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10.4 NARAVOSLOVNE PREISKAVE KOVINSKEGA GRADIVA Z GROBIŠČA PEZDIRČEVA NJIVA V PODZEMLJU

10.4 SCIENTIFIC EXAMINATIONS OF METAL ARTEFACTS FROM THE PEZDIRČEVA NJIVA BURIAL SITE IN PODZEMELJ

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UVOD

Pri naravoslovnih preiskavah kovinskega gradiva iz bakrovih zlitin in železa s Pezdirčeve njive so sodelovali številni strokovnjaki s področja kemije, fizike in metalurgije. Že na začetku preiskav smo ugotovili, da nam z neinvazivnimi preiskavami ne bo uspelo pridobiti zadovoljivih odgovorov na vprašanja o mehanizmih propadanja predmetov in tehnologiji izdelave. Zato se invazivnemu odvzemanju vzorcev nismo mogli popolnoma izogniti.

Preiskave je koordiniral Narodni muzej Slovenije[1] v sodelovanju z Naravoslovnotehniško fakulteto Univerze v Ljubljani. Pri preiskavah z rentgensko radiografijo smo sodelovali z Inštitutom za metalne konstrukcije (IMK). Z Institutom "Jožef Stefan" smo sodelovali pri preiskavah z rentgensko fluorescenčno spektroskopijo (XRF). Na Inštitutu za kovinske materiale in tehnologije so izvedli metalografske preiskave in analize korozijskih produktov. Pri interpretaciji stratigrafije korozijskih plasti smo sodelovali s Paleontološkim inštitutom Ivana Rakovca ZRC SAZU. Večina preiskav je bila povezana s proučevanjem negovske čelade, pozornost pa smo namenili tudi tehnološkim razlikam med najdbami iz grobov dolenjskega (D) halštatskega in mlajšega viniškega (V) kulturnega kroga (Grahek, Kovač 2020, 448; Grahek 2024).

[1] Preiskave so potekale v okviru raziskovalnega programa P6-0282 *Predmet kot reprezentanca: okus, ugled, moč (Raziskave materialne kulture na Slovenskem)*, ki ga vodi dr. Tomaž Lazar ter financira Javna agencija za znanstvenoraziskovalno in inovacijsko dejavnost Republike Slovenije (ARIS).

INTRODUCTION

The scientific examinations of the copper-alloy and iron artefacts from the Pezdirčeva njiva burial site involved a number of specialists in the fields of chemistry, physics, and metallurgy. At the very outset, we established that non-invasive methods would not yield adequate information about the mechanisms of artefact degradation and technology involved in their production. This was why we were unable to entirely avoid invasive sampling.

The examinations were coordinated by the National Museum of Slovenia[1] in collaboration with the Faculty of Natural Sciences and Engineering at the University of Ljubljana. X-ray radiography was performed in cooperation with the Institute for Metal Constructions (IMK). For X-ray fluorescence spectroscopy (XRF) analyses, we partnered with the Jožef Stefan Institute. The Institute for Metal Materials and Technologies was tasked with metallographic analyses and corrosion product characterisation. The interpretation of corrosion layer stratigraphy was a combined effort undertaken in cooperation with the ZRC SAZU Ivan Rakovec Institute of Palaeontology. Our analyses were predominantly focused on the Negova-type helmet, though we also examined the technological differences between finds from the graves of the Dolenjska (D) Hallstatt cultural group and those from the later Vinica (V) cultural group (Grahek, Kovač 2020, 448, Grahek 2024).

[1] The examinations ran in the framework of Research Programme P6-0282 *Objects and Prestige: Taste, Status, and Power (Research of Material Culture in Slovenia)*, which is headed by Dr Tomaž Lazar and financed by the Slovenian Research and Innovation Agency (ARIS).

Sl. 1: Podzemelj, Pezdirčeva njiva, grob 110. Ostanki železnega meča pred konserviranjem-restavriranjem in rentgenski posnetek: 85 kV, 4 mA, 30 s (preiskava: Janko Vodišek, IMK, foto: Nataša Nemeček).
Fig. 1: Podzemelj, Pezdirčeva njiva, grave 110. Remnants of an iron sword prior to conservation-restoration and an X-ray image: 85 kV, 4 mA, 30 s (examination: Janko Vodišek, IMK, photo: Nataša Nemeček).

PREISKAVE IZBRANIH PREDMETOV Z RENTGENSKO RADIOGRAFIJO (RTG)

Rentgenska radiografija je neinvazivna metoda, s katero pridobimo številne koristne informacije o stopnji ohranjenosti arheoloških predmetov še pred konservatorsko-restavratorskimi posegi.

Metoda

Rentgenski žarki so elektromagnetno valovanje z zelo kratko valovno dolžino (10.000-krat krajšo od vidne svetlobe), zato imajo veliko sposobnost prodiranja skozi snov. Glede na intenziteto žarkov, sestavo kovine, debelino predmeta in njegovo ohranjenost prepuščeni rentgenski žarki na rentgenski film odtisnejo različne odtenke potemnitve. Zlasti plemenite kovine v manjši meri prepuščajo žarke, zato filma skoraj ne počrnijo, sledita bron in železo (Milić, Šubic-Prislan 1997, 91–104). Preiskave smo izvedli na Inštitutu za metalne konstrukcije (IMK), kjer imajo dolgoletne izkušnje

X-RAY RADIOGRAPHIC ANALYSIS (RTG) OF SELECTED ARTEFACTS

X-ray radiography is a non-invasive method which yields numerous valuable insights into the level of preservation of archaeological artefacts ahead of conservation-restoration interventions.

Method

X-rays are a type of electromagnetic radiation with extremely short wavelengths (10,000 times shorter than visible light), which enables them to penetrate matter. Depending on the intensity of the rays, composition and thickness of an individual artefact, and the state of its preservation, the penetrating X-rays produce varying levels of darkening imprint on radiographic film. The least amount of darkening is produced by noble metals which resist X-ray penetration best, followed by bronze and iron (Milić, Šubic-Prislan 1997, 91–104). The examinations were conducted at the Institute for Metal Constructions (IMK), relying on their years of experiz rentgenskimi preiskavami arheološkega gradiva.[2] Rentgenziranje je bilo izvedeno na industrijskem rentgenskem aparatu. Predmete smo položili neposredno na film. Uporabili smo rentgenske žarke z napetostjo 85–100 kV, električnim tokom 4 mA in ekspozicijo 30–60 s. Pri preiskavah smo se osredotočili predvsem na predmete iz železa in bakrovih zlitin. Zanimala nas je ohranjenost predmetov pred začetkom konservatorsko-restavratorskih posegov, zato smo nekatere sklope najdb preiskali v zvitkih z zemljo.

Rezultati

Med zanimivejše posnetke z rentgensko radiografijo vsekakor lahko uvrščamo železni meč z delno ohranjeno nožnico iz groba 110 (*t. 55: 1*). Pri kovanem železnem meču so nas zanimale notranja struktura kovine, prisotnost morebitnih dekoracij in ohranjenost kovinskega jedra. Iz rentgenskega posnetka je razvidno (*sl. 1*), da je kovina na rezilu slabše ohranjena, kjer je material zaradi preoblikovanja s kovanjem sorazmerno najtanjši.[3] Zaradi korozije pa so vidne izrazitejše poškodbe kovine v zadnjem delu proti konici. Zaključni okov nožnice ima dobro ohranjeno kovinsko jedro.

Rentgenska radiografija je zelo uporabna tehnika za skupke kovinskih predmetov, saj lahko iz rentgenske slike ugotovimo njihovo prisotnost in medsebojno lego, česar s prostim očesom ni mogoče opaziti. Iz rentgenskega posnetka skupka najdb iz groba 45 (*t. 19 A*) so razvidni predmeti iz bakrovih zlitin – ti namreč filma skoraj ne počrnijo, in železa – delna počrnitev (*sl. 2*). Na drugem skupku predmetov, izkopanih pod negovsko čelado v grobu 100 (*t. 46:2; 50*), lahko opazujemo železno sekiro z dobro ohranjenim kovinskim jedrom, preostali pridatki iz železa so slabše ohranjeni, saj film le delno počrnijo (*sl. 3*).

PREISKAVE Z RENTGENSKO FLUORESCENČNO SPEKTROMETRIJO (XRF)

V prvi fazi – še pred konservatorsko-restavratorskimi posegi – smo na Institutu "Jožef Stefan" z rentgensko fluorescenčno spektrometrijo (XRF) izvedli 84 analiz na predmetih iz bakrovih zlitin.

[2] Vse preiskave je izvedel Janko Vodišek iz Laboratorija kovinskih konstrukcij IMK, za kar se mu najlepše zahvaljujemo.

[3] Kovanje ima tako pozitivne kot negativne vplive na korozijo. O negativnih govorimo, kadar nastanejo (mikro) razpoke v materialu, npr. pri hladnem kovanju. Na splošno pa kovanje izboljša korozijsko obstojnost v primerjavi z lito strukturo (poroznost).

ence in radiographic analysis of archaeological material.[2] An industrial X-ray apparatus was used. Artefacts were placed directly onto the film. X-rays were applied with voltages ranging from 85 to 100 kV, a current of 4 mA, and exposure times from 30 to 60 seconds. Our examination focused largely on iron and copper-alloy artefacts. Since we were interested in how preserved the artefacts were prior to conservation-restoration, we examined certain assemblages of finds without removing them from their soil blocks.

Results

One of the more interesting radiographs is certainly that of the iron sword with a partially preserved scabbard from grave 110 *(Pl. 55: 1*). In the case of the said forged iron sword, we were interested in the internal structure of the metal, presence of potential decorations, and level of preservation of its inner metal core. The radiograph (*Fig. 1*) shows that the blade metal was less well preserved where the material is comparativelly thinner.[3] Corrosion damage is more advanced along the final section towards the tip. Meanwhile the metal core of the terminal scabbard fitting is well preserved.

The technique of X-ray radiography is highly effective in the examination of groups of metal artefacts, as it can give us a view of their presence and spatial relationship, which are otherwise invisible to the naked eye. The radiograph of the assemblage from grave 45 (*Pl. 19 A*) clearly shows the presence of copper-alloy artefacts which produce no darkening on the film, and iron which darkens it partially (*Fig. 2*). Another assemblage, excavated from under the Negova-type helmet in grave 100 (*Pl. 46:* 2*; 50*), included an iron axe with a well-preserved metal core, while other metal fittings were less well preserved, as evident from the fact that they only partially darkened the film (*Fig. 3*).

X-RAY FLUORESCENCE SPECTROMETRY (XRF) ANALYSES

In the first phase of examination, ahead of the conservation-restoration interventions, we performed 84 X-ray fluorescence spectrometry (XRF) analyses on copper-alloy artefacts at the Jožef Stefan Institute.

[2] All the examinations were conducted by Janko Vodišek from the IMK metal Ccnstructions laboratory, for which he has our sincerest gratitude.

[3] Forging has both positive and negative effects on the progression of corrosion. Its effect is negative when it results in (micro)cracks in the material, e.g. in cold forging. In general, however, compared to cast structures (which tend to be porous) forging improves resistance to corrosion.


Najdišče
Koda
Datum
Najdba
Sekt./sonda
Kvadrant / mikrokvadrant
SE / plast
Arheoterra d.o.o.

Sl. 2 / Fig. 2 →

Sl. 3: Podzemelj, Pezdirčeva njiva, grob 100. Skupek predmetov pred konserviranjem-restavriranjem in rentgenski posnetek: 90 kV, 4 mA, 50 s (preiskava: Janko Vodišek, IMK, foto: Nataša Nemeček).
Fig. 3: Podzemelj, Pezdirčeva njiva, grave 100. An assemblage of artefacts prior to conservation-restoration and an X-ray image: 90 kV, 4 mA, 50 s (examination: Janko Vodišek, IMK, photo: Nataša Nemeček).

