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10.3 KONSERVATORSKO-RESTAVRATORSKI IZZIVI PRI OBDELAVI NEKERAMIČNIH NAJDB Z GROBIŠČA PEZDIRČEVA NJIVA V PODZEMLJU

10.3 CHALLENGES IN THE CONSERVATION AND RESTORATION OF NON-CERAMIC FINDS FROM THE PEZDIRČEVA NJIVA BURIAL SITE IN PODZEMELJ

Nataša NEMEČEK

UVOD

Konserviranje-restavriranje nekeramičnih najdb z grobišča na Pezdirčevi njivi je vključevalo zelo raznovrstne materiale: predmete iz bakrovih zlitin, železa, stekla, jantarja in v manjšem obsegu tudi srebra. Večinoma so bile najdbe odkrite v slabem stanju in izkopane skupaj z okoliško zemljino v paketu, številni posamezni predmeti pa povsem nerazpoznavnih oblik. Vzroki za tolikšno propadanje predmetov še niso zadovoljivo pojasnjeni, saj so meritve kislosti zemlje pokazale, da so vrednosti blizu nevtralnih (pH od 5,6 do 6). Ker so mehanizmi propadanja nekeramičnih arheoloških najdb izjemno kompleksni, je za njihovo razumevanje nujno sodelovanje strokovnjakov z različnih področij, predvsem metalografije, kemije in pedologije. Kljub slabemu stanju najdb nas je presenetilo, da je bilo skupaj z njimi ohranjenih razmeroma veliko organskih ostankov, predvsem mineraliziranega tekstila ter lesenih nasadišč za sekire in sulične osti. Če je bilo mogoče, smo te organske ostanke shranili za nadaljnje analize še pred konservatorsko-restavratorskimi posegi.

Pri konservatorsko-restavratorskih posegih sta ključna ustrezna metodologija in znanstveni pristop. Pri kovinskih predmetih iz bakrovih zlitin je pred vsakim posegom priporočljivo izvesti preiskave z rentgensko fluorescenčno spektrometrijo (XRF), s katero ugotovimo, iz kakšne zlitine je predmet izdelan. Pri predmetih iz železa so pred posegi pomembne preiskave z rentgensko radiografijo (RTG), s katerimi predvsem ugotavljamo stanje in ohranjenost predmetov. Sledi natančen pregled pod binokularnim oziroma stereomikroskopom, s katerim prepoznamo korozijske produkte. Nato se odločimo,

INTRODUCTION

Conserving-restoring non-ceramic finds from the Pezdirčeva njiva burial site involved a highly varied selection of materials: artefacts made from copper alloys, iron, glass, amber, and, to a lesser degree, silver. Artefacts were excavated in blocks, along with the surrounding soil, most finds were in poor condition, and many individual items were entirely unrecognisable. Thus far, the cause of such extensive deterioration has not yet been adequately explained, since soil pH values were measured to be close to neutral (pH between 5.6 and 6). The exceptional complexity of mechanisms governing the deterioration of non-ceramic archaeological finds necessitates the collaboration of experts in various fields, particularly metallography, chemistry, and pedology. We were surprised to find that, in spite of the poor state of the artefacts, a relatively high concentration of organic remains was preserved alongside them, mostly mineralised textiles and wooden shaft fittings for axes and spears. Wherever possible, these organic remains were set aside for further analysis ahead of conservation-restoration interventions.

Suitable methodology and scientific approach are the two key elements of conservation-restoration interventions. Before undertaking any interventions/treatment on copper-alloy metal artefacts, it is advisable to conduct X-ray fluorescence spectrometry (XRF) surveys to determine alloy composition. Meanwhile, it is beneficial to assess the state and condition of iron artefacts using X-ray radiography. This is followed by a detailed inspection under a binocular or stereomicroscope aimed at identifying corrosion products. Next,

Sl. 1: Delno restavrirani predmeti iz brona, železa, jantarja in stekla iz grobov na Pezdirčevi njivi v Podzemlju.
Fig. 1: Partially restored bronze, iron, amber and glass artefacts from graves at Pezdirčeva njiva in Podzemelj.

na kakšen način bomo izvedli posege. Konservatorsko-restavratorski postopki obsegajo čiščenje, stabilizacijo in restavriranje (*sl. 1*[1]).

PREDMETI IZ BAKROVIH ZLITIN

Po številu obravnavanih najdb s Pezdirčeve njive izstopajo predmeti iz bakrovih zlitin. Preiskave z metodo XRF so razkrile, da so poleg glavnih kovin – bakra, kositra in svinca – prisotni še arzen, srebro, železo in antimon. Vse te kovine v obdobju po zakopu tvorijo raznovrstne korozijske produkte. Kloridne soli v zemlji vplivajo na nastanek aktivnih korozijskih produktov, kar lahko nazadnje privede do popolnega propada predmeta. Dokaz o kompleksnem korozijskem delovanju je tudi debelina korozijskih produktov, ki so bili

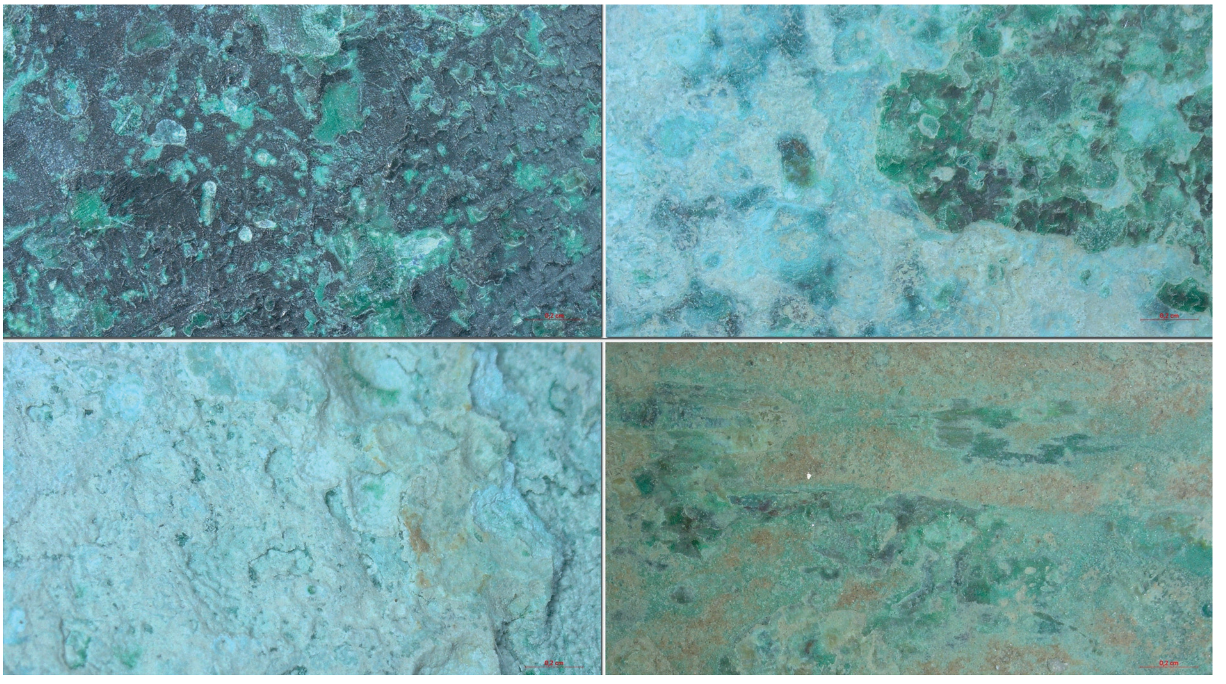
[1] Vse slike je pripravila avtorica.

it is time to select the appropriate course of treatment. Conservation-restoration procedures include cleaning, stabilisation, and restoration. (*Fig. 1*[1]).

