking centres in Carniola, with its central ironworking settlement named after iron; Železniki (in German “Eisnern”) (Blaznik 1973: 83–87) (Fig. 3).³

2 *eyznaer maister Jakomo Barthlomee Zaschs Murron Siluester Monfiodin Mathew und Jacob sein pruder.*

3 Iron = “železo” (Slovenian), “Eisen” (German).



Fig. 2 Malborghetto in Canal Valley (photo by: G. Oitzl)

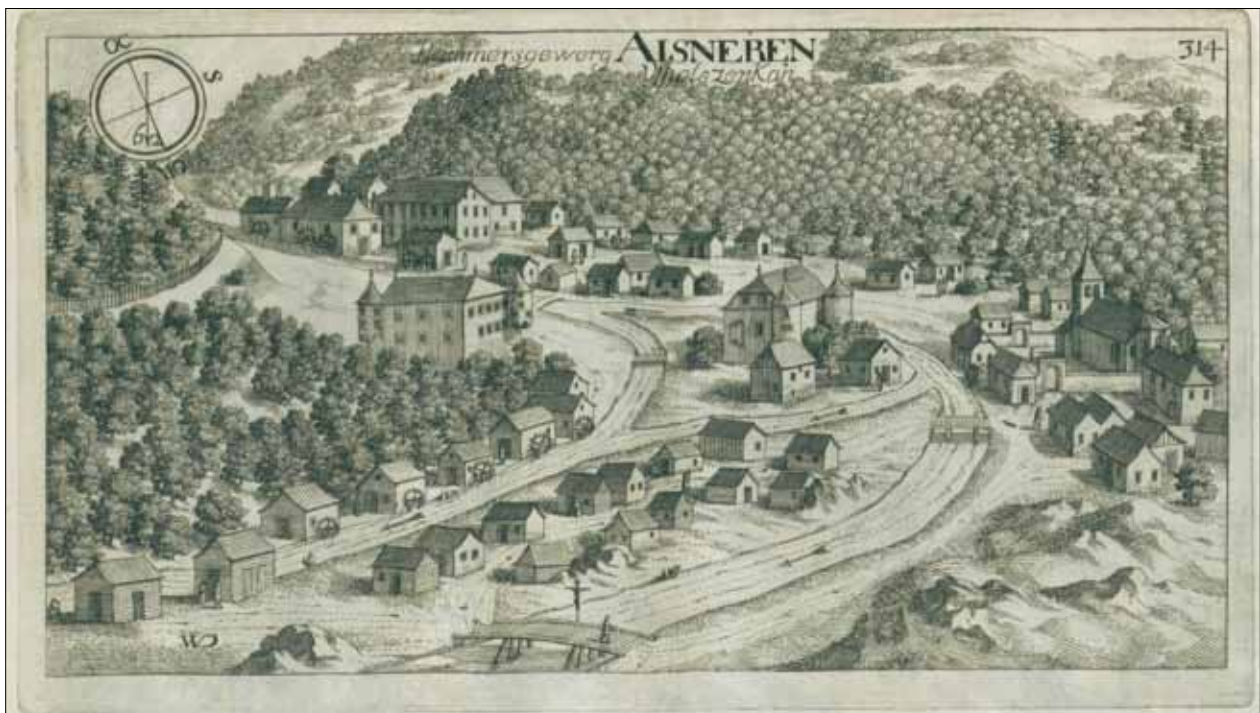


Fig. 3 Ironworking settlement Železniki in 1679 (Johann W. Valvasor, *Topographia ducatus Carnioliae modernae*, © dlib.si)

In 1381, there is a rather unambiguous reference to the use of waterpower for the operation of a forge on the Sava River (*schmittn an der Sau*) near Jesenice (currently the Stara Sava museum area), which had been previously set up by one *Wisser* (Lačen-Benedičič 2001: 17). Unlike the above-mentioned masters, and judging by his name, he did not hail from northern Italy, but clearly from a German-speaking area; alternatively, he could also have been a local man from the Jesenice area or other parts of Carniola.

