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# Investigation on Metal Adornments From Ancient Eastern Europe

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This study focuses on the investigation of certain bronze adornment objects from the First Iron Age (the so-called middle Hallstatt period), dating to the ninth–eighth c. BC. These objects are part of a bronze and iron hoard (labeled Cx 116) discovered in the present Romanian territory, at Tărtăria–Podu Tărtăriei vest archaeological site, in Alba County. Along with a second hoard of bronze and iron objects, this represents a unique discovery for the present Romanian territory, namely, for the inner Carpathian area and the Lower and Middle Danube Basin, where no such votive discovery had been made by archaeological excavations. The objects, approximately 450 bronze and iron objects—weapons, tools, adornments, and harnesses—were found in the two hoards, in the Southern ditch, which outlines the archaeological site. Digital radiography has been used to assess the physical state of the objects and to identify potential specific craftsmanship details. It showed a fairly good preservation status, with incipient corrosion processes located in the core of some of the objects and some specific traces of the crafting process and subsequent mechanical defects were highlighted. The relatively good state of preservation of the objects can result from the fact that they had been protected from the humid environment by the ceramic vessel they were placed in. XRF and LIBS were used to identify the materials and to stratigraphically evaluate the objects. XRF scanned the surface of the objects, revealing elements related to both the raw material—a copper alloy with tin and lead, together with trace elements related to the specific mining location of the ores, and the depositional environment of the objects–such as iron. LIBS allowed a more in-depth stratigraphic analysis, which indicated a higher copper ratio—compared to iron—as the kinetic series advance, fact that sustains the idea that the major iron input was coming from the depositional environment. Both XRF and LIBS results were consistent with high elemental variability, probably due to the nature of the original material and the influence of the deposition soil conditions.

**Keywords: archaeological bronze hoard, Bîlvăneşti-Vinţ series, X-ray fluorescence spectroscopy, laser-induced breakdown spectroscopy, digital radiography**



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## INTRODUCTION

### Archaeological Site

The study focuses on the investigation of certain bronze adornment objects from the First Iron Age (the so-called Hallstatt period), dating to the ninth–eighth c. BC. These objects are part of a very large bronze and iron hoard (labeled Cx 116), one of two such hoards, discovered in the present Romanian territory, at Tărtăria–Podu Tărtăriei vest archaeological site, in Alba County, along the Mureş river valley (**Figure 1**). This represents a unique discovery for the present Romanian territory, namely, for the inner Carpathian area and the Middle and Lower Danube Basin, where no such votive discovery had been made by archaeological excavations. The objects were found in two hoards, in the southern ditch (which is the site's Southern limit). Numerous water infiltrations (possibly natural springs) were observed along the ditch's path, thus resulting in a constant humid environment. Taking into account the two discoveries subsequent to the moment of the Hallstatt period depositions, namely, a monetary treasure (second–first c. BC) and a Roman period brooch (Borş et al., 2013), one can formulate the hypothesis that this southern ditch was still visible (being an opened structure, namely, not clogged) about five centuries after the chronological horizon when the depositions were made (the Middle Hallstatt period–Ha $B_3$–C, ninth–eighth c. BC, the time of the Basarabi pottery style).

## Description of the Tărtăria I Hoard

The hoard Tărtăria I (Cx 116) is the largest and most complex deposit of bronze and iron objects of the so-called Bîlvăneşti-Vinţ series (the horizon of bronze hoards VI = DFS VI), preliminary dated to the Ha $B_3$–$C_1$ horizon, and the first one at this chronological level uncovered up to now throughout an archaeological excavation in this geographical area (the present Romanian territory and–most probably–of the Carpathian Mountains zone and the Middle and Lower Danube basin). It comprises more than 450 objects, preliminary inventoried up to now (it is expected that at the end of this post-excavation procedures, a larger number of objects will be identified than the estimated one for its total content): besides adornments and jewelry, harness objects, and weapons, there are also a series of small casting remains, as well as certain elements of organic materials (wolf teeth and a wild boar tusk), which were identified and provided samples for 14C dating. These new 14C data are very important since they allowed to place the moment of the deposition of Tărtăria I hoard during the last quarter of the ninth c. BC, thus contributing to new understanding about the chronology of the early phase of the Basarabi pottery style and the Bîlvăneşti-Vinţ bronze hoard horizon and to reopen the discussion in general about the chronology of the Fizeşu Gherlii–Vetiş and Bîlvăneşti-Vinţ bronze hoard horizons (DFS V–DFS VI) as suggested by Metzner-Nebelsick (Metzner-Nebelsick 2005). The observations concerning the objects part of this hoard are still preliminary, since there are other three "nuclei" of objects which were only recently dismantled in the specialized laboratory of the museum, part of which entered into a restoration process.

Both Tărtăria I and Tărtăria II hoards are depositions with special characteristics. Relatively similar in general (at least to a certain extent, from a chronological point of view, and partially from a typological point of view), they have a series of peculiarities regarding the "structure" of the deposition. Thus, the two hoards' compositions are diverse from a typological point of view, as indicated by the synthesis in **Table 1**.