COPPER ALLOY ARTEFACTS

Of all the analysed finds at Pezdirčeva njiva, copper alloy artefacts were the most numerous. XRF research revealed that apart from primary metals, such as copper, tin, and lead, the alloys also include arsenic, silver, iron, and antimony. In burial, all these metals contribute to the formation of various corrosion products. Presence of chloride salts in the soil affects the creation of active corrosion products, which can ultimately result in the artefact's complete disintegration. Complex corrosive processes are also evidenced in the thickness of corro-

[1] All figures were prepared by the author.



Sl. 2: Različni korozijski produkti na negovski čeladi iz groba 100 na Pezdirčevi njivi v Podzemlju s plemenito patino – levo zgoraj in desno spodaj in škodljivo patino – desno zgoraj in levo spodaj.

Fig. 2: Different corrosion products on a Negova helmet from Grave 100 at Pezdirčeva njiva in Podzemelj with a noble patina – top left and bottom right and a harmful patina – top right and bottom left.

pri večjem številu predmetov debelejši od kovinskega jedra predmetov.

KOROZIJA BAKRA IN NJEGOVIH ZLITIN MED ZAKOPANOSTJO V ZEMLJI

Mehanizmi propadanja bakrovih zlitin so zelo kompleksni in odvisni od različnih dejavnikov. Korozija bakra in njegovih zlitin privede do tvorbe različnih bakrovih spojin (sulfati, karbonati, kloridi). Če je korozijski proces v prsti počasen, se po Robbioli (Robbiola et al. 1998, 2083–2111) oblikuje korozija tipa I, pri čemer se oblikuje plast plemenite patine. Če je korozija hitra, nastaja prašna ali krastava oblika – po Robbioli tip II, ki ni cenjena (tako imenovana škodljiva patina) (*sl. 2*). Korozijsko delovanje je odvisno od okolja, v katerem je predmet zakopan. Peščena tla dobro prepuščajo vodo, kisik in ogljikov dioksid. Korozija se začne z nastankom rdeče plasti bakrovega(I) oksida – kuprita (Cu_2O), ki se sčasoma pretvori v črni bakrov(II) oksid – tenorit (CuO). Ob prisotnosti CO_2 (pri pH 6) nastajata zeleni bakrov(II) karbonat hidroksid – malahit ($Cu_2CO_3(OH)_2$) ali modri bakrov(II) karbonat hidroksid – azurit ($Cu_3(CO_3)_2(OH)_2$). Sočasno poteka oksidacija kositra do kositrovega(IV) oksida – kasiterita (SnO_2) (Milič 2004, 3–7).

sion layers, which, in many cases, exceeded the thickness of the artefacts' metallic core.

THE CORROSION OF COPPER AND ITS ALLOYS DURING BURIAL

Mechanisms governing copper alloy degradation are highly complex and contingent on a variety of factors. The corrosion of copper and its alloys results in the formation of a variety of copper compounds, such as sulphates, carbonates, and chlorides. A slow corrosion process in the soil results in what Robbiola (Robbiola et al. 1998, 2083–2111) defines as type I corrosion, also referred to as noble patina. Quickly occurring corrosion, on the other hand, results in a powdery or encrusted layer, or Type II according to Robbiola, which is not valued (i.e. harmful patina) (*Fig. 2*). Corrosion processes depend on the environment in which the object is buried. Sandy soils are highly permeable to water, oxygen, and carbon dioxide. Corrosion begins with the formation of a red layer of copper(I) oxide–cuprite (Cu_2O), which gradually transforms into black copper(II) oxide–tenorite (CuO). The presence of CO_2 (with pH 6) can result in the formation of green copper(II) carbonate hydroxide–malachite ($Cu_2CO_3(OH)_2$) or blue copper(II) carbonate hydroxide–azurite ($Cu_3(CO_3)_2(OH)_2$). Meanwhile, tin oxidises to tin(IV) oxide–cassiterite (SnO_2) (Milič 2004, 3–7).

KONSERVATORSKO-RESTAVRATORSKI POSTOPKI

Za odstranjevanje korozijskih produktov na bakrovih zlitinah iz arheološkega konteksta so najprimernejše mehanske metode. Vse posege opravljamo pod stereomikroskopom. Predmeti so običajno prekriti z ostanki zemlje, ki vsebuje mineralne delce in organske ostanke, sprijete z različnimi korozijskimi produkti. Zemljo običajno odstranjujemo s čopiči z mehkimi dlakami ali steklenimi vlakni. Sledi odstranjevanje korozijskih produktov z ultrazvočnim (UZ) kladivcem, ki omogoča selektivno odstranjevanje korozije, ne da bi pri tem poškodovali originalne površine oziroma plasti plemenite patine, skrite pod korozijskimi produkti. Pri odstranjevanju korozijskih produktov si pomagamo tudi z mikromotorjem z različnimi nastavki (brusi, polirne gumice in podobno) (Nemeček 2023a, 10, 11).

Pogosto je treba predmete iz bakrovih zlitin pred nadaljevanjem čiščenja utrditi, kar lahko storimo na več načinov. Lahko jih utrdimo v triodstotni raztopini inhibitorja benzotriazola (BTA, $C_6H_5N_3$), v etanolu ali pa jih utrdimo s petodstotno raztopino metil metakrilatne smole Paraloid B 44 v vakuumski pečici. Tako smo za nadaljnjo mehansko obdelavo pripravljali tudi predmete s Pezdirčeve njive. Mehansko čiščenje predmetov iz bakrovih zlitin je namreč najprimernejše tudi z estetskega gledišča. Če z osnovnimi metodami mehanskega čiščenja nismo zmogli odstraniti trdovratnejših korozijskih produktov, smo izjemoma uporabili mikropeskanje s steklenimi ali plastičnimi kroglicami (prim. Nemeček 2023a, 15).

Kemijske metode so nepogrešljive pri odstranjevanju škodljivih soli – bakrovih kloridov (na primer nantokit–CuCl). V ta namen uporabljamo organsko topilo acetonitril (metil cianid, CH_3CN) v sanitarni vodi v razmerju 50 proti 50. Nato predmete večkrat prekuhamo v destilirani vodi. Prisotnost oziroma odsotnost kloridnih soli določamo kvalitativno s testom iz srebrovega nitrata in dušične kisline (Scott 2002, 372).

Za lakiranje predmetov iz bakrovih zlitin smo uporabljali raztopini metakrilne smole Paraloid B-72 in metil metakrilatne smole Paraloid B 44 v ksilenu ali raztopino Incralaka (Paraloid B-44 z dodatkom inhibitorja BTA), za dodatno zaščito pa poskrbi premaz renesančnega voska (*sl. 3*).