The (northern) Italian influence was more pronounced on the far northwest side of Carniola, close to the Canal Valley. Near Rateče, on the long uninhabited border area between Carniola and Carinthia, a new ironworking centre Fusine in Valromana (Bela Peč/Weissenfels) began to develop towards the end of the 14th century.⁴ The first known master ironworker is assumed to have come from Carinthia, as suggested by his name (*Niklas Hintenaus*) and the fact that the landlords of this area, the Counts of Ortenburg, also had estates in Carinthia (ARS, AS 1, box nr. 117, 45–46; Golec 2016: 390–392). It appears that the central role in the further development of this area in the late 14th and early 15th centuries was played by Bartolus Consurano from Malborghetto, who purchased one whole forge and a quarter of another one. His extensive estate was inherited by his two sons, Sanusch/Hans and Lazar, whose descendants can probably be traced in the Weissenfels Seigniorship rent-roll as far as 1498. Apart from this family, there were also other master ironworkers with Italian-sounding names active in Fusine, among them *Nicolo*, *Suan*, *Samus Galans*, and *Anndre Supperni* (Golec 2016: 390–392; Mlinar 2018: 82–83). Water-powered facilities were also common in Fusine; on the Rio del Lago Stream (Jezerški potok/Seebach), ironworks operated at three separate locations.

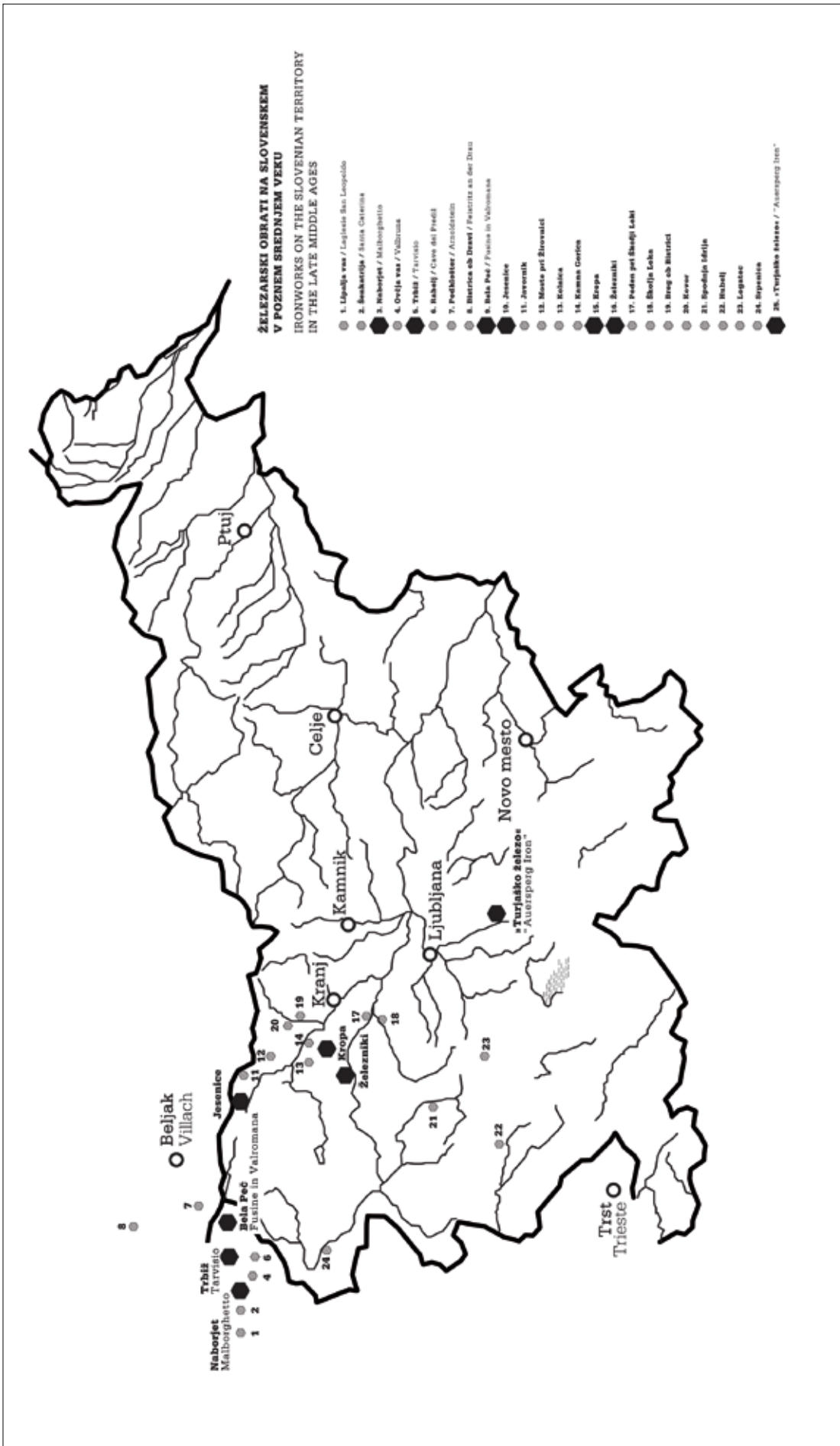
Water-powered ironworks were also present in other ironworking centres in Carniola that appear in sources from the 15th century. At the end of that century, the majority of works operating are recorded to have been present in the Jesenice area, where, according to the Weissenfels Seigniorship rent-roll, one of the seven smelting furnaces operating on the mountain pastures above Jesenice was located on the Beli Potok Stream (*Weisepach*), while the remaining ones must have therefore operated on the Črni Potok or Jesenica Streams. One of the trip hammers operating in the valley was located on the Sava River; the exact site of the other cannot be confirmed in sources, but it must have been located on the Jesenica, in the area of present-day Plavž (today part of Jesenice) (Mlinar 2018: 72). On the Završnica Stream, there was a forge in Moste near Žirovnica, which was bought in 1414 by one Marcus, son of Simon from Venzone in Friuli (CKSL, 1414 8/5), and there was a smelting furnace operating in the area around Radovljica, along the Sava River at the end of the 15th century (ARS, AS 1, box nr. 97, 124). On the Lipnica Stream, there were ironworking plants in Kamna Gorica, and on the Kroparica Stream ironworks were located in Kropa, a settlement that developed into another major ironworking centre in Carniola in the late 15th and during the 16th centuries. In Kropa, we can also assume that master ironworkers of Italian descent played a certain role in its development; at the end of the century, both trip hammers and three farms in the settlement were co-owned by one *Sann* and his associate *Jörn* (ARS, AS 174, box nr. 246, 104).