Metoda

Rentgenska fluorescenčna spektrometrija je hitra, enostavna in predvsem neinvazivna tehnika, s katero določimo elementno sestavo predmetov. Metoda XRF omogoča, da v kratkem času (300 s na vzorec) preverimo vsebnost vseh glavnih elementov v bakrovih zlitinah. Ob upoštevanju izsledkov novejših raziskav o sestavi prazgodovinskih bakrovih zlitin (prim. Northover 2011, 644–649) so nas zanimali naslednji elementi: baker (Cu), kositer (Sn), srebro (Ag), svinec (Pb), arzen (As),

Method

X-ray fluorescence spectrometry is a fast, simple, and, above all, non-invasive method of determining the elemental composition of artefacts. The XRF method allows us to very quickly (300 seconds per sample) detect all major elements present in copper alloys. Taking into account the results of recent research on the composition of prehistoric copper alloys (e.g. Northover 2011, 644–649), we were interested in the following elements: copper (Cu), tin (Sn), silver (Ag), lead (Pb), arsenic (As),

← *Sl. 2:* Podzemelj, Pezdirčeva njiva, grob 45. Skupek predmetov pred posegi in rentgenski posnetek: 90 kV, 4 mA, 50 s (preiskava: Janko Vodišek, IMK, foto: Nataša Nemeček).
Fig. 2: Podzemelj, Pezdirčeva njiva, grave 45. An assemblage of artefacts prior to conservation-restoration and an X-ray image: 90 kV, 4 mA, 50 s (examination: Janko Vodišek, IMK, photo: Nataša Nemeček).

bizmut (Bi), antimon (Sb), železo (Fe) in nikelj (Ni). V ta namen smo optimizirali analitsko metodologijo v smislu priprave vzorca ter dobljene rezultate interpretirali s sodobno in priljubljeno statistično metodo glavnih osi (PCA, Principal component analysis).

Pri metodi XRF predmete obsevamo z radioaktivnim virom. Vzbujeni elementi v zlitini se odzovejo v obliki rentgenskega fluorescenčnega sevanja, ki ga zaznamo v obliki karakterističnega, večelementnega fluorescenčnega spektra, iz katerega določimo kvalitativno in kvantitativno elementno vsebnost v merjencih v mas. odstotkih. Za presejalni test predmetov iz bakrovih zlitin sta najprimernejša dva monokromatska vzbujevalna vira, in sicer Am-241[4] z vzbujevalno energijo 59,5 keV in Cd-109[5] z vzbujevalno energijo 22,1 keV. Prvi učinkoviteje vzbuja kositer. Tako dobimo bolj optimalen fluorescentni spekter Sn, ki ga lahko natančneje kvantificiramo. Poleg kositra je vzbujevalna energija Am-241 primernejša, občutljivejša in natančnejša za vzbujanje elementov srebra in antimona, ker dobimo optimalen spekter njihovih najobčutljivejših K-črt, pri čemer seveda vzbujamo tudi preostale elemente bakra, svinca in podobno. Pri vzbujanju se K elektroni izbijejo iz atomskega ovoja. Nastane vrzel, ki se zapolni z elektronom iz višjega nivoja. Ta elektron odda energijo v obliki rentgenske fluorescence, ki jo zaznamo z detektorjem, pri čemer dobimo energijski fluorescentni spekter kositra. Po drugi strani pa je vzbujevalni vir Cd-109 optimalen za preostale elemente, torej za vzbujanje bakra, arzena, svinca, bizmuta, niklja in železa, ki so v konfiguraciji z vzbujevalnim virom Am-241 manj natančno določeni. Optimalen je torej kombinirani rezultat iz obeh merjenj.

Z vzbujevalnim virom Am-241 smo izvedli okoli 84 presejalnih meritev na bronastih predmetih in oblikovali večelementne preglednice sedmih elementov bakra, arzena, svinca, bizmuta, srebra, kositra in antimona. Za natančnejšo interpretacijo večelementne sestave (baker, kositer, svonec, bizmut, arzen, železo, nikelj) smo 30 presejalnih meritev ponovili še na vzbujevalnem viru Cd-109. Iz obeh meritev smo sestavili večelementne preglednice devetih elementov bakra, kositra, svinca, srebra, arzena, bizmuta, antimona, železa in niklja (prim. Pernicka 2014, 28–29).

Za interpretacijo pridobljenih meritev elementne sestave oziroma podatkovnih baz elementnih profilov smo uporabili multivariacijsko statistično metodo PCA. Ta sodobna in v arheometriji priljubljena statistična metoda pomaga dobiti nov uvid v izbrani set artefaktov. Metoda je linearna transformacija (rotacija) m-dimenzionalnega merskega prostora, ki omogoči ogled večdimenzionalnega sistema objektov z različnih zornih kotov. Rezultat modeliranja je dvodimenzionalni graf porazdelitve predmetov in izmerjenih parametrov

[4] Radioaktivni izotop americija-241.

[5] Radioaktivni izotop kadmija-109.

bismuth (Bi), antimony (Sb), iron (Fe), and nickel (Ni). For this purpose, we optimised the analytical methodology of sample preparation and interpreted the results using a contemporary and widely popular statistical technique of Principal Component Analysis (PCA).

The XRF method involves irradiating the artefacts with a radioactive source prompting the elements present in the alloy to respond by emitting X-ray fluorescence, which is then detected as a characteristic, multi-element fluorescence spectrum. This enables us to derive the qualitative and quantitative elemental composition of the samples. The two most suitable monochromatic excitation sources for the screening analysis of copper alloys artefacts are Am-241[4] (excitation energy 59.5 keV) and Cd-109[5] (excitation energy 22.1 keV). The 59.5 keV excitation energy of Am-241 excites tin more effectively, producing a more precise fluorescence spectrum, which can be quantified with greater precision. Furthermore, the excitation energy of Am-241 also excites silver and antimony with greater sensitivity and accuracy, as it yields the optimal spectrum of their most responsive K-lines. In line with expectations, copper, lead, and other elements are also excited. During the excitation process, K-shell electrons are ejected from their atomic orbitals, creating gaps, which are subsequently filled by electrons from a higher energy level; in the course of this exchange, the latter electron emits energy in the form of X-ray fluorescence. A detector measures this emission, providing the energy spectrum for tin. The Cd-109 source, on the other hand, is optimal for the excitation of other elements, such as copper, arsenic, lead, bismuth, nickel, and iron, which Am-241 would have detected less accurately. The most reliable analytical results are therefore achieved using the combined results of both measurement methods.

We screened approximately 84 bronze artefacts using Am-241 and compiled multi-element tables of seven elements: copper, arsenic, lead, bismuth, silver, tin and antimony. To achieve a more precise interpretation of the elemental composition of artefacts (copper, tin, lead, bismuth, arsenic, iron, nickel), we repeated 30 of these measurements using the Cd-109 source. Results of both measurement clusters were merged into combined tables of nine elements: copper, tin, lead, silver, arsenic, bizmuth, antimony, iron and nickel (cf. Pernicka 2014, 28–29).

In interpreting the resulting elemental composition measurements, i.e. element profile datasets, we employed the PCA multivariate statistical method. PCA is a popular contemporary statistical method in archaeometry that can aid in gaining new insight into the select set of artefacts. This method is a linear transformation (rotation) of an m-dimensional measurement space, allowing the multi-dimensional system of artefacts to be viewed

[4] Radioactive isotope of americium-241.

[5] Radioactive isotope of cadmium-109.

(elementov) v prostoru prvih dveh glavnih osi PCA1 in PCA2. Tako lahko vidimo grupiranje in podobnost predmetov, razberemo, kako so parametri (elementi) porazdeljeni po morebitnih skupinah in kako vplivajo na ločevanje ali združevanje teh skupin, poleg tega pa lahko ugotovimo tudi, kateri elementi so ključni za razlike ali podobnosti.

Dobljene rezultate elementne sestave artefaktov smo prenesli v preglednice in iz njih naredili podatkovne datoteke elementnih profilov. Te smo v nadaljevanju obdelovali s PCA. Preizkušali smo, ali lahko na podlagi 84 meritev razlikujemo med elementno sestavo predmetov iz dolenjske halštatske skupine (D) in mlajše viniške skupine (V) ter kateri prevladujoči elementi vplivajo na to grupiranje.

Rezultati

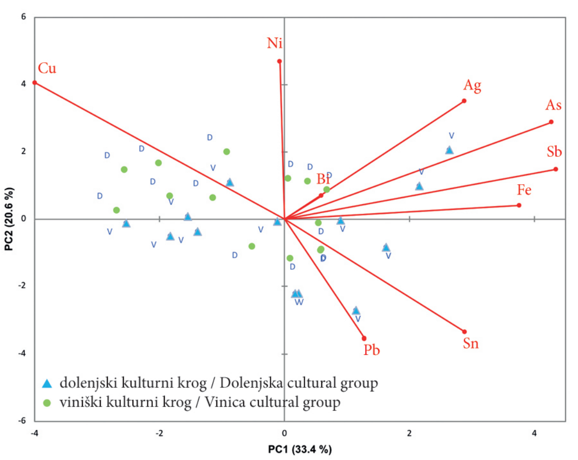
Zaradi večje preglednosti smo za obdelovanje s PCA naredili izbor analiziranih predmetov iz dolenjskega kulturnega kroga (*tab. 1*) in viniškega kulturnega kroga (*tab. 2*), prikazani so v dveh preglednicah. Pri pregledu preglednice elementne vsebnosti med analiziranimi predmeti različnih arheoloških kulturno-kronoloških skupin nismo zaznali večjih razlik. Obema skupinama predmetov so skupne visoka vsebnost kositra (27–78,2 mas. %), sorazmerno nizka vsebnost bakra (11,7–74,1 mas. %) in sorazmerno visoka vsebnost svinca (1,1–29,1 mas. %; *sl. 4*). Poleg glavnih elementov bakra, kositra in svinca so v zlitinah tudi arzen, srebro, bizmut, antimon, železo in nikelj. Višje vsebnosti srebra morebiti lahko nakazujejo, da so bili nekateri predmeti posrebreni. Vsebnosti srebra nad 1 mas. % smo zaznali pri certoških fibulah iz groba 96 (PN 302: 2,6 mas. % Ag) in groba 3 (PN 235: 1,3 mas. % Ag) ter pri šestrtastih fibulah z obrazno masko iz domnevnega groba 19 (PN 63: 1,7 mas. % Ag), groba 20 (PN 66: 1,5 mas. % Ag) in groba 44 (PN 178: 1,2 mas. % Ag). Ker je za prazgodovinske bakrove zlitine običajnejša vsebnost kositra od 8 do 12 mas. %

from multiple perspectives. In short, this modelling yields a two-dimensional graph showing the distribution of artefacts and measured parameters (elements) along the first two principal components (PCA1 and PCA2). It enables us to perceive groupings and similarities between artefacts, understand how parameters (elements) are distributed across any potential groupings, how they influence their dispersion or clustering, and which elements are critical to the observed variation.

We entered the obtained results of the elemental composition of artefacts into tables to generate datasets of elemental profiles, which we then analysed using PCA. Based on 84 measurements, we gauged whether we could distinguish between the elemental composition from the Dolenjska Hallstatt group (D) and the later Vinica group (V), and attempted to determine which dominant elements influenced the grouping.