PREDMETI IZ ŽELEZA

Tako kot pri bakrovih zlitinah so tudi pri železnih predmetih mehanizmi propadanja zelo kompleksni in odvisni od različnih dejavnikov. Korozijsko delovanje med zakopanostjo v zemlji privede do tvorbe različnih spojin (oksidi in oksihidroksidi). Da bi ugotovili stopnjo

CONSERVATION-RESTORATION PROCEDURES

In an archaeological context, corrosion products on copper alloys are best removed by means of mechanical methods. All procedures are conducted under a stereomicroscope. Artefacts are usually covered in soil residue, which includes mineral particles and organic remains combined with various corrosion products. The soil is usually removed with soft-bristled or glass-fibre brushes. Next, corrosion products are removed with an ultrasonic chisel, which allows for the corrosion to be removed selectively without damaging the original surface, i.e. the noble patina layer underneath the corrosion products. A micromotor equipped with a variety of attachments (burrs, polishing rubbers etc.) can further aid in removing corrosion products. (Nemeček 2023a, 10–11).

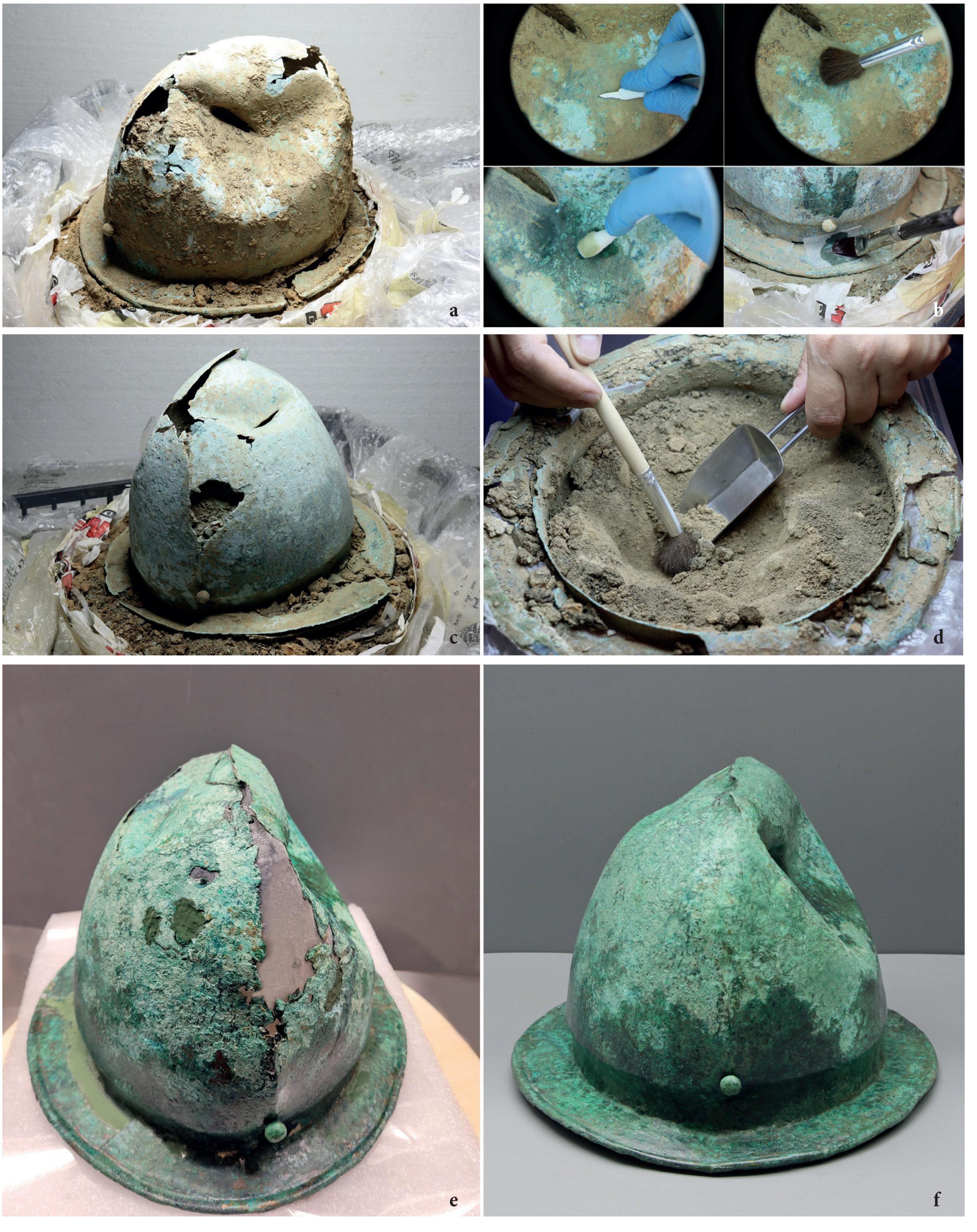
Copper alloys artefacts often need to be consolidated before further cleaning. This can be done in different ways. They can be consolidated in a 3% solution of corrosion inhibiting benzotriazole (BTA, $C_6H_5N_3$) in ethanol, or 5% solution of methyl methacrylate resin Paraloid B-44 in a vacuum oven. This was how artefacts from Pezdirčeva njiva were prepared for further mechanical treatment, particularly since mechanical cleaning of copper alloy objects is also the most suitable method from an aesthetical viewpoint. On the rare occasion, where basic mechanical cleaning methods did not suffice to remove the more persistent products of corrosion, micro-abrasive blasting with glass or plastic beads was used (cf. Nemeček 2023a, 15).

Chemical methods are indispensable in removing harmful salt–copper chlorides (e.g. nantokite–CuCl). This task is undertaken through the use of the organic solvent acetonitrile (methyl cyanide CH_3CN) diluted 50:50 in deionized water. Afterwards, the artefacts are repeatedly boiled in distilled water. The presence/absence of chloride salts is determined qualitatively by means of a silver nitrate and nitric acid test (Scott 2002, 372).

Copper alloy artefacts were lacquered using methacrylate resin Paraloid B-72 and the methyl methacrylate resin Paraloid B-44 in xylene as well as a solution of Incralac (Paraloid B-44 with added BTA inhibitor). Additional protection was provided by a coat of Renaissance Wax (*Fig. 3*).

IRON ARTEFACTS

Like copper alloys, iron artefacts are also subject to highly complex mechanisms of degradation, dependent on a variety of factors. Corrosion of iron in the soil results in the formation of different compounds (oxides and oxyhydroxides). Before undertaking any interven-



Sl. 3: Podzemelj, Pezdirčeva njiva. Konservatorsko-restavratorski posegi na negovski čeladi: stanje pred posegi razkriva obsežne poškodbe bronaste pločevine (a); posegi so vključevali: odstranjevanje zemlje s skalpelom, čopičem, tamponi in utrjevanje z japonskim papirjem (b); stanje čelade med restavriranjem po delni odstranitvi zemlje (c); odstranjevanje zemlje iz notranjosti (d); podlaganje poškodb z japonskim papirjem (e) in čelada po zaključenih posegih (f).
Fig. 3: Podzemelj, Pezdirčeva njiva. Conservation and restoration works on the helmet: the state before the works reveals extensive damage to the bronze sheet (a); the works included: removal of soil with a scalpel, brush, swabs and consolidation with Japanese paper (b); the state of the helmet during the restoration after partial soil removal (c); removal of soil from the interior (d); lining of the damage with Japanese paper (e); and the helmet after the works were completed (f).

ohranjenosti predmetov je pred posegi priporočljivo opraviti preiskave z rentgensko radiografijo (RTG).[2]