One question that remains is the origin of these master ironworkers with Italian sounding names. Given the relative geographical proximity and the advanced stage of development of the ironworking technology, it might be safe to assume that they came from northern Italy, perhaps from Lombardy, specifically from the Alpine valleys above Bergamo and Brescia, or from the neighbouring Friuli, from where Marcus, who bought the forge in Moste, had also come. The popular tradition in Železniki says that master ironworkers migrated there from the Palmanova area (Globočnik 1867: 2); however, no sources attest to an advanced stage of ironworking activities in this area, making the argument untenable. Even so, Friuli could be one of the possible areas of origin of master ironworkers, as ironworking in Friuli's Alpine valleys of the Carnic Alps was at an advanced stage of development even before the mid-14th century. In this respect, the close geographical proximity and intensive trade connections between Upper Carniola and Friuli since at least 14th century are also worth highlighting (Gestrin 1965: 210–211; Sprandel 1968: 112; Degrassi 2014: 80) (Map 1).

INDIRECT IRONMAKING PROCESS AND ITS INTRODUCTION IN THE SLOVENIAN TERRITORY

The second progress crucial for the development of ironworking technology in the pre-industrial era is the transition from the direct to indirect process. Instead of a bloom, the indirect ironmaking process yielded pig iron with high carbon content which had to be reduced through decarbonisation in special hearths in finery forges. The main difference was in the higher temperature in smelting facilities, leading to progressively bigger furnaces. These new facilities, which produced pig or crude iron, are called "blast furnaces", and enabled the production of iron in one continuous process, resulting in

4 Part of Carniola since the Middle Ages, Fusine in Valromana became part of the Kingdom of Italy in 1920.



Map 1 The map shows the locations of ironworking plants mentioned in written sources until 1500 (map: P. Strman, concept: G. Oitzl).

higher production quantities and also higher consumption of charcoal (Sprandel 1968: 226; Šorn 1984: 137–140) (Fig. 4).

To date, researchers have not been able to come to a full consensus on the issue of the invention and development of the blast furnace technology. Possible territories for the development of the indirect ironmaking process include Lombardy, the Rhineland, and Sweden, with the timeframe of the invention placed into the 13th and 14th centuries. The new technology took some time to spread into other European lands. Where the direct ironmaking technology was well developed, blast furnaces did not spread or prevail until the 18th or 19th centuries. Such example is the Eastern Alps area, where facilities with the old and the new technology coexisted side by side for several centuries (Sprandel 1968: 227–241; Sella 1974: 102–103; Gimpel 1993: 67; Pleiner 2000: 82–85, 283–285).