Results

For better clarity, we made a selection and compiled two tables of analysed artefacts from the Dolenjska cultural group (*Tab. 1*) and the Vinica cultural group (*Tab. 2*) for PCA modelling. In reviewing the tables of elemental content, we detected no significant differences between the artefacts of the two different archaeological-cultural chronological groups. Both groups shared high tin contents (27–78.2 wt.%), relatively low copper levels (11.7–74.1 wt.%), and moderately high lead contents (1.1–29.1 wt.%; *Fig. 4*). In addition to the main elements, i.e. copper, tin, and lead, represented alloys also included arsenic, silver, bismuth, antimony, iron, and nickel. Higher silver content could potentially be signalling that certain artefacts were silvered. More than 1 wt.% silver content was measured in Certosa fibulae from graves 96 (PN 302: 2.6 wt.% Ag) and 3 (PN 235: 1.3 wt.% Ag), as well as in the six-knobbed fibulae with a face mask from supposed graves 19 (PN 63: 1.7 wt.% Ag), 20 (PN 66: 1.5 wt.% Ag), and 44 (PN 178: 1.2 wt.% Ag). Since prehis-



Sl. 4: Projekcija rezultatov elementne sestave bakra, kositra in svinca ter elementov v sledovih srebra, arzena, bizmuta, antimona, železa in niklja v ravnini PC1/PC2, ki pripadajo skupini analiziranih predmetov iz dolenjskega in viniškega kulturnega kroga (avtor: Marijan Nečemer).

Fig. 4: Projection of copper, tin, and lead elemental composition and trace elements of silver, arsenic, bismuth, antimony, iron and nickel in the PCA1/PCA2 plane for a group of analysed objects from the Dolenjska and Vinica cultural group (author: Marijan Nečemer).

	Predmet / Artefact		Cu	Sn	Pb	Ag	As	Bi	Sb	Fe	Ni
1	312-1 D gr. 92 (*t. 42A:* 7)	CD	74,1	30,3	7,7	0,4	0,3	0,09	0,7	2,7	0,1
		AM	52,3	30,3	8,4	0,4	7,2	0,4	0,7		
2	238 D gr. 79 (*t. 34:* 1)	CD	14,2	73,4	10,2	0,5	0,7	0,2	0,7	0,8	0,1
		AM	14,2	73,4	7,4	0,5	3,3	0,3	0,7		
3	302-1 D gr. 96 (*t. 44A:* 1)	CD	29,1	51,9	9,8	0,4	1,1	1,1	0,7	0,4	0,07
		AM	29,1	51,9	9,5	0,4	7,2	1,1	0,7		
4	302-2 D gr. 96 (*t. 44A:* 2)	CD	56,9	27,7	6,5	2,6	0,5	0,8	0,3	0,3	0,1
		AM	56,9	27,7	7,2	2,6	4,4	0,7	0,3		
5	334 D gr.102 (*t. 51:* 5)	CD	72,1	5,86	8,6	0,4	0,5	0,2	0,7	0,3	0,1
		AM	72,1	5,86	17,1	0,4	3,4	0,3	0,7		
6	290K D gr. 91 (*t. 40A:* 2)	CD	66,7	6,85	19,5	0,2	0,5	0,3	0,3	0,4	0,1
		AM	66,7	6,85	21,9	0,2	3,6	0,3	0,3		
7	251 D gr. 67 (*t. 27B:* 1)	CD	58,2	34,9	6,3	0,4	0,8	0,2	0,5	0,6	0,1
		AM	58,2	34,9	1,1	0,4	4,4	0,3	0,5		
8	235LF D gr. 3 (*t. 3A:* 1)	CD	28,7	54,6	12,6	1	1,5	3,4	0,7	1,7	0,08
		AM	28,7	54,6	7,3	1	4,5	3	0,7		
9	175LF D gr. 52 (*t. 21C:* 4)	CD	15,3	76	8,6	0,6	0,9	0,1	1	1	0,1
		AM	11,7	77,3	11,7	0,6	3,4	3,4	0,8		
10	264 D gr. 86 (*t. 37C:* 1)	CD	12,8	69,4	17,3	0,9	1	0,2	1,6	2,1	0,1
		AM	12,8	69,4	14	0,9	0,9	0,1	1,6		

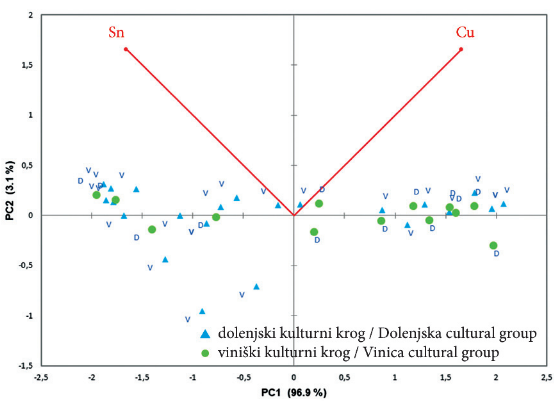
Tab. 1: Rezultati nekaterih meritev XRF v mas. % z dvema monokromatskima vzbujevalnima viroma (Am-241 in Cd-109) na predmetih iz dolenjskega kulturnega kroga (D).
Table 1: Selected XRF measurement results in wt.% using two monochromatic excitation sources (Am-241 and Cd-109) on artefacts from the Dolenjska cultural group (D).

(prim. Nørgaard 2017, 113), smo sprva pomislili, da so bili analizirani predmeti predvsem pokositreni. Vzroke za to anomalijo moramo vendarle iskati še v drugih dejavnikih. Visoke vrednosti kositra so najverjetneje posledica korozijskih produktov, ki nastajajo na površini artefakta. Korozijski mehanizmi, njihova struktura in stopnje ali faze razpadanja bronastih zlitin so odvisni od časa zakopa, predvsem pa od okolja, v katerem je predmet zakopan. To okolje določajo kislost zemlje, elementna vsebnost zemlje, količina in dostopnost padavin, klimatske spremembe, gnojenje in podobno. Korozijski mehanizmi v zgodnjih fazah pospešujejo razgradnjo oziroma dekuprifikacijo (odtapljanje) bakra iz zlitine (Robbiola et al. 1993, 153–154). Dekuprifikacija v poznejših fazah mobilizira kositer in poviša njegove vsebnosti na površini v obliki korozijskega produkta

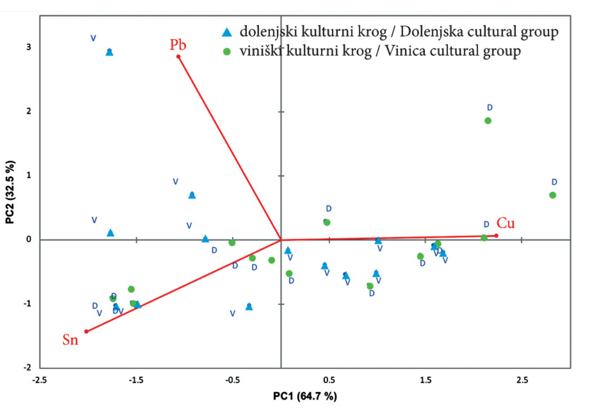
toric copper alloys more typically contain 8—12 wt.% tin (cf. Nørgaard 2017, 113), we initially thought that most analysed artefacts were tinned. However, reasons behind this anomaly must also be sought elsewhere. Elevated tin values are most probably the result of corrosion products on the artefact surface. Corrosion mechanisms, their structure, and stages of copper alloy degradation depend on the duration of interment as well as and especially on the environment in which the artefact was buried. This environment is defined by soil acidity, elemental composition, quantity and exposure to rainfall, climate change, fertilisation etc. In early stages, corrosion mechanisms accelerate the degradation, i.e. de-cuprification of copper in the alloy (Robbiola et al. 1993, 153–154). In later stages, de-cuprification mobilises tin, increasing its content on the surface in the form of the corrosion product cassiterite

	Predmet / Artefact		**Cu**	**Sn**	**Pb**	**Ag**	**As**	**Bi**	**Sb**	**Fe**	**Ni**
1	63 V gr. 19 (*t. 10A:* 1)	CD	23	52,7	19,1	1,7	2,4	0,2	2	1,3	0,1
		AM	23	52,7	11,3	1,7		0,5	2		
2	63G1 V gr. 19 (*t. 10A:* 1)	CD	23,5	36,9	7,8	1,5	2,4	0,06	1,3	7,1	0,08
		AM	23,5	36,9	29,1	1,5	7,1	0,4	1,3		
3	113 V gr. 28 (*t. 12D:* 2)	CD	12,7	78,2	8,8	0,4	0,5	0,1	0,8	1,9	0,04
		AM	12,7	78,2	3,2	0,4	4,3	0,2	0,8		
4	131sd V gr. 45 (*t. 19A:* 4)	CD	16,5	75,9	8,5	0,4	0,6	0,1	0,8	1,9	0,03
		AM	15,4	75,9	4	0,4	3,2	0,2	0,8		
5	150 V gr. 45 (*t. 19A:* 3)	CD	58,7	29,2	5,4	0,8	1,5	0,1	0,7	2,5	0,09
		AM	58,9	29,2	5,6	0,8	4,4	0,3	0,7		
6	66GL V gr. 20 (*t. 10B:* 1)	CD	19,6	51	2,8	1,5	4,9	0,6	1,9	1,5	0,1
		AM	37,1	51	2,8	1,5	4,9	0,6	1,9		
7	178GS V gr. 44 (*t. 18:* 3)	CD	25,7	57,8	13,9	1,2	1,4	0,4	1,1	1,5	0,1
		AM	25,7	57,8	8,3	1,2	4,9	0,7	1,1		

Tab. 2: Rezultati nekaterih meritev XRF v mas. % z dvema monokromatskima vzbujevalnima viroma (Am-241 in Cd-109) na predmetih iz viniškega kulturnega kroga (V).
Table 2: Selected XRF measurement results in wt% using two monochromatic excitation sources (Am-241 and Cd-109) on artefacts from the Vinica cultural group (V).



Sl. 5: Projekcija rezultatov elementne sestave bakra in kositra v ravnini PC1/PC2, ki pripadajo skupini analiziranih predmetov iz dolenjskega in viniškega kulturnega kroga. Na podlagi PCA grafa lahko ugotavljamo, da je bilo korozijsko delovanje, katerega posledica so višje vrednosti kositra na površini predmetov iz viniškega kulturnega kroga izrazitejše kot pri dolenjskem kulturnem krogu (avtor: Marijan Nečemer).
Fig. 5: Projection of copper and tin elemental composition results in the PC1/PC2 plane for a group of analysed objects from the Dolenjska and Vinica cultural groups. Based on the PCA plot, we may infer that objects from the Vinica cultural group show higher corrosive activity and resultant higher tin levels than those from the Dolenjska cultural group (author: Marijan Nečemer).



Sl. 6: Projekcija rezultatov elementne sestave bakra, kositra in svinca v ravnini PC1/PC2, ki pripadajo skupini analiziranih predmetov iz dolenjskega in viniškega kulturnega kroga. Poleg višjih vrednosti kositra na površini predmetov iz viniškega kulturnega kroga, pri njih opažamo tudi višje vrednosti svinca (avtor: Marijan Nečemer).
Fig. 6: Projection of copper, tin, and lead elemental composition results in the PCA1/PCA2 plane for a group of analysed objects from the Dolenjska and Vinica cultural groups. Aside from higher tin values on their surface, the objects from the Vinica cultural group also show elevated lead content (author: Marijan Nečemer).

kasiterit (SnO_2), s katerim skuša zadržati nadaljnje razpadanje zlitine (Nørgaard 2017, 106).

Pri modeliranju s PCA so se pri dveh glavnih elementih – bakru in kositru – pokazale razlike v razvojnih fazah korozije na analiziranih artefaktih. Kažejo, da je bilo korozijsko delovanje z višjimi vsebnostmi kositra na površini predmetov iz viniškega kulturnega kroga izrazitejše kot pri predmetih iz dolenjskega kulturnega kroga (*sl. 5*). Prav tako so pri viniškem kulturnem krogu višje vrednosti svinca (*sl. 6*).