KOROZIJA ŽELEZA MED ZAKOPANOSTJO V ZEMLJI

Korozija ima za arheološke predmete iz železa vrsto uničujočih posledic, ki lahko privedejo do izgube kovinskega jedra, s čimer izgubimo informacije o funkciji predmeta in tehnoloških značilnostih. Korozija železa v zemlji ob prisotnosti vlage in kisika je elektrokemijski proces. Zanjo je značilna večplastna struktura, ki je v grobem sestavljena iz dveh delov. Prvi del sestavljajo korozijski produkti iz železovih oksidov in oksihidroksidov z nižjim oksidacijskim stanjem tik nad kovinskim jedrom ter hkrati označujejo nivo originalne površine predmeta. Tipičen produkt v tej plasti je železov(II,III) oksid – magnetit (Fe_3O_4) črne barve. Drugo, zunanjo plast pa sestavljajo korozijski produkti železovih(III) oksihidroksidov – običajno je to goetit (α-FeOOH) oranžne barve, v katerega so vključeni še sedimenti iz zemlje, kot so kamenčki, kristali in glina. V kolikšni meri bo železo v zemlji korodiralo, je odvisno od koncentracije kloridnih ionov, ta pa je odvisna od pH-vrednosti zemlje. Za železo je značilno, da korodira v nizkem, torej kislem pH-območju. Ciklično korozijsko dogajanje vpliva na pojav razpok, por in odprtih površin, v katerih se kopiči kisla raztopina železovega(II) klorida – feroklorida ($FeCl_2$) (Turgoose 1993). Z raziskavami so ugotovili, da zaradi cikličnega korozijskega delovanja v zemlji korozijski produkti volumensko v veliki meri nadomestijo kovinsko jedro. Tako je v nekaterih primerih od kovinskega jedra ostalo samo 24 odstotkov, 62 odstotkov predstavljajo korozijski produkti in 19 odstotkov zemlja (prim. Bernabale et al. 2022, 6125). Po izkopu so predmeti izpostavljeni novim okoljskim "izzivom", ki vplivajo na nastanek novih poškodb in korozijskih produktov, kot je na primer železov(III) oksihidroksid – akaganeit (β-FeOOH) (Selwyn 2004, 295–296).

KONSERVATORSKO-RESTAVRATORSKI POSTOPKI

Za večino predmetov iz železa s Pezdirčeve njive so značilne številne poškodbe z močno razpokano površino, s koščki, ki odpadajo, in oranžnim prahom, ki nakazujejo, da je bila prst zelo vlažna in zračna. Za nekatere predmete so bile značilne izjemno debele korozijske plasti. V teh primerih je korozija odstopala od kovinskega jedra, zanjo so bile značilne razpoke in razplastitve. V nevtralni prsti se namreč železovi ioni oborijo kot oksidi ali karbonati in ostanejo na mestu nastanka. V tem primeru se predmet ohrani v obliki korozijskih produktov (oksidov, karbonatov). Volumen predmeta se poveča in njegova oblika se

[2] Glej tu poglavje 10.4.

tion, X-ray radiography is advisable to determine the degree to which the artefacts are preserved.[2]

CORROSION OF IRON DURING THE BURIAL

The range of destructive effects of corrosion on iron archaeological artefacts can result in total loss of their metal cores, which means a loss of information on the artefact's function and technological characteristics. Corrosion of iron in the soil in the presence of moisture and oxygen is a multi-layered electro-chemical process, which can roughly be divided into two parts. The inner part immediately above the metal core, which is made up of corrosion products consisting of iron oxides and oxyhydroxides with a lower state of oxidation, marks the level of the artefact's original surface. A typical product found in this layer is black iron(II, III) oxide – magnetite (Fe_3O_4). The other, outer layer is comprised of corrosion products of iron(III) oxyhydroxides – typically orange goethite (α-FeOOH) fused with soil sediments, such as pebbles, crystals, clay. The level of the iron's corrosion in the soil depends on the concentration of chloride ions, which in turn depends on the soil's pH value. Iron typically corrodes in low, i.e. acidic pH environments. Cyclical corrosion processes have an effect on the appearance of cracks, pores, and open surfaces wherein acidic solutions of iron(II) chloride – ferrous chloride ($FeCl_2$) accumulate (Turgoose 1993). Research has shown that cyclical corrosion processes in the soil lead to corrosion products largely replacing the volume of the metallic core. And so, in certain instances, only 24% of the metallic core remained, with corrosion products representing 62%, and soil 19% of the artefact's volume (e.g. Bernabale et al. 2022, 6125). Following the excavation, the artefacts are exposed to new environmental "challenges", which effect new damage and the formation of corrosion products, such as e.g. iron(III) oxyhydroxide —akaganéite (β-FeOOH) (Selwyn 2004, 295–296).

CONSERVATION–RESTORATION PROCEDURES

Most artefacts from Pezdirčeva njiva suffered excessive damage, most typically heavily cracked surfaces, flaking bits, and orange dust, all of which indicates very humid and airy soil. Some artefacts displayed exceptionally thick corrosion layers. In these instances, corrosion detached from the metallic core, showing cracking and delamination. In neutral soil iron ions precipitate as oxides or carbonates and remain in place where they appeared. In these instances, the artefacts are preserved in the shape of corrosion products (oxides, carbonates). The artefact's volume increases while its shape is often entirely altered, retained only

[2] See Chapter 10.4.

Sl. 4: Konservatorsko-restavratorski posegi na meču z nožnico iz groba 110: meč pred začetkom posegov (a); po peskanju s korundom (b); detajl med posegi (c) in meč po zaključenih posegih (d).

Fig. 4: Conservation and restoration works on the sword with scabbard from Grave 110: sword before the works (a); after corundum blasting (b); detail during the works (c) and sword after the works (d).

velikokrat popolnoma spremeni. Predmet ohrani svojo obliko le še v kompaktni črni plasti magnetita, ki označuje originalno površino predmeta – originalna površina je torej skrita znotraj voluminozne korozijske plasti (Milić 2004, 3). Pri predmetih z dobro ohranjenim kovinskim jedrom – ti so bili sicer v manjšini – pa so bile velika težava visoke koncentracije kloridnih ionov, ki nam jih kljub večmesečnemu namakanju predmetov v alkalno-sulfitni raztopini (0,5M NaOH in 0,5M Na_2SO_3) ni uspelo izločiti iz predmetov – taki predmeti zahtevajo posebno stroge pogoje hranjenja in razstavljanja (Schmidt-Ott in Oswald 2006, 128).

Po alkalno-sulfitnem postopku, v katerem iz predmetov izločimo kloridne ione, sledijo prekuhavanje v destilirani vodi, sušenje in mehanska obdelava. Pri slednji najpogosteje uporabljamo mikropeskanje s korundom (Al_2O_3), ki pa je zelo zamudno, zlasti v primerih, ko so korozijske plasti izjemno debele in kompaktne in se le s težavo prebijamo do plasti magnetita, ki označuje nivo originalne površine predmeta. Pri tanjšanju korozije si lahko pomagamo z različnimi brusi, ki pa so primerni le, če so predmeti stabilni. Pogosto ni tako, zato moramo predmete sproti utrjevati z akrilnimi smolami. Po mehanski obdelavi so sledili nanos tanina, sušenje in nato lakiranje predmetov, pri katerem smo uporabili razto-

in the compact black layer of magnetite, which delineates the artefact's original surface; the original surface is therefore concealed within a voluminous layer of corrosion (Milić 2004, 3). Meanwhile, objects with a preserved metallic core, here in the minority, were highly problematic due to their high concentrations of chloride ions, which we were unable to separate from the artefacts, even after treatment by immmersion in an alkaline-sulphite solution (0.5M NaOH and 0.5M Na_2SO_3) for several months. Such artefacts demand particularly strict storage and exhibition conditions (Schmidt-Ott, Oswald 2006, 128).