Fig. 4 Blast furnaces in Heft, near Hüttenberg, Carinthia. The building complex has been preserved from the mid-19th century (photo by: G. Oitzl)



Once again, master ironworkers and entrepreneurs from northern Italy played a critical role in the transfer of the new technology to iron industry in the Slovenian territory. They also introduced the new ironmaking process for the production of quality steel, called “Brescian” steel after its region of origin. The smelting facilities using the new technologies are referred to in sources as Brescian blast furnaces (*brescianischer Plaofen*), and the iron-processing facilities as Brescian (*Pressawerisch Werchgaden*) and “Italian” trip hammers (*wällischen hammer*).

In the Slovenian territory, the use of the “Brescian” process for iron smelting was probably introduced in the second half of the 1530s. In 1538, the permission to set up two Brescian blast furnaces in the area of present-day Jesenice (Sava and Plavž) was allegedly granted to Bernard Bucelleni, whose family originated from the area above Bergamo and Brescia in Lombardy. A year before, Matthias Seenuss from Fusine in Valromana was granted a concession for producing steel in the “Brescian”

Fig. 5 The coat of arms of the Bucelleni family, 17th century (kept by the Upper Sava Valley Museum Jesenice, photo by: S. Kokalj)

manner in Slovenski Javornik. It is not entirely clear if he also built a blast furnace there, while he was mostly processing pig iron from Hüttenberg. Since at least mid-16th century, another branch of the Bucelleni family operated in Javornik, with Gabriel Bucelleni as one of its first representatives recorded in sources (Müllner 1909: 381–382; Pirchegger 1937: 144; Mugerli 2019: 51–55) (Fig. 5).

Another family to have had a profound impact on the development of iron industry in Upper Carniola were the Locatellis, who are believed to have migrated from the Brescia region in the 1540s. The first reference to their existence in Upper Carniola dates back to 1544, when Anton Locatelli traded in Carniolan iron. The family had estates both in Jesenice and Bohinj. Other families involved in the iron industry in Carniola include the Coronini, Nani, Milano, Gneckho, among others. In the second half of the 16th century, Italian entrepreneurs and master ironworkers were present in about one third of ironworking facilities in Carniola. Their capital and their knowledge helped introduce the new technology to the significant part of the ironworking centres; the list of ironworking facilities in Carniola and Gorizia provinces from 1581 reveals a total of 22 smelting plants, of which at least seven, perhaps even eight, were of Brescian type (ARS, AS 1, box nr. 234, 214–216; Müllner 1909: 383–384, 476–478; Gestrin 1981: 235).

Unlike in the Late Middle Ages, the persons referred to above were not master ironworkers but rather nobles and burghers, who engaged primarily in the financial and operational issues of introducing the new technology to their facilities. The execution part, however, was in the hands of master ironworkers, whom these entrepreneurs had often brought with them to work in Carniola. Such was the case of the factory-based workshops of Veit Khisl and Hans Weilhamer, both burghers of Ljubljana, who in 1529/30 established a copper processing plant and an iron foundry near Ljubljana and hired 15 Italian workers to work there (Gestrin 1991: 208).

The situation was quite different in the nearby Carinthia. Like in Upper Styria, the production of pig iron in smelting furnaces was present during the Late Middle Ages; however here, the pig iron was an unplanned by-product of the direct iron-smelting process, with the amount of iron obtained in this way rather low and used for each subsequent loading in the smelting process. The first blast furnace used for a systematic production of pig iron was set up in 1541 in Kremsbrücke, followed by another in Eisentratten in 1566. Both blast furnaces operated in the Gmünd Seigniorship, while the iron ore came from the mines in the Krems Valley. Unlike the ironworking centres of Carniola, where blast furnaces were owned by entrepreneurs from northern Italy, the facilities here were owned by the mining and ironworking company from Krems, composed of entrepreneurs from Austrian provinces.⁵ There are no references in sources to any master ironworkers from Italy. In 1555, for example, there is a mention of Veit Schmelzer as the foreman of the company (KLA, Lodron, 27-B-907 St). In the following years, blast furnaces in Carinthia were built by “local” investors; in 1578, the blast furnace in Urtl above Althofen was built by the burghers of St. Veit an der Glan (Wiessner 1953: 51, 147–150; Dinklage 1974: 327).