SKLEP

Za določitev realistične elementne sestave osnovne zlitine z metodo XRF bi torej morali s površine analiziranih predmetov odstraniti velik del korozijskih produktov, kar pa ni v skladu z etičnimi načeli. S pridobitvijo nove raziskovalne opreme smo lahko izbrali drugo, delno invazivno možnost, pri kateri smo na artefaktih pobrusili površino v velikosti 1 mm^2 in nato na očiščenem delu opravili meritev s spektrometrom μXRF. Preliminarni, še ne objavljeni rezultati kažejo, da je večina analiziranih predmetov izdelana iz brona ali svinčevega brona. S preiskavami površine predmetov z metodo XRF smo dokazali, da so visoke vrednosti kositra posledica zapletenih korozijskih procesov med zakopom predmetov v zemlji.

ARHEOMETALURŠKE PREISKAVE NEGOVSKE ČELADE

Največ naravoslovnih preiskav – in tudi najraznovrstnejših – je bilo izvedenih na čeladi iz groba 100 (*t. 47–49*). Osredotočali smo se na proučevanje mehanizmov propadanja in tehnologijo izdelave. Na čeladi smo najprej izvedli preiskave z rentgensko radiografijo (RTG) in nato še neinvazivne preiskave površine čelade z rentgensko fluorescenčno spektrometrijo (XRF). Za razumevanje korozijskih mehanizmov smo z metodo SEM-EDS stratigrafsko analizirali kovinsko jedro in korozijske plasti. Vrste korozijskih produktov smo določili z metodo XRD in izvedli še metalografske preiskave.

PREISKAVE Z RENTGENSKO RADIOGRAFIJO (RTG)

Metoda

Natančne preiskave čelade z RTG smo še pred začetkom konservatorsko-restavratorskih posegov izvedli na Inštitutu za metalne konstrukcije (IMK). Rentgeniziranje smo opravili na industrijskem rentgenskem aparatu, pri katerem smo od zemlje neočiščeno čelado

(SnO_2), which acts to inhibit further degradation of the alloy (Nørgaard 2017, 106).

PCA modelling revealed differences in copper and tin behaviour related to corrosion development in the analysed artefacts, indicating that corrosive processes involving higher surface concentrations of tin were more pronounced on artefacts from the Vinica cultural group than those from the Dolenjska group (*Fig. 5*). Likewise, elevated lead values were more prominent in the Vinica cultural group (*Fig. 6*).

CONCLUSION

In order to determine an accurate elemental composition of the base alloy using XRF, a large part of corrosion products would need to be removed from the surface of the analysed artefacts, which goes against ethical principles. The acquisition of new research equipment allowed us to choose an alternative, only partially invasive option of polishing a surface area of no more than 1 mm^2 and performing a measurement with a μXRF spectrometer on it. Preliminary, presently as yet unpublished results indicate that the majority of analysed artefacts are made of bronze or leaded bronze. XRF surface analyses indicated that elevated tin values were the result of complex corrosion processes occurring during the period of the artefacts' interment.

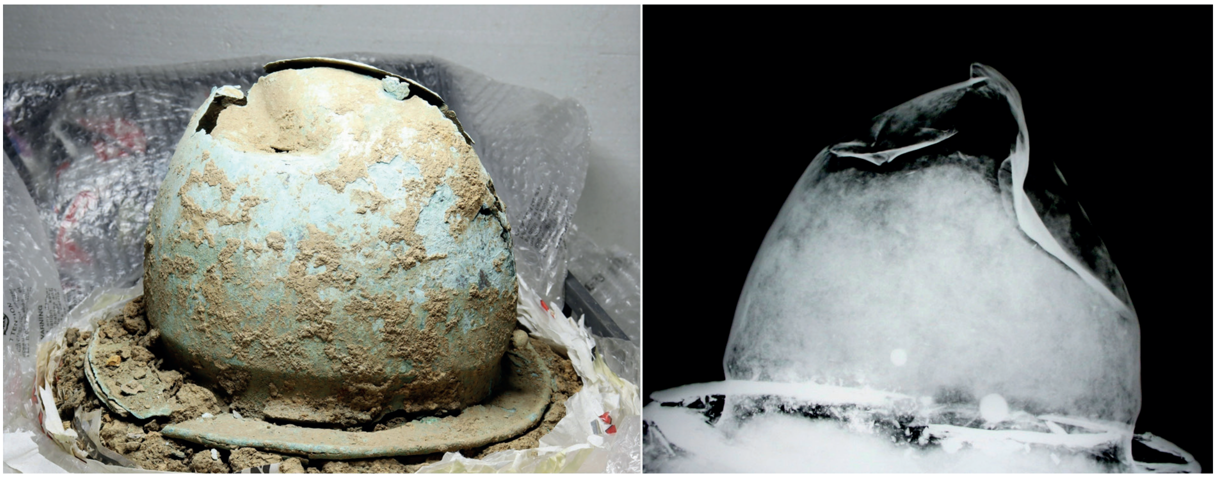
ARCHAEOMETALLURGICAL INVESTIGATIONS OF THE NEGOVA-TYPE HELMET

The most numerous and varied scientific examinations were conducted on the helmet from grave 100 (*Pls. 47–49*). They focused on the study of the mechanisms of degradation and technology of manufacture. The helmet was first examined using X-ray radiography (RTG) followed by non-invasive X-ray fluorescence spectrometry analysis (XRF) of its surface. To learn more about corrosion mechanisms, we conducted stratigraphic analyses of the metal core and corrosion layers using SEM-EDS. Types of corrosion products were identified with X-ray diffraction (XRD). Additionally, metallographic examinations were also performed.

X-RAY RADIOGRAPHIC EXAMINATIONS (RTG)

Method

Detailed RTG examinations of the helmet were conducted at the Institute for Metal Constructions (IMK) ahead of conservation-restoration interventions. Irradiation was performed using an industrial X-ray ap-



Sl. 7: Podzemelj, Pezdirčeva njiva, grob 100. Čelada pred posegi in rentgenski posnetek čelade (stranski pogled): 150 kV, 4 mA, 60 s (preiskava: Janko Vodišek, IMK, foto: Nataša Nemeček).
Fig. 7: Podzemelj, Pezdirčeva njiva, grave 100. Helmet prior to conservation-restoration and an X-ray image of the helmet (side view): 150 kV, 4 mA, 60 s (examination: Janko Vodišek, IMK, photo: Nataša Nemeček).

položili neposredno na film. Uporabili smo rentgenske žarke z napetostjo 150 kV, električnim tokom 4 mA in ekspozicijo 60 s. (*sl. 7*).

Rezultati

Iz rentgenskega posnetka je razvidno, da je čelada slabo ohranjena zlasti v zgornjem delu. Slaba ohranjenost pločevine je vidna tudi na krajcih, kjer svetlejša mesta na posnetku nakazujejo še prisotnost svinca na robu. Svetleje sta prikazana tudi gumba, ki sta bila ulita iz masivne bakrove zlitine.

PREISKAVE Z RENTGENSKO FLUORESCENČNO SPEKTROMETRIJO (XRF)

Metoda

Pred konservatorsko-restavratorskimi posegi smo z rentgensko fluorescenčno spektrometrijo (XRF) analizirali dva vzorca – s krajca čelade in grebena kalote. Za ugotavljanje elementne sestave obeh vzorcev smo uporabili monokromatski vzbujevalni vir Cd-109 z vzbujevalno energijo 22,1 keV, ki je primeren za vzbujanje bakra, arzena, svinca, bizmuta, niklja in železa.

Rezultati

Pri analizah površine obeh vzorcev z metodo XRF smo ugotovili visoko vsebnost kositra (krajec: 38,4 mas. % Sn in 61,1 mas. % Cu; greben kalote: 35,1 mas.

paratus; without the soil still attached, the helmet was placed directly onto the film. X-rays were set at 150 kV, 4 mA for a 60-second exposure. (*Fig. 7*)

Results

The radiograph reveals that the helmet, particularly its upper part, was not well preserved. The poor condition of the sheet metal is also evident at the edges, where brighter spots on the radiograph indicate the presence of lead. The buttons, which were cast from a solid copper alloy, are also rendered lighter.

X-RAY FLUORESCENCE SPECTROMETRY (XRF)

Method

Before going in for conservation-restoration interventions, two samples were analysed using X-Ray Fluorescence Spectrometry (XRF): one from the rim of the helmet and the other from the crest of the calotte. We determined the elemental composition of both samples by employing monochromatic excitation source Cd-109 with the excitation energy of 22.1 keV, suitable for the excitation of copper, arsenic, lead, bismuth, nickel, and iron.

Results

XRF analyses of the surfaces of both samples revealed elevated tin content caused by selective leaching of copper from the base (measuring at the rim: 38.4 wt.% Sn

% Sn in 63,4 mas. % Cu), ki je posledica selektivnega odtapljanja bakra iz osnovne kovine. Meritve smo opravili tudi na brušenem delu vzorcev (krajec: 15,3 mas. % Sn in 84,4 mas. % Cu; greben kalote: 17,8 mas. % Sn in 81,5 mas. % Cu). Vsebnost kositra se je sicer znižala, vendar je bila še vedno visoka.

PREISKAVE Z ELEKTRONSKO VRSTIČNO MIKROSKOPIJO IN ENERGIJSKO DISPERZIJSKIM SPEKTROMETROM (SEM-EDS)

Metoda

Analize vzorcev, zalitih v dvokomponentno epoksidno smolo, so bile izvedene z vrstičnim elektronskim mikroskopom (SEM) JEOL JSM-IT100, opremljenim z energijsko disperzijskim spektrometrom (EDS) za elementno analizo. Pri tem smo uporabili napetost 15 kV in delovno razdaljo 10 mm.

Rezultati

Rezultate, pridobljene z elektronsko vrstično mikroskopijo in energijsko disperzijskim spektrometrom (SEM-EDS), smo primerjali z že izvedenimi analizami SEM-EDS prazgodovinskih čelad, ki so jih našli na ozemlju današnje Slovenije, Češke, Hrvaške, Madžarske, Italije in Nemčije, kjer je vsebnost kositra v zlitini od 6,3 mas. % do največ 12 mas. % (cf. Mödlinger et al. 2013, 29; Mödlinger 2014, 166). Vsebnost kositra v zlitini je bila okoli 8 mas. %.

Neinvazivne raziskave z metodo XRF na korozijskih plasteh praviloma ne zagotavljajo pravih informacij o sestavi analiziranih arheoloških predmetov iz bakrovih zlitin, ker korozijski mehanizmi pospešujejo odtapljanje oziroma dekuprifikacijo bakra iz zlitine in hkrati vplivajo na povišano vrednost kositra na površini predmetov. Tudi z brušenega dela površine čelade informacije o njeni sestavi niso bile dovolj natančne, saj je bila vsebnost kositra še vedno previsoka za prazgodovinske zlitine. Najzanesljivejši so bili rezultati analiz z metodo SEM-EDS.

PREISKAVE STRATIGRAFIJE KOROZIJSKIH PLASTI Z METODO SEM-EDS

Korodiranje arheoloških predmetov iz brona (zlitina bakra in kositra) poteka po zapletenih mehanizmih, odvisnih od sestave kovine in okolja, v katerem je predmet. Ob tem nastajajo različni korozijski produkti bakra in kositra, kot so kuprit (Cu_2O), malahit ($Cu_2CO_3(OH)_2$) in kasiterit (Sn_2O). Identifikacija in stratigrafska razporeditev korozijskih produktov je pomembna zato, da lažje ugotavljamo stanje predmeta (Oudbashi, Russell 2024, 303).

and 61.1 wt.% Cu; on the crest of the calotte: 35.1 wt.% Sn and 63.4 wt.% Cu). We also performed measurements on the polished areas of the samples (rim: 15.3 wt.% Sn and 84.4 wt.% Cu; crest of the calotte: 17.8 wt.% Sn and 81.5 wt.% Cu). Tin content, though reduced, was still high.