The alkaline-sulphite procedure, which removes chloride ions from the artefacts, is followed by boiling in distilled water, drying, and mechanical treatment. The latter commonly involves micro-abrasive blasting with corundum (Al_2O_3), a highly very time-consuming process making it difficult to reach the magnetite layer, which marks the artefact's original surface layer. We can thin the corrosion layers using various abrasives, but only if the artefacts are stable. This is often not the case, necessitating continuous consolidation of the artefacts with acrylic resins.

After the mechanical treatment was completed, the artefacts were coated in tannin, dried, and finally

Sl. 5: Podzemelj, Pezdirčeva njiva. Primer poškodb jantarja na jagodi z železne žičnate fibule iz groba 176.
Fig. 5: Podzemelj, Pezdirčeva njiva. Example of amber damage on a bead from an iron wire fibula from Grave 176.

pino akrilne smole Paraloid B-72, za dodatno zaščito pa je poskrbel premaz renesančnega voska (Cronyn 2004, 202–210). Po konservatorsko-restavratorskih posegih naše delo še ni končano (*sl. 4*), saj moramo predmetom zagotoviti tudi ustrezne pogoje hranjenja in razstavljanja. Za arheološke predmete iz železa so ti pogoji še posebej zahtevni. Ustrezna relativna zračna vlažnost (RH) za arheološke železne predmete je v idealnih razmerah čim bližje 0-odstotni relativni zračni vlažnosti. Kot varne pogoje se navaja RH pod 12 oz. 15-odstotno relativno zračno vlažnostjo, do 30-odstotne relativne zračne vlažnosti pa so korozijski procesi relativno počasni.

JAGODE IZ JANTARJA

Tako kot za večino kovinskih najdb je tudi za jagode iz jantarja značilna slaba ohranjenost. Značilne poškodbe jantarja s Pezdirčeve njive so krhkost, razpokanost, plastenje oziroma luščenje in beljenje površine (*sl. 5*).

SESTAVA JANTARJA IN MEHANIZMI PROPADANJA

Jantar je fosilna smola iglavcev in listavcev iz drevesnih družin Arauacariaceae, Fabaceae, Leguminoase. Nastajala je milijone let od obdobja krede do neogena (145–5 milijonov let). Ima dokaj zapleteno in nestabilno kemično sestavo, ki jo poenostavljeno zapišemo kot $C_{10}H_{16}O$. Smola vsebuje terpene, terpenoide, fenole in v manjši meri alkohole, kisline, maščobe ter redkeje aminokisline. Sestava je raznolika in je odvisna od številnih dejavnikov, kot so provenienca, geološka zgodovina, paleookolje in paleobotanični izvor. V tisočletjih preobrazbe se smola kemijsko preoblikuje v polimer.

lacquered with acrylic resin solution Paraloid B-72 with an added a coat of Renaissance Wax for additional protection (Cronyn 2004, 202–210). However, our work was not done when conservation-restoration procedures were completed (*Fig. 4*), we also had to ensure that the artefacts would be stored and exhibited in suitable conditions. These are particularly strictly defined for iron archaeological artefacts The ideal relative humidity (RH) for archaeological iron objects is as close to 0% RH as possible. Safe conditions are considered to be RH below 12% or 15% RH, while corrosion processes are relatively slow up to 30% RH.

AMBER BEADS

Like most metal finds, amber beads are also characteristically poorly preserved. The representative forms of deterioration at Pezdirčeva njiva were brittleness, cracking, delamination or flaking, and surface whitening (*Fig. 5*).

AMBER COMPOSITION IN DEGRADATION MECHANISMS

Amber is fossilised resin from coniferous and deciduous trees of the Araucariaceae, Fabaceae, and Leguminosae families, formed over millions of years from the Cretacious to the Neogene period (145–5 million years ago). Its chemical composition, commonly simplified as $C_{10}H_{16}O$, is complex and unstable. Resin contains terpenes, terpenoids, phenols, and to a lesser degree alcohols, acids, fats, and less frequently still – amino acids. Its composition varies depending on numerous factors, such as provenance, geological history, paleoenvironment, and

Sl. 6: Podzemelj, Pezdirčeva njiva. Ostanki železne fibule z oblogo iz jantarnih jagod (a); čiščenje jagod z bambusovo (b) in vatirano palčko ter mešanico etanola in destilirane vode (c); ostanki fibule po čiščenju jagod.
Fig. 6: Podzemelj, Pezdirčeva njiva. Remains of an iron fibula with amber beads lining (a); cleaning of the beads with a bamboo (b) and cotton bud and a mixture of ethanol and distilled water (c); remains of the fibula after cleaning the beads.

Smola sprva otrdi, ker izgubi svoje hlapne komponente (alkohol) in postane v vmesni fazi smola kopal. Jantar se oblikuje v zadnji fazi polimerizacije zaradi nadaljnje izgube hlapnih sestavin. Barve segajo od jasne svetlo rumene do globoke rdeče. Glede na jasnost poznamo transparentne, poltransparentne, prosojne in neprozorne jantarje (Ivanova, Kuleff 2009, 23).

Glede na zgodovinsko ozadje in strukturno karakterizacijo (osnovni polimer) razlikujemo pet razredov oziroma vrst jantarja. Za nas je najpomembnejši baltski jantar iz severne Evrope in z območja Baltika. Vsebuje sukcinsko kislino $(CH_2)_2(CO_2H)_2$ iglavcev, borovcev družine *Sciadopityaceae*, zato jih imenujemo sukciniti (Triantafyllou 2016, 5).

Baltski jantar je zelo občutljiv za fizikalne in kemijske okoljske dejavnike. Propada zaradi atmosferske oksidacije (oksidacija terpenoidov v kislino), vročine in svetlobe (UV-sevanje povzroči termalno in fotooksidacijo), relativne zračne vlažnosti (občutljiv je tako za visoke kot nizke vrednosti RH, še posebej za nizke, ki privedejo do površinskih razpok, krhkosti in izrazite neprozornosti) in onesnaževal. Prav tako je občutljiv

palaeobotanical origin. In the course of millennia, the resin chemically transforms into a polymer. First, the loss of its volatile components (alcohol) results in the resin hardening and entering the intermediate phase known as copal. Further loss of volatile components in the final stage of polymerisation result in the formation of amber.

Its colours range from a clear yellow to a deep red. Based on clarity, ambers can be classified as transparent, semi-transparent, translucent, or opaque (Ivanova, Kuleff 2009, 23).

Based on historical background and structural characterisation (primary polymer), we distinguish five classes or types of amber. In this context, Baltic amber from northern Europe and the Baltic region is the most relevant. It derives succinic acid $(CH_2)_2(CO_2H)_2$ from coniferous pine trees of the *Sciadopityaceae* family, which is why it is also known as succinite (Triantafyllou 2016, 5).