The presence of master ironworkers and entrepreneurs of northern Italian origin in the iron industry of Carinthia was stronger in the iron-processing facilities located in the valleys of southern Carinthia, especially in the Canal Valley. In 1578 in Malborghetto, as many as 20 of the total of 66 burghers of the market town engaged directly in ironworking, of which at least seven had an Italian-sounding family name (Wiessner 1953: 256). While this does not imply that they came from the northern Italian area, their ancestors certainly might have.

Master ironworkers and entrepreneurs from (northern) Italy also appeared in other settlements of the Canal Valley; in the mid-16th century, there is a mention in Tarvisio of a “Perdieller” trip hammer, which was apparently set up by a master ironworker with the Italian-sounding name of *Perdieller* (KLA, Allgemeine Urkundenreihe, 418-B-A 4744 St). Some master ironworkers of Italian descent hailed from the nearby area, among them Piero Fillafero, who operated in Malborghetto and in 1584 lived near Hermagor in Gail Valley, but originally came from the Friulian part of Pontebba, near the border with Carinthia (KLA, Urkunden des Marktes Malborghet, 99-B-27 St). A reference to master ironworkers from northern Italy is also found in the Rosental Valley; before the mid-16th century, Suan Maria Delango, a wire puller (*Drahtzieher*), set up a small trip hammer plant in Feistritz im Rosental, where wire was produced, apparently (Wiessner 1953: 208–209).

In the valleys of southern Carinthia, in the 16th century, Italian (and other) masters would set up trip hammer facilities where they practised ironworking in the Italian manner; hence the trip hammers were called “Italian” trip hammers (*wällischen hammer*). At least one such trip hammer operated near Malborghetto (KLA, Allgemeine Urkundenreihe, 418-B-A 2333 St), and at least two in the Bad Eisenkappel area, one of them on the Ebriach Stream in the immediate vicinity of the Bad Eisenkappel market town, and the other on the Vellach River below Rechbach. In the latter two instances, the owners were not of Italian descent (KLA, Eberstein und Hornburg, Christalnigg, 227-B-37 St; Wiessner 1953: 273–275). Such

⁵ Upon its establishment in 1538, eight stakes were divided among six owners, and by 1567 they were concentrated in the hands of two owners: one half was owned by the Khevenhüller brothers and the other by Christoph Pflügl (Wiessner 1953: 149–150).

trip hammers were a rare occurrence north of the Drava River, one of the rare examples dating back to around 1565 when a Brescian type ironworking facility (*Pressawerisch Werchgaden*), the owners of which were not from Italian lands, was set up near Friesach (Wiessner 1953: 195–196).

As there is almost no trace of Italian influence in the Late Middle Ages and 16th century on ironworking in Carinthia north of the Drava River, the question arises as to where the new technologies used in these ironworking centres (Hüttenberg, Waldenstein and Krems) came from, or if perhaps they were the product of local knowledge and expertise. The resources currently available cannot establish an unambiguous connection to other iron industry centres in Europe. Especially conspicuous in this regard is the absence of intensive connections to one of the largest iron industry centres in pre-industrial Europe, Erzberg in Styria, which would be expected given its relative geographical proximity.

One of the few masters from the Upper Styrian iron industry centre to have worked in Carinthia was Siegmund Griesser, a resident of the market town of Eisenerz, who owned a smelting furnace in Erzberg. In late 1535, from his sisters-in-law, he bought the estate of Pfannhof on the Wimitz River above St. Veit an der Glan, which also included ironworking facilities (a trip hammer, a nail forge, and a scythe forge) (KLA, Allgemeine Urkundenreihe, 418-B-A 2055 St). A few years later, Griesser sold the estate back to the same sisters-in-law (KLA, Allgemeine Urkundenreihe, 418-B-A 2137 St).

In contrast, the ban on the export of the Carinthian iron northwards and the resulting geographical orientation in the distribution of Styrian and Carinthian iron products suggest an intense competition between the two centres; while the products from Styria were exported to the north (Austrian and south German area) and west (Tyrol), the majority of products from Carinthia were sold to the south, southwest and east, to Italian, Hungarian, and Croatian lands (Wiessner 1953: 24–31).