EXAMINATIONS WITH SCANNING ELECTRON MICROSCOPY AND ENERGY-DISPERSIVE SPECTROMETRY (SEM-EDS)

Method

Samples were embedded in two-component epoxy resin and examined using a JEOL JSM-IT100 scanning electron microscope, equipped with an energy-dispersive spectrometer (EDS) for elemental analysis. Measurements were carried out at 15 kV with a working distance of 10 mm.

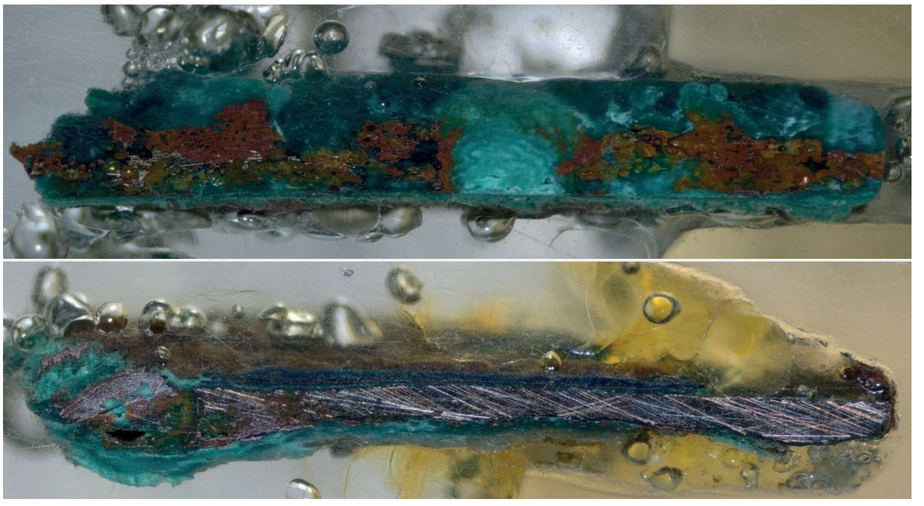
Results

We compared the Electron Microscopy and Energy-Dispersive Spectrometry (SEM-EDS) results with previously attained SEM-EDS analyses of other prehistoric helmets found in the space of present-day Slovenia, Czech, Croatia, Hungary, Italy, and Germany, where tin content typically ranges between 6.3 wt.% and 12 wt.% (cf. Mödlinger et al. 2013, 29; Mödlinger 2014, 166). The alloy tin content was approximately 8 wt.%.

Non-invasive XRF analyses of corrosion layers do not usually yield accurate information about the composition of coper alloy archaeological artefacts because corrosion mechanisms accelerate copper leaching, i.e. de-cuprification of the alloy while simultaneously effecting elevated tin values on artefact surfaces. Data on the composition of the helmet sourced at its polished area were also insufficiently precise, being that tin content still measured too high for prehistoric alloys. Here, SEM-EDS analysis results proved the most reliable.

STRATIGRAPHY OF CORROSION LAYERS EXAMINATIONS USING THE SEM-EDS METHOD

The mechanisms governing the corrosion of bronze (copper-tin alloy) archaeological artefacts are complex and contingent on metal composition as well as the environment in which the artefacts are located. They result in various copper and tin corrosion products, such as cuprite (Cu_2O), malachite ($Cu_2CO_3(OH)_2$), cassiterite (SnO_2), and others. Identifying and stratigraphically distributing corrosion products is important as it facilitates assessing the artefacts' condition (Oudbashi, Russell 2024, 303).



Sl. 8: Podzemelj, Pezdirčeva njiva, grob 100. Vzorca s krajca čelade (zgoraj) in grebena kalote čelade (spodaj) v dvokomponentni smoli (foto: Andrea Martín Pérez, Paleontološki inštitut Ivana Rakovca, ZRC SAZU).
Fig. 8: Podzemelj, Pezdirčeva njiva, grave 100. Samples from the rim (above) and crest (below) of the calotte in two-component resin (photo: Andrea Martín Pérez, Ivan Rakovec Institute of Palaeontology, ZRC SAZU).

Metoda

Korozijske produkte bronaste pločevine smo proučevali na dveh vzorcih, vzetih s krajca čelade in grebena kalote (*sl. 8*). Vzorca sta bila zalita v dvokomponentno epoksidno smolo, ki se je pri sobni temperaturi strdila po 48 urah. Zalita vzorca sta bila nato zlepljena z ogljikovim trakom in vpeta v nosilec. Analizirana sta bila pod nizkim vakuumom v načinu povratno sipanih elektronov (BES). Analize so bile izvedene z vrstičnim elektronskim mikroskopom (SEM) JEOL JSM-IT100, opremljenim z energijsko disperzijskim spektrometrom (EDS) za elementno analizo. Pri tem smo uporabili napetost 15 kV in delovno razdaljo 10 mm.

Rezultati

Stratigrafska razporeditev korozijskih produktov vzorca s krajca čelade je bila zelo nedefinirana, medtem ko so bile korozijske plasti vzorca z grebena kalote lepo vidne. Kovinsko jedro vsebuje višji odstotek bakra (68,4 mas. %) in manjši odstotek kositra (8,46 mas. %), sledi plast kuprita, prisotni so tudi kloridi, nad njo je plast z izrazito interkristalno korozijo, obogatena s kositrom in kositrovimi oksidi, ki označujejo mejo originalne površine (*sl. 9b*). Vzorec s krajca čelade ima manj definirane plasti in slabše ohranjeno kovinsko jedro iz zlitine Cu-Sn-Pb. V korozijskih plasteh so bakrovi in kositrovi oksidi ter aluminij (Al) in silicij (Si) iz glinene zemlje (*sl. 9a*).[6]

[6] Analize je izvedla dr. Andrea Martín Pérez s Paleontološkega inštituta Ivana Rakovca na ZRC SAZU, za kar se ji najlepše zahvaljujemo.

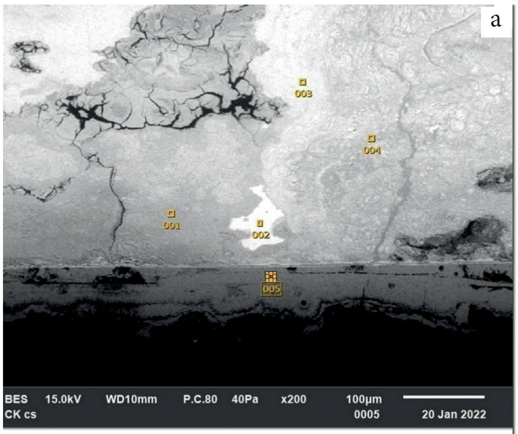
Method

Corrosion products of bronze sheet metal were studied in two samples taken from the helmet's rim and the crest of the calotte (*Fig. 8*). The samples were embedded in two-component epoxy resin, which cured at room temperature in 48 hours. The embedded samples were then affixed with carbon tape, mounted onto a support, and analysed under low vacuum in backscattered electron (BES) mode. Elemental analysis was performed using a JEOL JSM-IT100 scanning electron microscope equipped with an energy-dispersive spectrometer (EDS), operating at 15 kV and a 10 mm working distance.

Results

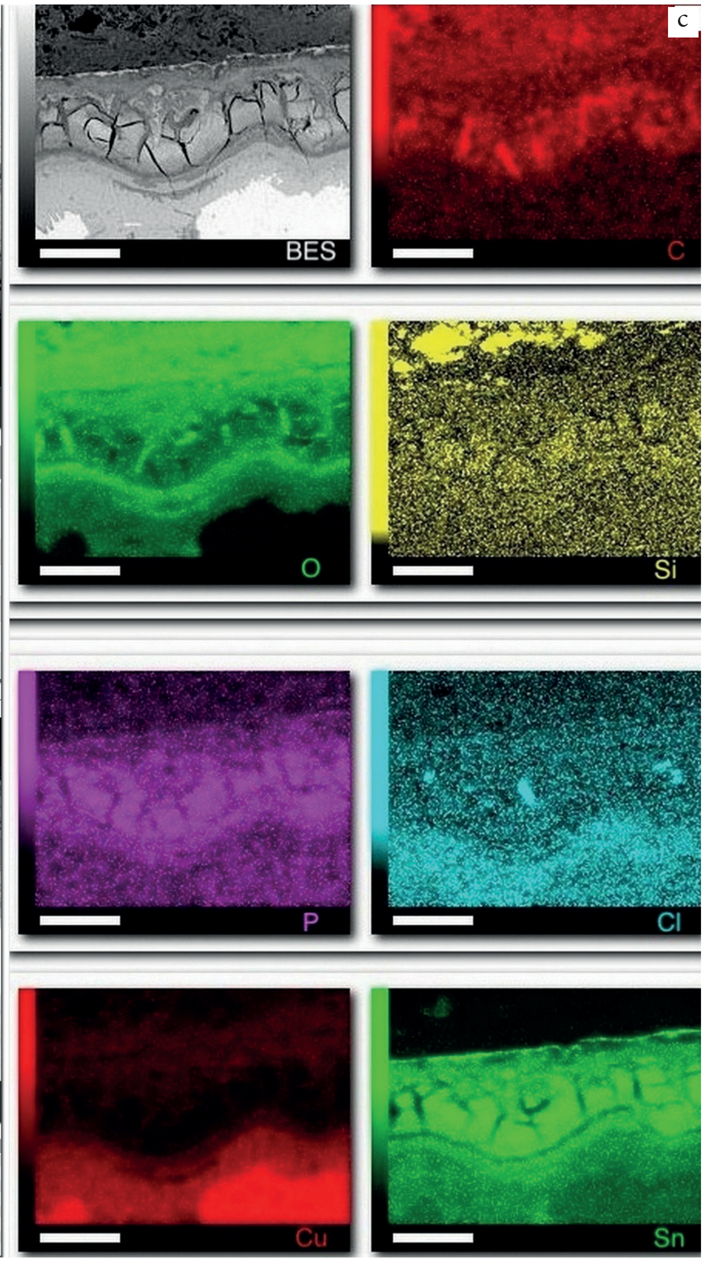
The stratigraphic distribution of corrosion products in the helmet rim sample was poorly defined while corrosion layers of the sample from the crest of the calotte were clearly visible. The metal core contains a higher percentage of copper (68.4 wt.%) and a smaller percentage of tin (8.46 wt.%), followed by a cuprite layer, which also contained chlorides. Above it lies a tin-rich corrosion layer marking the original surface (*Fig. 9b*). The rim sample showed less distinct layers and a poorly preserved Cu-Sn-Pb core, with copper and tin oxides along with aluminium (Al) and silicon (Si) from clay soil (*Fig. 9a*).[6]

[6] Analyses were conducted by Dr Andrea Martín Pérez from the Ivan Rakovec Institute of Palaeontology at ZRC SAZU, for which we extend our sincerest gratitude.