Baltic amber is highly sensitive to physico-chemical environmental factors. It deteriorates due to atmospheric oxidation (oxidation of terpenoids into acids), exposure to heat and light (with ultraviolet radiation causing both thermal and photo-oxidation), fluctuations in relative za kisli in alkalni pH (Pastorelli 2009, 62, 93–95). Kisle in alkalne pH-vrednosti zemlje povzročijo agresivne kemijske procese, ki vplivajo na ohranjenost jagod, zlasti če so spremembe iz močno bazičnih v rahlo kisle pogoje hitre, kar se običajno zgodi pri razgradnji zakopanih človeških teles. Pri tem nastajajo značilne poškodbe, kot so beljenje površine, mikrorazpoke, nabrekanje in odstopanje. Posledica vseh teh procesov je izguba originalne površine, zato je interpretacija tehnologije izdelave otežena.

KONSERVATORSKO-RESTAVRATORSKI POSTOPKI

Za odstranjevanje ostankov zemlje smo uporabili destilirano vodo in različne pripomočke, kot so vatirane palčke in zobotrebci za odstranjevanje zemlje iz luknjic. Odvečno tekočino smo popivnali s papirnato brisačo. Po čiščenju smo jagode posušili na zraku (*sl. 6*). Za lepljenje smo uporabili raztopino Paraloida B 72 v acetonu. V preteklosti so za utrjevanje krhkih jantarnih jagod uporabili različna utrjevalna sredstva, kot so damar, glicerin, terpentin in podobno. V novejšem času izstopa uporaba tako imenovane kanadske smole (Canada balsam) in Paraloida B 72 v različnih topilih (ksilen, *white spirit*). V primeru jantarnih jagod s Pezdirčeve njive smo se odločili, da predmetov ne bomo utrjevali, saj so številne raziskave pokazale, da za jantar ni primerne zaščite oziroma utrjevalnih sredstev. Še več, številna utrjevalna sredstva pospešujejo propadanje predmetov iz jantarja (Jeberlein 2000, 65–68). Prav tako različni materiali za utrjevanje – z izjemo parafina, vplivajo na identifikacijo jantarja v infrardečem spektru. Zato je zelo pomembno, da jantar hranimo in razstavljamo pod strogimi določenimi pogoji. Priporočljivo je, da so predmeti iz jantarja shranjeni v temnem prostoru brez kisika, s stalno temperaturo pri 17 stopinjah Celzija in 50-odstotno relativno zračno vlažnostjo. Ker kisik vpliva na propadanje jantarja, priporočamo uporabo absorberjev za vitrine oziroma shranjevanje brez kisika in stabilizator relativne zračne vlažnosti (Thickett et al. 1995, 217–226).

JAGODE IZ STEKLA

Tako kot pri kovinskih predmetih tudi na steklo med zakopanostjo v zemlji vplivajo različni parametri: raven vlažnosti, sestava in kislost zemlje, mikroorganizmi in drugo. Ti dejavniki povzročajo preperevanje (angleško *weathering*) in korozijo stekla. Med poškodbami prevladujejo krhkost in mehanske poškodbe v obliki razpok različnih oblik ali pa se na površino začnejo izločati alkalne komponente. Ohranjenost jagod je odvisna tudi od tehnike izdelave. Jagode s Pezdirčeve

humidity (it is sensitive to both high and low RH levels, particularly to low RH, which causes surface cracking, brittleness, and pronounced opacity), and pollutants. It is also sensitive to acidic and alkaline pH (Pastorelli 2009, 62, 93–95). Acidic and alkaline pH values of the soil cause aggressive chemical processes, which effect the preservation of the beads, particularly if the change from strongly alkaline to slightly acidic conditions occur quickly, which is typically what occurs when buried human bodies decompose. The resulting characteristic types of degradation include surface whitening, microcracking, swelling, and delamination. All these processes disintegrate the original surface, which makes it harder to infer what manufacturing technology was used.

CONSERVATION-RESTORATION PROCEDURES

Soil residues were removed from small cavities using distilled water and a variety of implements, such as cotton swabs and toothpicks. Surplus liquid was "blotted" with paper towels. After the cleaning process was complete, the beads were air-dried (*Fig. 6*).

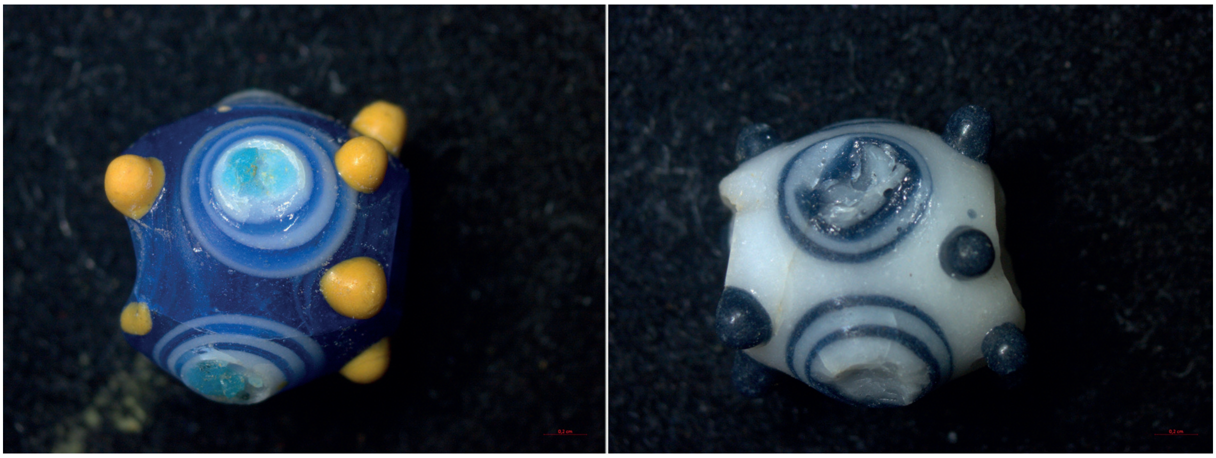
A solution of Paraloid B-72 in acetone was used for adhesion. In the past, fragile amber beads were consolidated with a variety of consolidants, such as damar resin, glycerine, turpentine, et. sim. More recently, the use of so-called Canada balsam and Paraloid B-72 in different solvents (xylene, white spirit) has become common.

In the case of Pezdirčeva njiva, we decided not to consolidate the artefacts, being that numerous studies have demonstrated that no suitable protection or consolidating agents for amber exist. Furthermore, many consolidants even accelerate degradation of amber artefacts (Jeberlein 2000, 65–68).

Likewise, most consolidants, with the exception of paraffin, interfere with the identification of amber in the infrared (IR) spectrum. This is why it is of utmost importance to store and exhibit amber under strict conditions. It is advisable to store amber artefacts in a dark, oxygen-free environment, at a constant temperature of 17° C and at 50% relative air humidity. Since oxygen affects amber degradation, oxygen absorbers in display cases or oxygen-free storing are recommended, as well as a relative humidity stabiliser (Thickett et al. 1995, 217–226).

GLASS BEADS

Like metal objects, glass is also subject to the influence of various parameters during burial, such as humidity levels, soil composition and acidity, microorganisms and the like. These factors cause glass to weather and corrode. The predominantly occurring types of damage are fragility and mechanical damage in the form of variously shaped cracks, while alkaline components begin



Sl. 7: Podzemelj, Pezdirčeva njiva. Pogoste poškodbe steklenih jagod v obliki finih morfoloških razpok.
Fig. 7: Podzemelj, Pezdirčeva njiva. Frequent damage to glass beads in the form of fine morphological cracks.

njive so bile izdelane s tehniko navijanja ali s tehniko prepogibanja (Purowski 2022, 70–71). Pri slednji je spoj običajno krhek in se lahko hitro razlomi.