Attention should also be given to the existence of more intensive connections to the Bavarian or south German area. In the late 15th century, at the invitation of King Maximilian, Hans Hamer, a burgher of Nuremberg who specialised in iron sheet production, established an iron sheet forge in the vicinity of St. Veit an der Glan (Dinklage 1953: 132–133). The fairly extensive estate of the Bamberg Diocese in Carinthia, where two large ironworking centres developed, specifically in the Upper Lavant (Waldenstein) and Canal Valleys, also suggests possible connections to southern Germany. The entourage of the Bishop of Bamberg included burghers and ministeriales who moved from Franconia to Carinthia (Dinklage 1953: 59); the same could be assumed for master ironworkers, who could have transferred to Carinthia the ironworking technology used in ironworking centres in southern Germany, particularly in the developed ironworking centre in Oberpfalz. Dinklage also suggests that the waterpower technology might have spread from Bamberg or German area, though he believes that it most probably spread to Carinthia from northern Italy. In contrast, he also states that the blast-furnace technology spread to Carinthia from the west German area (Dinklage 1974: 318, 327).

The influence of master ironworkers from southern Germany is evident also in the family name of Peyr or Payr, suggesting a person resettled from this area, or their descendant (Fräss-Ehrfeld 1984: 450). Persons carrying this family name can be also found around 1500 in the territory in question, specifically in the mountains above Jesenice, where Wolf Peyr and Simon Peyrl owned smelting furnaces, and in Friesach, where Hans Payr was the foreman in the ironworking plant composed of the two smelting furnaces and one trip hammer (Pirchegger 1936: 97–100; Mlinar 2018: 72).

MOTIVES BEHIND THE TECHNOLOGY TRANSFER AND ITS CONSEQUENCES

The key role in the arrival of foreign master ironworkers and the transfer of new technologies, at least in the Late Middle Ages, was played by the landlords. A good example of this is the development in the Selca Valley, where Albert II, Bishop of Freising most likely played the crucial part in the beginnings of an intensive iron industry in the Škofja Loka Seigniorship. In 1354, he initially granted the master ironworkers, who had recently migrated to the Selca Valley, the right to ironworking and determined the amount of their dues. Four years later, he determined the borders of their lands and granted them rights to exploit forests and use of the paths (BayHStA, HL 4, Hochstift Freising, fasz. 135, 1379 4/29; CKSL, 1354 6/9, 1358 10/16). It is possible that these masters came to the Freising estate following his initiative. His other actions support this assumption, as he was able to considerably improve the economic position of the diocese, which he headed from 1349 to his death in 1359 (Krüger 1953: 127–128).⁶

The second important figure to have greatly influenced the development of the iron industry in Carniola was Count Frederick III of Ortenburg. In 1381, seeking to attract masters and ironworkers from other, technologically more advanced regions, he issued the Ortenburg mining regulations for the mining and ironworking area in Jesenice. The oldest mining

⁶ Albert descended from the family of the Counts of Hohenberg from Swabia. From the 1330s onward, he held several important clerical and secular offices, and spent some time as the imperial chancellor and provincial attorney in Alsace.

regulation for any ironworking area in the Eastern Alps, this extensive document governed the relations and rights of various social and work groups in the area and established a mining court presided by a mining magistrate. Frederick thus established conditions for the beginning of an intensive mining and ironworking industry in the Jesenice area (Lačen-Benedičič 2001; Mlinar 2016: 51). He also played an important part in the establishment of the ironworking centre in Fusine in Valromana, where he initially acquired an estate and then proceeded to attract master ironworkers to settle in this unpopulated area. The first of them was allegedly one Hintenaus from Carinthia, but later, there is a notable influence of master ironworkers from the Canal Valley, among them Bartolus Consurano from Malborghetto, and Oton from Camporosso (Žabnica/Saifnitz) (Golec 2016: 390–392).

By taking initiative in the iron industry, landlords primarily pursued financial and economic goals. With the introduction of new technologies, and in many places also with the establishment of iron production, they sought to increase the earnings of their estates, especially after the potential for further agrarian colonisation had been fully exploited.

The main reasons for the relocation of master ironworkers and entrepreneurs are believed to have been primarily related to various rights and privileges, as well as relatively low duties offered to them in new environments and the possibility for economic and social progress. For some, the reasons might have been the troubles they faced in their areas of origin; for others, these might have been political conditions. In the 16th century at least, the large majority of entrepreneurs migrated to Carniola from Lombardy, where parts of the nobility had traditionally allied with the dukes of Milan, but during the Austro-Venetian war they supported Maximilian and, after the war, some of them moved to Austrian lands apparently. One typical example is the above-mentioned Bucelleni family (Mugerli 2019: 51–55). A similar assumption could be made for the less-studied Locatelli family; some of the sources from the 1570s and 1580s refer to Hans Locatelli, a member of the family, as *Zuan Locatelli dicto Gebellin* (ARS, AS 1, box nr. 234, 422–425; Müllner 1909: 631–632), the then already archaic addition to the name pointing to his family's loyalty to the German king.