	P	O	Pb	C	Si	Cl	Cu	Sn
001	0.28	21.91	2.55	23.90	0.59	0.36	30.59	19.83
002		12.43		24.96	0.34	0.32	51.84	10.11
003	0.16	18.29	2.44	21.54	0.49	0.29	40.56	16.23
004		24.50	2.35	21.22	0.51	0.25	33.83	17.34
005		30.77		28.72	0.50	0.39	33.51	6.12
Average	0.22	21.58	2.45	24.07	0.49	0.32	38.07	13.92
Deviation	0.08	6.85	0.10	3.04	0.09	0.06	8.52	5.64

	P	Fe	K	O	C	Mg	Al	Si	S	Cl	Ca	Ti	Cu	Sn
1	0.15	2.53	1.09	33.51	37.26	0.48	5.14	6.76	0.09	0.52	0.26	1.39	9.30	1.48
2				35.34	27.18		0.27	1.16		0.30			33.75	1.99
3				38.64	28.95		0.17	19.76		0.23			10.62	1.63
4				34.33	26.27		0.26	0.57		0.32			35.63	2.62
5	1.11			15.92	18.49		0.20	0.84		0.35			30.17	32.92
6				5.39	18.69			0.46		0.16			66.84	8.46
verage	0.63	2.53	1.09	27.19	26.14	0.48	1.21	4.92	0.09	0.31	0.26	1.39	31.05	8.18
eviation	0.68	0.00	0.00	13.35	7.02	0.00	2.20	7.66	0.00	0.12	0.00	0.00	20.98	12.40



Sl. 9: SEM posnetek vzorcev s krajca (a) in grebena kalote (b) z rezultati meritev na posameznih mestih v mas. % in kartiranje elementov vzorca z grebena kalote (c): vzorec, ogljik (C), kisik (O), silicij (Si), fosfor (P), klor (Cl), baker, kositer (foto: Andrea Martín Pérez, Paleontološki inštitut Ivana Rakovca, ZRC SAZU).
Fig. 9: SEM image of samples from the rim (a) and crest (b) of the calotte with measurement points in wt.%, and elemental mapping of the crest sample (c): sample, carbon (C), oxygen (O), silicon (Si), phosphorus (P), chlorine (Cl), copper, tin (photo: Andrea Martín Pérez, Ivan Rakovec Institute of Palaeontology, ZRC SAZU).

Pri vzorcu z grebena kalote smo prepoznali korozijo tipa I po Robbioli in Blenginu (Robbiola et al. 1998, 2083–2111), ki jo imenujemo tudi plemenita patina, zanjo pa je značilna enakomerna in svetleča površina. V prerezu ima dvojno strukturo – zunanjo z bakrovimi korozijskimi produkti in površino, "obogateno" s kositrovimi korozijskimi produkti, ki se jim pridružujejo elementi iz okolja (npr. karbonati, sulfati in silikati), ter notranjo strukturo zlitine Cu-Sn (*sl. 9b*). Za korozijo

On the calotte crest sample, we identified Type I corrosion, as defined by Robbiola and Blengino (Robbiola et al. 1998, 2083–2111), also known as noble patina, which is characterised by a uniform shiny surface. Its cross-section shows a two-layered structure: an outer layer of copper corrosion products, with its surface enriched by tin corrosion products and environmental elements (e.g., carbonates, sulphates, silicates), and a second inner Cu-Sn structure (*Fig. 9b*). Conversely, tipa II je značilna neenakomerna površina z debelejšimi korozijskimi plastmi. V prerezu ima trojno strukturo (*sl. 9a*): zunanjo z bakrovimi produkti, vmesno z bakrovimi oksidi in notranjo s (preoblikovanimi) kovinskimi strukturami (Robbiola et al. 1998, 2083–2111). Strukturo korozije tipa II ima vzorec s krajca čelade (Nemeček et al. 2022, 353).

ANALIZE KOROZIJSKIH PRODUKTOV Z RENTGENSKO DIFRAKCIJO (XRD)

Metoda

Za rentgensko difrakcijo (XRD) smo uporabili rentgenski difraktometer PANalytical 3040 na Inštitutu za kovinske materiale in tehnologije. Difraktograme smo posneli na treh različnih vzorcih: na vzorcu prahu, ki smo ga postrgali s čelade, ter na ravnem koščku odlomljene čelade z notranje in zunanje strani. Difraktograme smo posneli v območju kotov 2Θ med 15° in 95°, s korakom 0,002° in časom na korak 120 s. Med snemanjem smo vzorce vrteli s hitrostjo 4 obrate na minuto. Uporabili smo anodo Cu (valovna dolžina sevanja Kα1 λ = 0,15406 nm) pri napetosti 45 kV in toku 40 A. Difraktograme smo obdelali v programu *HighScorePlus*, za njihovo primerjavo pa smo uporabili bazo podatkov COD2013 (*Crystallography Open Database*). Z Rietveldovo metodo (Rietveld 1969, 65–71) smo simulirali rentgenske difraktograme in za praškast vzorec določili deleže posameznih kristalnih faz v vzorcih.

Rezultati

Prah korozijskih produktov je zelenkaste barve (*sl. 10a*), vsebuje baker, kositer in kisik, lahko tudi žveplo (S), svinec, klor in drugo. Na podlagi difraktogramov in podatkovnih kartic za posamezne faze iz podatkovne baze COD2013 prah lahko najbolje primerjamo s stopnjo korozije mushistonite, $CuSn(OH)_6$. To spojino so pri koroziji arheoloških najdb bronastih predmetov največkrat opazili, kadar je bil predmet najden v morski vodi ali jezerih (Armetta et al. 2021, 1–11). Poznejše analize EDS so pokazale, da je pri oksidirani plasti razmerje atomskih deležev Cu : Sn 1 : 1, kar dodatno potrjuje prisotnost te stopnje. Analiza difraktograma z Rietveldovo metodo je pokazala dobro ujemanje tudi z manjšo vsebnostjo faz korozijskih produktov na osnovi klora (nantokit in atakamit), žvepla (kovelit) in kositrovega oksida (kasiterit). Malahita, ki je najpogostejši korozijski produkt bakra, v tem primeru ne zaznamo v bistvenih količinah. Ob tem je pomembno poudariti, da je meja detekcije za posamezno stopnjo okrog 3–5 vol.%.

Za analizo korozijskih produktov na zunanji in notranji strani čelade smo raven košček postavili na

Type II corrosion is characterised by an uneven surface and thicker corrosion layers. Its cross-section shows a three-part structure (*Fig. 9a*): an outer layer of copper products, a middle layer of copper oxides, and an inner core of (altered) metal structures (Robbiola et al. 1998, 2083–2111). Type II corrosion is present on the sample from the helmet rim (Nemeček et al. 2022, 353).

ANALYSES OF CORROSION PRODUCTS USING X-RAY DIFFRACTION (XRD)

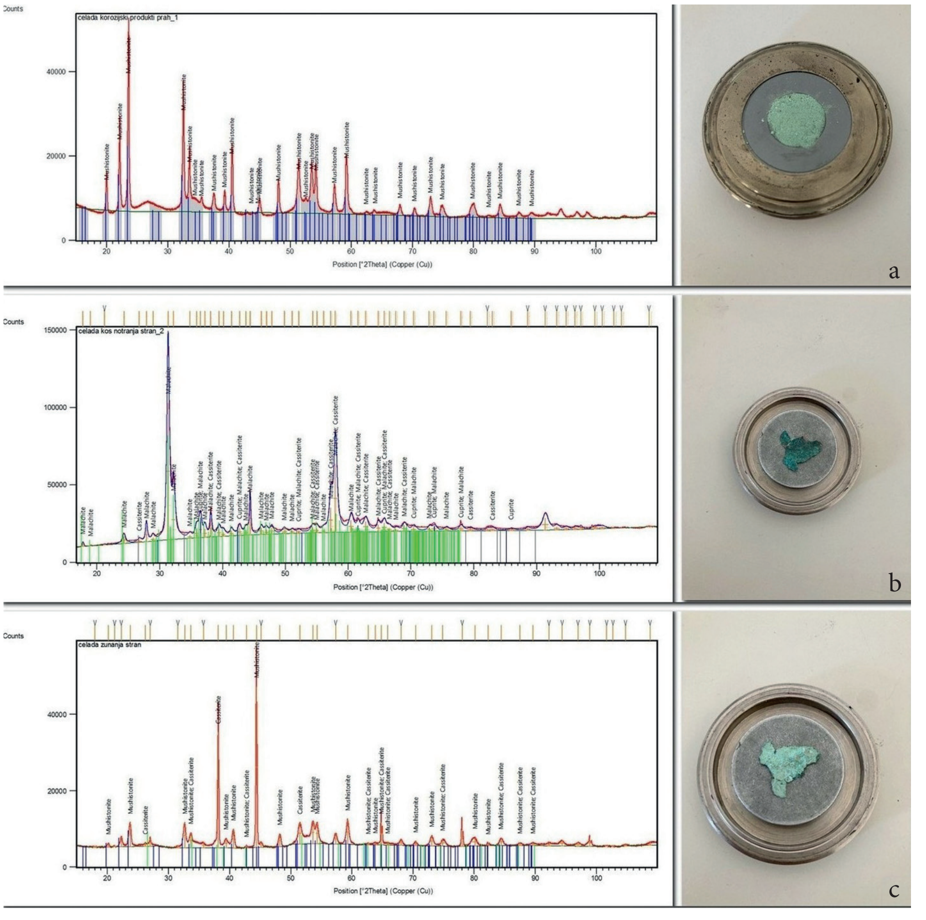
Method

X-ray diffraction (XRD) was conducted at the Institute for Metal Materials and Technologies using a PANalytical 3040 diffractometer. Diffractograms were recorded on three different samples: a sample of powder scraped from the helmet, and two sides of the flat broken off helmet fragment. The diffractograms were recorded in the 2Θ range between 15° and 95°, with a step size of 0.002° and a dwell time of 120 seconds per step. During scanning, the samples were rotated at 4 revolutions per minute. A copper anode (Kα1 radiation wavelength λ = 0.15406 nm) was used at a voltage of 45 kV and a current of 40 A. The diffractograms were processed using *HighScorePlus* software, and phase comparison was performed using the COD2013 (*Crystallography Open Database*). The Rietveld method (Rietveld 1969, 65–71) was applied to simulate X-ray diffractograms and quantify the proportions of individual crystalline phases in the powder sample.

Results

The powder of corrosion products is greenish in colour (*Fig. 10a*) and contains copper, tin, oxygen, as well as possibly sulphur (S), lead, chlorine, etc. Based on the diffractograms and phase reference cards from the COD2013 database, it is most closely comparable to the mushistonite corrosion phase, $CuSn(OH)_6$. This compound is most frequently observed in corroded bronze artefacts found in sea water or lake environments (Armetta et al. 2021, 1–11). Subsequent EDS analyses demonstrated that the atomic ratio of Cu:Sn in the oxidised layer is 1:1, further confirming the presence of this phase. Rietveld analysis of the diffractogram also showed a good match with minor phase content of chloride-based corrosion products (nantokite and atacamite), sulphur-based compounds (covellite), and tin oxide (cassiterite). Malachite, which is typically the most common copper corrosion product, was not detected in noteworthy amounts. Here, it is important to note that the detection limit for each phase is approximately 3 vol.%–5 vol.%.

For the analysis of corrosion products on the interior and exterior surfaces of the helmet, the flat fragment



Sl. 10: XRD analiza vzorca prahu čelade ter notranjega in zunanjega vzorca čelade (avtor: Barbara Šetina Batič).
Fig. 10: XRD analyses of a powder sample from the helmet and of the inner and outer helmet sample (author: Barbara Šetina Batič).

nosilec. Difraktograma se bistveno razlikujeta, zato lahko sklepamo na različno sestavo korozijskih produktov na notranji in zunanji strani čelade. Prav tako opazimo, da je zunanja stran čelade svetlejša, medtem ko je notranja stran čelade temno zelenega videza. Na podlagi poznavanja kemijske sestave čelade, katere pločevina vsebuje baker, kositer in manjši delež svinca, zaradi korozije pa so na obeh straneh koščka čelade prisotne še spojine z elementi oksida, žvepla in klora. Ker vzorca nista bila v praškastem stanju, z Rietveldovo metodo nismo določili vsebnosti posameznih korozijskih stopenj, temveč smo le identificirali najpomembnejše vrhove v difraktogramu (*sl. 10b, c*). Na notranji strani čelade opazimo vrhove, ki potrjujejo prisotnost malahita, ne zaznamo pa stopnje mushistonite; kar nakazuje različne mehanizme korozije na zunanji in notranji strani čelade.