SESTAVA STEKLA IN MEHANIZMI PROPADANJA

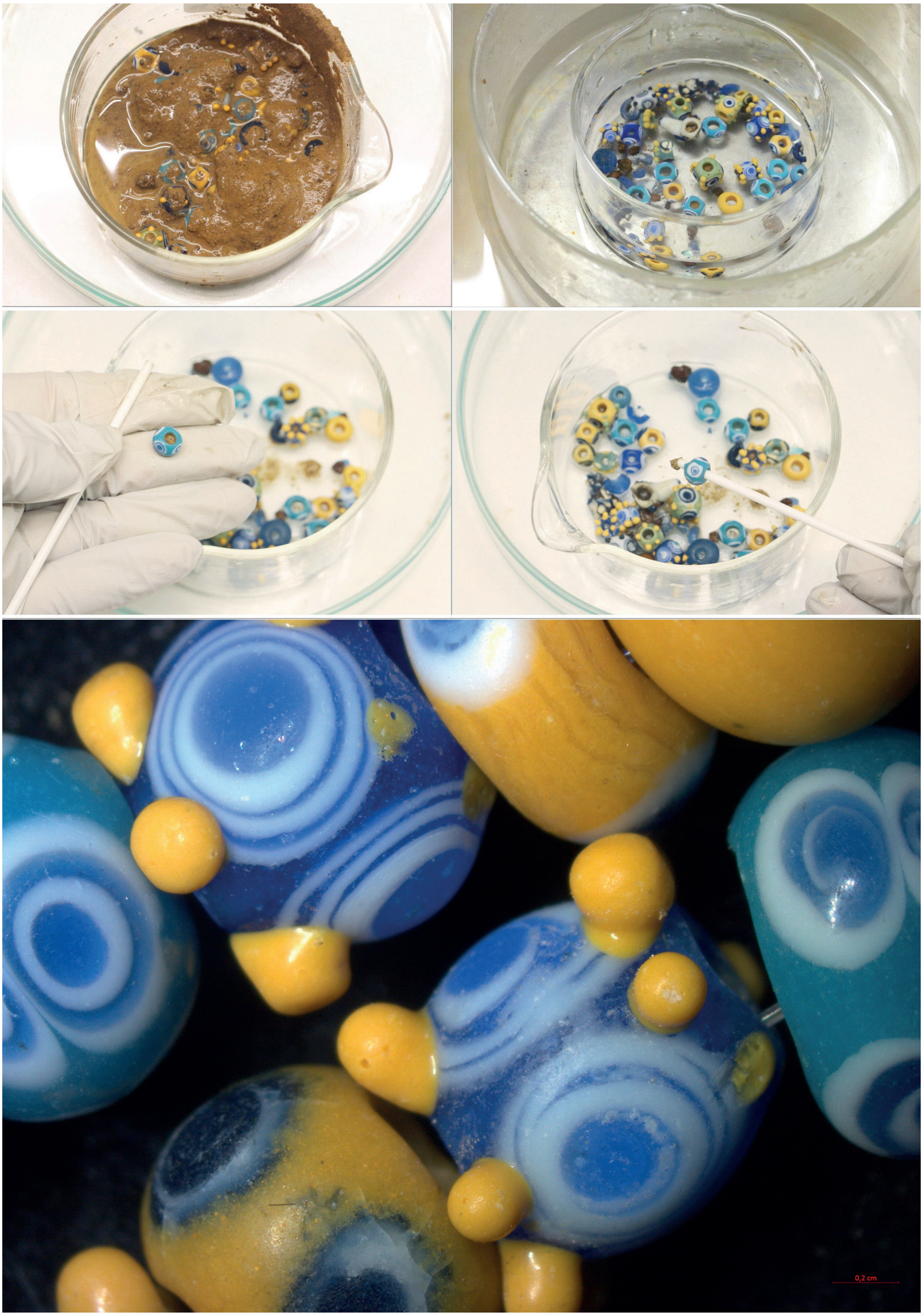
Steklena masa je sestavljena iz štirih sestavin. Glavna sestavina stekla je silicijev dioksid (kremen, SiO_2), ki ima zelo visoko tališče okoli 1700 stopinj Celzija. Z dodatkom alkalnih talil (Na_2O, K_2O, PbO) se tališče zniža pod 1000 stopinj Celzija. Kemijska stabilnost stekla se poveča z dodatkom stabilizatorjev (MgO, CaO). Za obarvanje steklu dodajo različna barvila oziroma sredstva za motnjenje (Co, Sb, Ni in podobno) (Lončarić, Costa 2023, 3838–3841). Za bronastodobne steklene jagode je značilna visoka vsebnost magnezija (MgO), in sicer od tri- do petodstotna, ter kalija (K_2O), od dva do tri odstotke (HMG = high Mg), ki ju vsebuje talilo iz pepela slanoljubnih rastlin (halofitov). Obdobje železne dobe zaznamujejo številne tehnološke spremembe, ki se odražajo tudi v proizvodnji stekla. V zgodnji železni dobi so sicer recepti za izdelavo stekla še vedno zelo raznovrstni (na primer steklo z visoko vsebnostjo magnezija in nizko vsebnostjo kalija – HMLK = high Mg-low Ca; steklo z nizko vsebnostjo magnezija in srednjo vsebnostjo kalija – LMMK = low Mg-medium Ca in podobno). Od 8. stoletja pr. n. št. pa začne prevladovati tako imenovano natronsko oziroma natronovo steklo ali steklo z nizko vsebnostjo magnezija (LMG = low Mg), saj vsebuje manj kot 1,5 odstotka MgO in K_2O (Šmit et al. 2020, 1; Lončarić, Costa 2023, 3841–3853). Ker talilo natron[3] (natrijev

[3] Natron so pridobivali iz sedimentov suhih egiptovskih jezer. Natronsko steklo prevladuje skoraj tisoč let, vse do 7. st.

exuding to the surface. The level to which glass beads are preserved also depends on the manufacturing method itself. Beads from Pezdirčeva njiva were produced either using the winding or the folding technique (Purowski 2022, 70–71). The latter is usually characterised by a fragile joint, prone to breaking.

GLASS COMPOSITION AND DEGRADATION MECHANISMS

Glass matter is composed of four components. The main ingredient is silicon dioxide (quartz, SiO_2), whose melting point is very high at approximately 1700° C. Adding alkaline fluxes (Na_2O, K_2O, PbO) lowered the melting point to below 1000˚ C. Next, the chemical stability of glass was increased with the addition of stabilisers (MgO, CaO). Glass was then dyed with the addition of different colouring or opacifying agents (Co, Sb, Ni etc.) (Lončarić, Costa 2023, 3838–3841). Bronze-Age glass beads typically have a high magnesium and potassium content –MgO 3–5%, K_2O 2–3% (HMG = high Mg), contained in the flux derived from the ash of halophytes. The Iron Age is characterised by numerous technological advancements, which are also reflected in glass manufacture. Early Iron-Age glass recipes are still highly diverse (e.g. glass with high magnesium and low calcium content – HMLK = high Mg-low Ca; glass with low magnesium and medium calcium content – LMMK = low Mg-medium Ca, etc.). From the 8th c. BCE onward, so-called natron glass, i.e. glass with low magnesium content (LMG = low Mg) containing less than 1,5% MgO and K_2O begins to prevail (Šmit et al. 2020, 1; Lončarić, Costa 2023, 3841–3853). Since, compared to halophyte-derived



Sl. 8: Podzemelj, Pezdirčeva njiva. Čiščenje steklenih jagod in detajl po zaključenih posegih.
Fig. 8: Podzemelj, Pezdirčeva njiva. Cleaning the glass beads and detail after the procedures.