Apart from the advanced stage of development, one of the factors influencing the arrival of masters from northern Italy was also close geographical proximity and the resulting intensive trade links between northern Italy and the Slovenian (also Austrian) territory. The vast majority of iron and iron products from Carniolan and Carinthian iron-producing centres was exported to Friuli and North Adriatic ports (Venice, Trieste, and Rijeka). In the 16th century, in particular, a significant part of the entrepreneurs from northern Italy was merchants trading in iron and iron products. In the Late Middle Ages, it was the Canal Valley that attracted masters and entrepreneurs from northern Italy; located right next to the border between Carinthia and Friuli (the Venetian Republic after 1420), which in the Middle Ages ran along the Pontebbana Stream, it provided an ideal location to set up iron-processing facilities. The valley also represented the most favourable transport link connecting Austria and northern Italy by way of Eastern Alps. The development of the iron industry in the valley was further enabled by its natural conditions, particularly water and forests (Gestrin 1981: 234–235; Fräss-Ehrfeld 1984: 659–667) (Fig. 6).

In time, some of the masters and entrepreneurs from northern Italy, who were active in the Slovenian territory, settled there and blended in with the rest of the population, and records of their descendants can be found in the following decades and centuries. Master *Jacomat*, who in 1379 is mentioned as the representative of master ironworkers in Železniki, had a son Nicholas, who in 1405 was an active ironworker in the Selca Valley and at the time also a burgher of Škofja Loka (BayHStA, HL 4, Hochstift Freising, fasz. 137, 1405 8/17). Bartolus Consurano from Malborghetto, who was probably a descendant of an unknown master from Friuli or northern Italy who had migrated to Malborghetto in mid- or late 14th century, operated in Fusine, where there is a record of his two sons (Lazar and Sanusch/Hans) in the mid-15th century, and possibly of their descendants at the end of the century (ARS, AS 1, box nr. 117, 54–55; CKSL, 1455 10/20; Mlinar 2018: 82). The descendants of Bernard and Gabriel Bucelleni also left a strong mark on the iron industry in Upper Carniola; over approximately two centuries, they were instrumental in helping the ironworking area in Jesenice become the most technologically advanced region of Carniola in the Early Modern Period (Mugerli 2016: 464–470; 2019: 51–55).⁷

The masters of northern Italy and the extensive trade exchange with northern Italy have also had a discernible impact on the development of Slovene ironworking terminology. The most common term derived from the Friulan or Italian language is “fužina”, which stands for an ironworking plant, predominantly for forge or trip hammer (Paulin 1995: 67; Snoj 2009: 134).⁸ The term only rarely occurs in sources from the Late Middle Ages, with the oldest known mention (*fusinis*) dating back to 1396 in a Škofja Loka Seigniorship account book (Blaznik 1963: 270). Attention should also be given to the

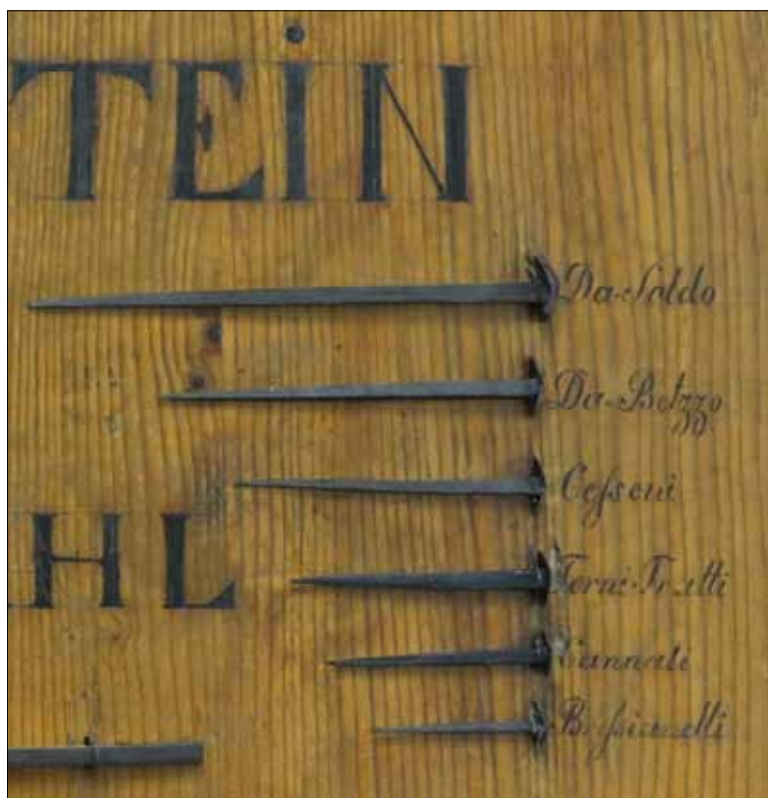
7 They lost their last facilities (on the Sava) in the mid-18th century, when they had to go into administration due to outstanding debts. The facilities were bought in 1764 by creditors from Trieste and sold two years later to Valentin Ruard.