Z metodo XRD smo pridobili podatke o raznovrstnih korozijskih produktih, ki so bili prepoznani na čeladi in so posledica različnih pogojev v obdobju, ko je bila čelada zakopana v zemlji. Ugotovili smo, da je v svetlo zelenem prahu, ki smo ga postrgali s čelade, hidroksid bakra in kositra, $CuSn(OH)_2$. Prav tako smo prepoznali

was placed on a sample holder. The two diffractograms differ significantly, allowing us to posit that corrosion product compositions on the inside of the helmet were different than those on the outside. We also noticed that the outside helmet fragment was lighter in colour while the inside was dark green. We were able to identify compounds present on both sides of the helmet based on the known chemical composition sheet metal, which contains copper, tin and a small proportion of lead. As a result of corrosion, compounds containing oxygen, sulfur, and chlorine were also detected. Since the samples were not in powder form, Rietveld refinement was not used to determine the proportions of individual phases. Only the most prominent peaks in the spectra were identified (*Fig. 10b, c*). On the helmet interior peaks corresponding with malachite presence were identified while no mushistonite was evidenced; this indicates that the external side of the helmet was impacted by different corrosion mechanisms than its internal side.

Using the XRD method, we obtained information on a variety of corrosion products on the helmet as results of different conditions during the time of its interment. We determined the presence of copper-tin hykorozijske produkte s klorom in žveplom, ki izhajata iz zemlje, v kateri je bil predmet zakopan. Analiza notranje in zunanje strani čelade pa nam je pokazala, da so korozijski produkti na eni in drugi strani različni. Na zunanji strani čelade smo tako našli več korozijskih produktov, povezanih s klorom (atakamit, paratakamit) in žveplom (kovelit), medtem ko je na notranji strani čelade dokaj stabilen malahit.

METALOGRAFSKE PREISKAVE

Metoda

Za določitev kemijske sestave in mikrostrukture čelade smo odvzeli vzorca z grebena in krajca čelade. Vzorca sta bila na površini korodirana in prekrita s plastjo prsti, ki je je bilo manj na notranji strani čelade (*sl. 11*). Proučevali smo tudi drobec svinčeve spajke v notranjem obodu krajca (*sl. 12*).

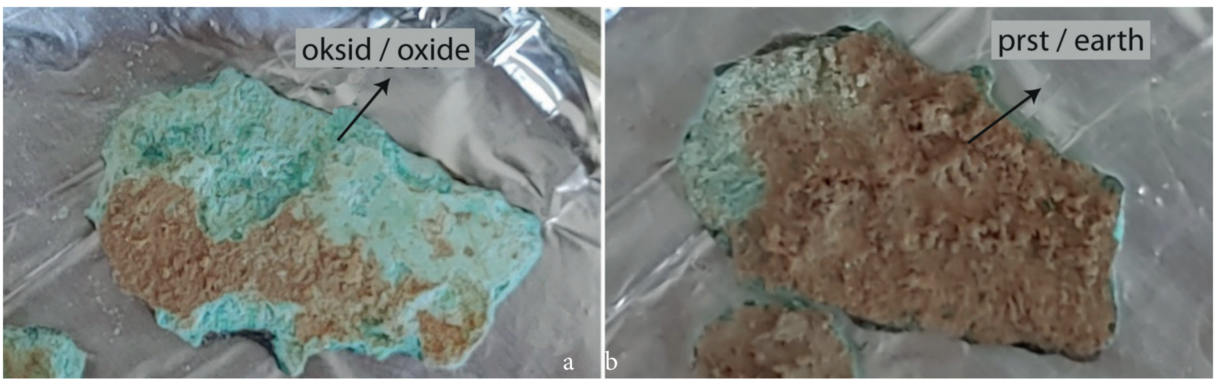
Za metalografsko analizo z vrstičnim elektronskim mikroskopom z energijsko disperzijskim spektometrom

droxide, $CuSn(OH)_2$ in the light green powder scrapped from the helmet. Furthermore, we also identified corrosion products containing chlorine and sulphur. These are likely linked to the soil in which the artefact was buried. Analysis revealed different corrosion products on the interior and exterior sides of the helmet. The exterior exhibited a higher concentration of chlorine- (atacamite, paratacamite) and sulphur-based (covellite) corrosion compounds of copper, while the interior surface was predominantly covered with relatively stable malachite.

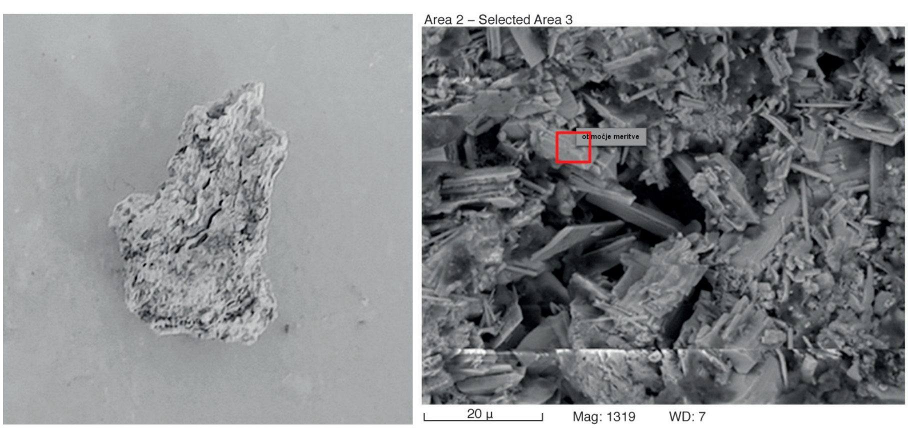
METALLOGRAPHIC EXAMINATIONS

Method

In order to determine the helmet's chemical composition and microstructure, samples were taken from its crest and rim. The surface of the samples was corroded and covered with a layer of soil, which was thinner on the interior side (*Fig. 11*). A fragment of lead

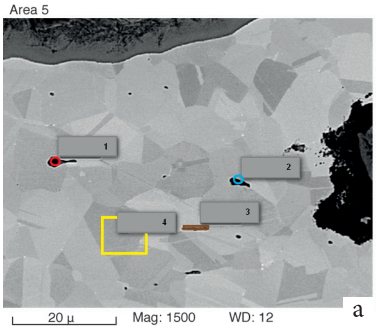


Sl. 11: Vzorec z grebena čelade: a – notranja stran, b – zunanja stran (foto: Barbara Šetina Batič).
Fig. 11: Sample from the helmet's crest: a – interior, b – exterior (photo: Barbara Šetina Batič).



Element	
C	9,1
O	19,1
Al	5,2
Si	1,0
Pb	65,6

Sl. 12: Svinčeva spajka z zunanjega roba krajca in SEM-EDS kemijska sestave spajke v mas. % z označenimi mesti (foto: Barbara Šetina Batič).
Fig. 12: Lead solder from the external edge of the rim and SEM-EDS chemical composition analysis of the solder in wt.%, with marked measurement points (photo: Barbara Šetina Batič).



Območje / Area	1	2	3	4
O	17,8	12,3	2	1,5
Al	0,4	0,2	0	0
P	0,1	0,7	0,1	0
S	2,3	0,3	2,5	0
Mn	3	4,3	0	0,1
Fe	23,7	10,2	0,6	0,2
Cu	46,8	65,8	85,9	88,5
Sn	3,6	5,5	8	9,6
Pb	2,3	0,7	0,9	0,1

b

	Krajec A Rim A	Krajec A Rim A	Krajec A Rim A	Krajec B Rim B	Greben Crest	Povprečna sestava Average comp.
Cu	90,8	91,0	90,0	91,0	90,9	90,7
Sn	9,0	8,8	9,0	8,7	9,1	8,9
Pb	0,2	0,3	0,7	0,2	0,0	0,3
Mn	0,0	0,0	0,2	0,1	0,0	0,1

c

Sl. 13: Metalografski vzorec (a), SEM-EDS kemijska analiza sestave čelade in vključkov z označenimi merilnimi mesti (1-4) v mas. % (b) in povprečje meritev kemijske sestave čelade v mas. % z EDS analizo (c) (foto: Barbara Šetina Batič).
Fig. 13: Metallographic sample (a), SEM-EDS chemical analysis of the composition of the helmet and inclusions with marked measuring points (1-4) in wt. % (b), and the average of the chemical composition measurements of the helmet in wt. % by EDS analysis (c) (photo: Barbara Šetina Batič).

(SEM-EDS) smo vzorce prerezali po debelini, jih postavili v kalup in zalili s hladno maso. Tako pripravljeni metalografski vzorec smo nato zbrusili in spolirali. Preiskovali smo prečni presek vzorcev. Z metodo uklona povratno sipanih elektronov EBSD smo analizirali še mikrostrukturo brona, velikost in obliko zrn ter dvojčične meje.

Rezultati

Glede na kemijsko sestavo je čelada narejena iz bronaste pločevine (*sl. 13*) s povprečno sestavo 90,7 mas. % bakra, 8,9 mas. % kositra, vsebuje pa tudi nizke vsebnosti svinca (0,3 mas. %) in mangana (0,1 mas. %). Baker in kositer tvorita trdno raztopino, medtem ko svinec najdemo v sulfidnih, mangan pa v oksidnih nekovinskih vključkih. Nizke vsebnosti železa, žvepla in svinca so pogoste v prazgodovinskih bronih ter so neposredno povezane s procesi taljenja bakrove rude (Pernicka 1999, 165–166).

Kemijsko analizo smo opravili tudi na svinčevi spajki, katere površina je bila močno oksidirana. Oksidna plast je večinsko sestavljena iz svinca (65,6 mas. %) in kisika (19,1 mas. %), torej svinčevega oksida. Predvidevamo, da vsebnosti aluminija, silicija in ogljika verjetno izhajajo iz prsti (*sl. 12*).

Pri analizi mikrostrukture pločevine smo ugotovili, da je ta sestavljena iz drobnih α kristalnih zrn z različno kristalografsko orientacijo. Največji del slikane površine zasedajo zrna premera 30 µm, in sicer 14 %. Na splošno je največji delež premera od 20 µm do 40 µm, obsega 60 %. Delež večjih zrn premera 55 µm je 7 %, delež zrn s premerom, manjšim od 20 µm, pa približno 20 % (*sl. 14*). V zrnih je mnogo deformacijskih dvojčkov, ki jih zlahka opazimo že pri SEM posnetkih mikrostrukture, vendar

solder from the inner circumference of the rim was also examined (*Fig. 12*).

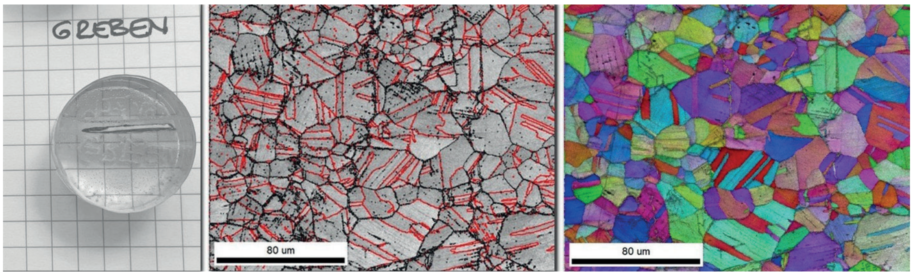
For metallographic scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), samples were sectioned through their thickness, placed in moulds, and embedded in cold-curing resin. The thus prepared metallographic samples were then ground and polished. Cross sections were examined. Next, electron backscatter diffraction (EBSD) was used to analyse the bronze's microstructure, grain size and shape, and the presence of twin boundaries.

Results

The helmet is made of typical bronze sheet metal (*Fig. 13*) with an average chemical composition of 90.7 wt.% copper, 8.9 wt.% tin, and trace amounts of lead (0.3 wt.%) and manganese (0.1 wt.%). Copper and tin form a solid solution, whereas lead is found in sulphidic inclusions and manganese in oxidic non-metallic inclusions. Low concentrations of iron, sulphur, and lead are common in prehistoric bronze and directly linked to copper ore smelting processes (Pernicka 1999, 165–166).