Sl. 9: Podzemelj, Pezdirčeva njiva. Ogrlica iz steklenih in jantarnih jagod.
Fig. 9: Podzemelj, Pezdirčeva njiva. Glass and amber beads necklace.

karbonat dekahidrat) v primerjavi s pepelom halofitnih rastlin ne vsebuje dovolj kalija, so steklu dodali še stabilizatorje, kot so apnenec ($CaCO_3$) in školjke. Za obarvanje steklenih jagod so uporabljali različne kovinske pigmente, kot so baker (rdeče, turkizno in zeleno steklo), kobalt in nikelj (modro steklo), kositer (rumeno in belo steklo), krom, titan, arzen in antimon (rumeno in belo steklo), ter sredstva za motnjenje, kot sta kalcij in svinčev antimonat (bela in rumena barva) (Lončarić, Costa 2023, 3840–3841).

Značilne poškodbe steklenih jagod s Pezdirčeve njive so obsegale površinsko izločanje alkalnih komponent (tako imenovana dealkalizacija) – kot posledica pogostih ciklov vlažnosti, jamice, mehanske poškodbe različnih oblik in globin ter fine morfološke razpoke (*sl. 7*). Naštete patologije so posledica različnih pogojev med tisočletnim zakopom (prim. Aguaa et al. 2017, 129).

KONSERVATORSKO-RESTAVRATORSKI POSTOPKI

Pri čiščenju jagod iz stekla imamo omejeno izbiro primernih metod. Uporabljamo predvsem mehansko čiščenje in tampone z destilirano vodo, etanolom ali mešanico etanola in vode v razmerju ena proti ena. Običajno pri čiščenju najprej uporabimo mehanske metode, pri čemer so nam v pomoč različna orodja, kot

n. št., ko je zaradi političnih dogodkov v Egiptu dostop do natrona otežen, znova pa se začne pojavljati steklo iz rastlinskega pepela. Glej Knific, Šmit 2018, 376.

ash, natron flux[3] (sodium carbonate decahydrate) does not contain enough potassium, stabilisers such as limestone ($CaCO_3$) or mollusc shells were added to the glass. Glass beads were tinted using various metal pigments, for example copper (red, turquoise, and green glass), cobalt and nickel (blue glass), tin (yellow and white glass), chromium, titanium, arsenic, and antimony (yellow and white glass), and opacifying agents, e.g. calcium and lead antimonate (white and yellow) (Lončarić, Costa 2023, 3840–3841).

Most frequently encountered damage to the glass beads from Pezdirčeva njiva included: surface leaching of alkali (i.e. dealkalisation) – as a consequence of frequent humid cycles, pitting, mechanical damage of various shapes and depths, and fine morphological cracking (*Fig. 7*). These pathologies were caused by different conditions in the course of millennia under ground (cf. Aguaa et al. 2017, 129).

CONSERVATION-RESTORATION PROCEDURES

The choice of suitable cleaning methods for glass beads is limited. Primarily, mechanical cleaning is used, as well as tampons with distilled water, ethanol, or a 1:1 mixture of ethanol and water. Usually we start with

[3] Natron was sourced from sediments in dry Egyptian lakes. Natron glass prevailed for nearly a millennium, until the 7th century CE, when political events in Egypt resulted in obstructed access to natron, leading to the resurgence of plant-ash glass. See Knific, Šmit 2018, 376.

Sl. 10: Podzemelj, Pezdirčeva njiva. Predmeti iz brona in jantarja po zaključenih posegih.
Fig. 10: Podzemelj, Pezdirčeva njiva. Bronze and amber artefacts after the interventions have been completed.

so mehke ščetke, vatirane palčke, čopiči in podobno, s katerimi odstranjujemo ostanke zemlje. Če so jagode stabilne, lahko uporabimo tudi ultrazvočno kopel, ki ostanke zemlje v veliki meri odstrani tudi iz notranjosti jagod (*sl. 8, 9*).

SKLEP

Za kovinske predmete z grobišča na Pezdirčevi njivi v Podzemlju je značilno, da so bili prekriti z debelimi plastmi korozije. Delovanje kloridnih soli v zemlji je bilo intenzivno, posledice tega pa so bile izrazitejše predvsem pri železnih predmetih z dobro ohranjenim kovinskim jedrom. Skupni imenovalec predmetov iz jantarja in stekla je krhkost, ki je posledica tisočletnih ciklov vlaženja in sušenja v zemlji (*sl. 10*). Glede na slabo ohranjenost izkopanih predmetov je doktrina o varovanju nepremične arheološke dediščine pred nenujnimi, zaščitnimi terenskimi raziskavami vprašljiva (Hollesen 2022), saj z njo tvegamo izgubo dragocenih arheoloških predmetov. Konservatorsko-restavratorski posegi na tako poškodovanih predmetih zahtevajo izjemno veliko časa. Predmetom iz železa ter deloma tudi iz bakrovih zlitin moramo po posegih zagotoviti ustrezne pogoje hranjenja pri nizki relativni zračni vlažnosti (RH). To je povezano z velikimi finančnimi vložki in teh institucije, ki hranijo takšno gradivo, pogosto nimajo. Morebiti bi bila lahko rešitev v zgraditvi visokotehnoloških centralnih depojev z optimalnimi pogoji za hranjenje, s

mechanical methods, removing soil residues with the aid of soft brushes, cotton swabs, and fine brushes etc. If the beads are stable, we may employ an ultrasonic bath, which also largely removes soil residues from within the beads (*Figs. 8, 9*).

CONCLUSION

Metal artefacts from the Pezdirčeva njiva burial site in Podzemelj were characterised by thick layers of corrosion. Chloride salts in the soil were very aggressive and more pronounced on iron artefacts with well-preserved metal cores. The common denominator in the damage observed on amber and glass artefacts was fragility caused by millennia of alternating wet and dry conditions (*Fig. 10*).

The poor condition of the excavated artefacts contests the doctrine of safeguarding immovable archaeological heritage by avoiding non-vital rescue field research (Hollesen 2022), as it could result in loss of valuable archaeological artefacts. Conservation–restoration of artefacts in such poor condition is exceptionally time consuming. Even after the course of their treatment, iron artefacts, and to an extent also those made of copper alloys, require appropriate storage conditions at a low relative humidity (RH). This entails considerable financial investment, often surpassing the capabilities of the institutions charged with storing them. One potential solution may lie in the construction of high-tech central katerimi bi ohranili dragoceno arheološko dediščino tudi za prihodnje generacije.[4]

repositories, which would provide optimall storage conditions and ensuring the preservation of valuable archaeological heritage for future generations.[4]

[4] Kot vzorčni primer so lahko centralni depoji na Finskem, ki jih upravlja finska agencija za kulturno dediščino, koordinira pa Narodni muzej Finske. Glej Nemeček 2023b, 120.

[4] Central repositories in Finland can serve as a model example; they are managed by the Finnish Heritage Agency and coordinated by the National Museum of Finland. See Nemeček 2023b, 120.

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