8 Derived from the Friulan (*fusine*) or Venetian Italian (*fusina*), Italian Standard *fucina*, in the meaning of “smelting plant” or “forge”.



Fig. 6 Rijeka (photo by: G. Oitzl)

significant impact of the Italian language on the designation for some types of nails, which until the end of the 19th century were the main end product of Carniolan iron industry in Italian markets. These designations appeared in the Early Modern Period at the latest and did not change until the end of the 19th century, among them *canalli*, *tratti*, *terni*, *ceseni*, *brescianelli*, *gondolini*, and others (Müllner 1909: 320–326; Žontar 1955: 85–86; Gašperšič 1956: 44–46).



Although the questions of identity fall outside of the limited scope of this paper, a few points of interest with regard to the subject at hand should nevertheless be pointed out, as the memory of the background of immigrants remained preserved among themselves and the surrounding population alike. Thus, people from around Železniki referred to Železniki as “Lahovše” well into the 19th century (Globočnik 1867: 2).⁹ Also, in the second half of the 16th century, when the number of Italian-speaking master ironworkers and entrepreneurs increased considerably, the senior mining magistrate in Carniola had to be fluent in the Slovenian and German as well as in the Italian language (*der theitsch, windisch und wälisch khan*) (Müllner 1909: 132) (Fig. 7).

Fig. 7 Names of various types of nails are preserved on the sample table with nails and semi-products, which was made in the ironworks above Kamnik in the mid-19th century (kept by the National Museum of Slovenia, photo by: T. Lazar).

9 Derived from the word “Lah”, at the time the designation for a person coming from Italy; today, the term is considered to be pejorative.

CONCLUSION

In the Slovenian territory in the pre-industrial era, ironworkers and entrepreneurs from northern Italy emerged as key players in the transfer of ironworking technology from their area, which at the time was one of technologically most advanced iron industry regions in Europe. During the 14th century, master ironworkers were responsible for introducing water power to the operation of ironworking facilities in at least Canal and Selca Valleys, and they played an important role in the establishment of the iron industry in Fusine. In the 16th century, entrepreneurs, who had come predominantly from Lombardy, introduced to Carniola the indirect iron production process and financed the construction of first blast furnaces. They also had a profound influence on the development of the iron industry in Jesenice area.

In the Late Middle Ages, the main initiative for the transfer of technology came from landlords, who sought to improve the profitability of their estates, while in the 16th century, entrepreneurs took a more active role in this. Both the arrival of foreign master ironworkers and entrepreneurs and the introduction of new technology represented a significant step forward for the hitherto underdeveloped iron industry in the Slovenian territory; consequently, they had a vital role in the economic development of these areas, which were generally poorly developed due to their less favourable geographical conditions.

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 AS 174, Terezijanski kataster za Kranjsko, box nr. 246, Urbar radovljiškega gospostva 1498.
 BayHStA – Bayerisches Hauptstaatsarchiv.
 HL 4, Hochstift Freising.
 KLA – Kärntner Landesarchiv.

KLA 27, Lodron.
 KLA 418, Allgemeine Urkundenreihe (AUR).
 KLA 99, Urkunden des Marktes Malborghet.
 KLA 227, Eberstein und Hornburg, Christalnigg.
 ZIMK SAZU – Zgodovinski inštitut Milka Kosa, Slovenska akademija znanosti in umetnosti.
 CKSL = Božo Otorepec, Centralna kartoteka srednjeveških listin za Slovenijo.

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