We also chemically analysed the lead solder, whose surface was heavily oxidised. The oxide layer consisted predominately of lead (65.6 wt.%) and oxygen (19.1 wt.%), i.e. lead oxide. We postulate that aluminium, silicon, and carbon content probably originated in the surrounding soil (*Fig. 12*).

Analysis of the sheet metal's microstructure revealed that it consisted of small α-phase grains with various crystallographic orientations. The largest share of the imaged surface area comprised grains 30 µm in diameter (14%). In general, grains between 20–40 µm comprised the majority of the area (60%), grains larger



Sl. 14: Analize dvojčičnih mej ter velikosti in oblike zrn z metodo EBSD na vzorcu grebena (foto: Barbara Šetina Batič.)
Fig. 14: Twin boundary analysis and analyses of the grain shape and size using the EBSD method on a sample from the crest (photo: Barbara Šetina Batič).

Sl. 15: Kovanje bakrene pločevine v vbočeno obliko na vdolbeni matrici–levo in dviganje stožčastega polizdelka na okroglem trnu–desno (foto: Nataša Nemeček).
Fig. 15: Hammering a copper sheet into a concave shape on a concave anvil (left) and raising a conical preform on a round mandrel (photo: Nataša Nemeček).

nam metoda EBSD omogoča bistveno lažjo analitiko dvojčičnih mej kristalnih zrn (*sl. 14*: rdeče črte). Te so dokaz o intenzivni hladni deformaciji, v tem primeru kovanja (Mödlinger 2014, 167).

Sklep

Na podlagi metalografskih analiz, kemijske sestave s SEM-EDS in metodo uklona povratno sipanih elektronov EBSD smo torej ugotovili, da je bila čelada izdelana iz surovca brona. Ocenjujemo, da je bil to v peščeno mešanico ulit disk debeline okoli 4 mm in premera okoli 220 mm. Za oblikovanje čelade iz surovca so uporabili postopek hladnega kovanja. Ko se je bron med kovanjem utrdil do stopnje, da je bilo kovanje težko nadaljevati, so ga za približno 15 minut dali v ognjišče na temperaturo 550–650° C ter ga nato ohladili v vodi. S tem postopkom so bron zmehčali in omogočili nadaljnje kovanje. Postopek je bilo treba nekajkrat ponoviti. Iz mikrostrukture grebena čelade je razvidno, da je bila ta po kovanju znova žarjena. Za izdelavo čelade s Pezdirčeve njive je kovač uliti disk skoval v okroglo ploščo, pri čemer se je

than 55 µm made up 7%, and grains smaller than 20 µm around 20% (*Fig. 14*). Numerous deformation twins were visible in the grains and could even be identified in SEM micrographs; however, EBSD enabled significantly easier identification of twin boundaries (red lines in *Fig. 14*). These are indicative of intense cold deformation – in this case, forging (Mödlinger 2014, 167).

Conclusion

Based on metallographic analyses, chemical composition determined through SEM-EDS, and the Electron Backscatter Diffraction EBSD method, we determined that the helmet was manufactured from a bronze blank. We estimate that a 4 mm-thick disc measuring circa 220 mm in diameter had first been cast in a sand mould. It was cold forged into a helmet. Once the bronze hardened to a point at which further forging was difficult, it was placed in a hearth for approximately 15 minutes to anneal at 550–650° C before being cooled in water. This procedure, which softened the bronze and facilitated further forging, needed to be debelina postopno zmanjševala od 1,5 mm na sredini do 0,5 mm na robu. Kaloto je oblikoval z uporabo bodisi vdolbenega nakovala bodisi okroglega trna (*sl. 15*; Mödlinger 2014, 172–173).

SKLEPNE UGOTOVITVE

Naravoslovne preiskave kovinskih arheoloških najdb še pred začetkom konservatorsko-restavratorskih posegov nam omogočajo proučitev stopnje ohranjenosti posameznih predmetov in snovanje najboljše strategije konserviranja in restavriranja. Pri tem so nam v veliko pomoč tudi popolnoma neinvazivne ali delno invazivne preiskave površine z metodo XRF, s katero ugotavljamo kemijsko sestavo predmetov. Z metodo XRF smo skušali ugotavljati morebitne pomenljive razlike v sestavi bakrovih zlitin, iz katerih so bili izdelani predmeti, najdeni v grobovih dolenjske halštatske in mlajše viniške skupine z grobišča na Pezdirčevi njivi v Podzemlju. Poleg povišanih vrednosti srebra, ki nakazujejo, da so bili nekateri predmeti morebiti posrebreni, smo z multivariacijsko statistično metodo PCA ugotovili, da je bilo korozijsko delovanje s povišanimi vrednostmi kositra in svinca na površini presenetljivo izrazitejše pri predmetih iz mlajše viniške skupine (*sl. 5*).

Čeprav nam z metodo XRF ni uspelo kvantitativno določiti vsebnosti posameznih elementov, lahko na podlagi opravljenih raziskav predlagamo najprimernejše protokole in metodologijo za analize artefaktov takoj po izkopu. Na podlagi rezultatov lahko ugotavljamo, da je za verodostojno določitev elementne vsebnosti v osnovni zlitini bronaste artefakte treba analizirati na pobrušenem delu površine z drugo metodo, denimo μXRF.

Na površini predmetov iz bakrovih zlitin, zakopanih v zemlji, se v tisočletjih oblikujejo številni korozijski produkti, na katere poleg osnovne sestave predmetov in časa zakopa močno vplivajo tudi okoljski dejavniki in sestava tal. Korozijske produkte smo natančno proučevali na negovski čeladi iz groba 100 (*t. 47–49*). Razumevanje korozijskih procesov je namreč ključno za razumevanje propadanja dragocenih arheoloških najdb tako pred odkritjem kot tudi po odstranitvi iz najdiščnih kontekstov ali po arheoloških izkopavanjih. Razumevanje korozijskih procesov je pomembno tudi za konservatorje-restavratorje, saj se glede na prisotnost oziroma odsotnost določenih korozijskih produktov odločajo o vrsti posegov in načrtujejo strategijo preventivnega konserviranja.[7]

[7] Preventivno konserviranje obsega vse ukrepe in dejavnosti za preprečevanje in čim večje zmanjšanje propadanja in izgube. Izvaja se v okolju, kjer je predmet ali pogosteje skupina predmetov, ne glede na starost in stanje predmetov. Ukrepi preventivnega konserviranja so posredni, ne posegajo v snov in strukturo predmetov ter ne spreminjajo njihovega videza.

repeated a few times. The microstructure of the helmet crest suggests that the helmet was annealed again after the forging was completed. To manufacture the helmet from Pezdirčeva njiva, the smith forged the disc into a circular plate with a gradually reducing thickness from 1.5 mm at the centre to 0.5 mm at the edge. The calotte was shaped either on a concave anvil or using a round mandrel (*Fig. 15;* Mödlinger 2014, 172–173).

FINAL REMARKS

Above all else, scientifically examining metal archaeological finds ahead of conservation and restoration interventions enables us to inspect the level of preservation of individual artefacts and to determine the best strategy for their conservation-restoration. We are greatly aided in these efforts by entirely non-invasive or partially invasive XRF surface analysis methods, which determine the chemical composition of the artefacts. We utilised XRF to identify potential notable differences in the composition of copper alloys between artefacts found in the graves of the Dolenjska Hallstatt group and in the later Vinica group at Pezdirčeva njiva in Podzemelj. Aside from elevated levels of silver possibly suggesting the possibility that certain artefacts may have been silvered, multivariate PCA statistical analysis led us to the surprising conclusion that corrosion effects involving elevated concentration of tin and lead content were more pronounced on artefacts from the later Vinica group (*Fig. 5*).

Even though the XRF method proved unable to quantify the levels of individual elements, our analysis enabled us to propose the most suitable protocols and methodology for analysing artefacts immediately upon their unearthing. Based on these results, we were able to conclude that reliable elemental compositions of bronze alloys can only be obtained by analysing polished areas utilising other methods, such as μXRF.

Over the course of millennia underground, numerous corrosion products form on the surfaces of the artefacts. In addition to their own base composition and the duration of interment, these are also greatly impacted by environmental factors and soil composition. A detailed study of corrosion products was conducted on the Negova-type helmet from grave 100 (*Pls. 47–49*). Indeed, understanding corrosion products is crucial in gaining insight into the degradation of invaluable archaeological finds both prior to their discovery and after their removal from the contexts of the site or after archaeological excavations. Understanding corrosion processes is also important to conservators and restorers, since accounting for the presence or absence of certain corrosion processes informs their choice of treatment and their planned preventive conservation strategy.[7]

[7] Preventive conservation includes all measures and activities aimed at preventing and minimising deterioration and

Tehnologijo izdelave smo proučili tudi z arheometalurškega vidika. Z različnimi metodami smo ugotavljali tako vrsto in kemijsko sestavo zlitine kot tudi njeno mikrostrukturo (*sl. 12 in sl. 14*). Z analizo smo pridobili podatke o mikrostrukturnih sestavinah ter velikosti, obliki in usmerjenosti kristalnih zrn, ki odražajo zgodovino oblikovanja, preoblikovanja in eventualnih toplotnih obdelav predmeta. Tako smo lahko rekonstruirali tehnološko pot izdelave obravnavane čelade. Izdelana je bila iz sprva ulitega diska, ki ga je prazgodovinski kovaški mojster preoblikoval v okroglo in nato v vse tanjšo ploščo pločevine. Iz nje je z uporabo bodisi vdolbenega nakovala bodisi okroglega trna naposled oblikoval kaloto čelade in njen krajec. Pri izdelavi krajcev si je pomagal še s svinčevo spajko.

Čelada s Pezdirčeve njive v Podzemlju pa ni samo pomembna arheološka najdba, je tudi slabo ohranjen bronasti predmet, ki za konservatorje-restavratorje pomeni velik izziv, kako predmet čim bolje ohraniti in varovati kot dragoceno muzealijo. Z vsemi predstavljenimi naravoslovnimi preiskavami kovinskega gradiva smo tako želeli dopolniti vedenje o znanju in sposobnostih prazgodovinskih metalurgov in kovačev, ob tem pa tudi prispevati k implementaciji in popularizaciji naravoslovnih analitskih metod v okviru konservatorsko-restavratorske srenje. Le z razumevanjem korozijskega delovanja tudi po končanih posegih bomo dragocene arheološke najdbe lahko kakovostneje varovali in ohranjali za prihodnje rodove.

We also reviewed the manufacturing technology from the archaeometallurgical perspective. We applied various methods to determine alloy type, its chemical composition, and its microstructure (*Figs. 12, 14*). Our analysis yielded information on the microstructural components of the artefacts, as well as size, shape, and orientation of grains, which reflect the history of the object's formation, transformation, and potential thermal treatments. This enabled us to reconstruct the technological sequence of the helmet's manufacture. The process began by casting a bronze disc, which the prehistoric master smith shaped into a circular and gradually thinning sheet. Using either a concave anvil or a round mandrel, he finally fashioned it into the helmet's calotte and rim. In manufacturing the rim, he also employed a lead solder.

The helmet from Pezdirčeva njiva in Podzemelj is a significant archaeological find, but it is also a poorly preserved bronze object. Preserving and safeguarding such a precious museum piece poses a considerable challenge to conservers-restorers. The scientific analyses presented above were therefore undertaken not only to enhance our understanding of the skills and technologies of prehistoric metallurgists and smiths, but also to promote the use and wider adoption of scientific analytical methods within the conservation-restoration community. Only by understanding corrosion processes, even after interventions are complete, will we be able to provide a better quality of care and preservation of archaeological finds for future generations.

loss. It is conducted in situ, i.e. in environments where an artefact, or more commonly a group of artefacts, is located – regardless of their age or state. Preventive conservation measures are indirect and do not interfere with the substance or structure of the artefacts, nor do they alter their appearance.

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