## Archaeological Analogies

Regarding the adornments discovered at this site, it was possible to determine a series of preliminary analogies: for the torques—the similar finds from the hoard of Vaidei (or possibly a funerary inventory), Vinţu II, Coldău II and Bîlvăneşti (Petrescu-Dîmboviţa 1977) if to consider only the

**TABLE 1** | Composition of the two hoards.

| Category | Sub category | Hoards | |
|---|---|---|---|
| | | Tărtăria I | Tărtăria II |
| Weapons | Iron short swords (so-called *Kurzschwert*) | √ | — |
| | Iron spears | — | √ |
| | Iron daggers | √ | — |
| Tools | Iron socketed axes (so-called *Tüllenbeile*) | √ | — |
| | Iron double axes | √ | — |
| | Iron winged axes (so-called *Ärmchenbeile*) | √ | √ |
| | Iron small knifes | √ | — |
| Horse harnesses | A bridle mouthpiece | √ | — |
| | Links | √ | — |
| | *Phalerae* | √ | √ |
| | Buttons | √ | √ |
| | *Tutuli* | √ | √ |
| Adornments and jewelry | Various types of torques | √ | √ |
| | Various types of bracelets (simple, spiral ones, with open endings, for both arm and foot) | √ | √ |
| | Brooches (spectacles brooches–so-called *Brillenfibeln* and with nodosities) | √ | √ |
| | Various types of pendants | √ | √ |
| | Multispiral hairpins with single or double loop ("8" shape) endings (so-called *Lockenringe*) | √ | — |
| | Various types of beads | √ | — |
| | Saltaleoni | √ | √ |
| | A cone | √ | — |
| | A diadem | √ | — |

current territory of Romania, but there are other finds of this kind in the West Balkan area (Pabst 2012); for the spectacles brooches–the objects of this kind of the hoards Vinţu II and Vinţu III, to which one can add other finds from Banat, along the Danube valley and the West Balkan area (Pabst 2012); for the multispiral hair pins with single or double loop ("8" shape) endings—the similar objects found in the prehistoric settlement from Teleac or in the necropolis from Vajuga-Pesak (Popović et al., 1998); for the diadem—a series of similar finds uncovered in funerary contexts in the West Balkan area (Ložnjak Dizdar 2009).

## Scientific Approach

The analytical analysis of such objects can offer valuable information regarding the socio-economic development and


**FIGURE 1 | (A)** the position of Tărtăria archaeological site; **(B)** location of the archaeological material within the boundaries of archaeological site Tărtăria–Podu Tărtăriei vest.

the civilization level of specific settlements, as well as, when compared to other similar objects, highlight commerce routes. The aim of the study was to gain a better understanding of our ancestors' way of living, focusing on how and what their adornments were made from, by collecting information about the original material and their degradation following long-term storage in the ground. Thus, a broader perspective was sought on a selection of women's adornment objects. The importance of the study derives from the significance of the discovery made on the above-mentioned archaeological site, the hoards found here probably being the most complex findings of the Bîlvăneşti-Vinţ series from the Eastern part of Europe, in Romania, Hungary, Serbia and Croatia by size, typological diversity and structure, but also to the extent that certain artifacts pertaining to these two deposits of bronze and iron objects from Tărtăria do not have known close analogies. The purpose of the deposits is yet unclear, possibly being votive depositions in relation to ancient beliefs and customs. Copper and bronze were known to have been used for manufacturing of tools, weapons, and jewellery in many cultures, often being buried with the deceased (Krebs and Krebs 2003; Álvarez-Mon, Basello, and Wicks 2018). For our aim, non- and micro-invasive analysis techniques have been employed, so as to obtain both structural and compositional information: digital radiography (DR), X-ray fluorescence spectroscopy (XRF), and laser-induced breakdown spectroscopy (LIBS). These methods have proven useful during the last years for the understanding of metal objects (Figueiredo et al., 2011; Arafat et al., 2013; Fernandes, van Os, and Huisman 2013; Awasthi et al., 2016; Simileanu 2016; Nørgaard 2017; Chris and Vicky 2018).

## MATERIALS AND METHODS

The selected objects included bracelets, torques and a spectacle fibula, shown in **Figure 2**. Immediately after their discovery the objects were brought for restoration to the Metal Laboratory of the National History Museum of Romania. The objects have been selected based on the fact they were in a relatively good preservation state, showing a thin, relatively uniform patina on the surface, but also with more degraded areas. These objects are all different, and they can be related to a certain category of ancestors, probably belonging to the wealthier class of the society. Although copper and bronze were used for common objects, such as tools and weapons, they were also used for manufacturing jewels (Krebs and Krebs 2003). Adornments, especially such as bronze torques, which are rare, were a sign of wealth and a high social status (Rustoiu 1996).

A short description of the items is presented in **Table 2**, all part of Tărtăria I hoard.

Due to their importance and the fact that this discovery has no close spatial and temporal analogies (Borş et al., 2013), no sampling, and neither any mechanical nor solvent cleaning were performed on the objects prior to analysis. Only non- and micro-destructive methods were chosen for the imaging and compositional investigation: digital radiography (DR), X-ray fluorescence spectroscopy (XRF), and laser-induced breakdown spectroscopy (LIBS). Both XRF and LIBS are surface analysis methods, whose penetration depth can reach, according to the sample's features, mm or less (Denker et al., 2005; Noll 2012; Šatović et al., 2013; Fulminante and Unavane 2020).

DR images were recorded with ISOVOLT Mobile 160 complex computerized radiography station, using the integrated Rhythm RT data acquisition and storage software. The experimental parameters were set at 140 kV, 5 mA, for 30 s exposure time. Images were processed with Rhythm Review software.

XRF spectra were collected with the portable energy-dispersive X-ray fluorescence equipment, TRACER III-SD (Bruker), with ultra-thin Rh foil anode and high-resolution Silicon Drift Detector with typical resolution of 145 eV at 100,000 cps. The working regime was set to 40 kV, 10.60 μA, 60 s analysis time, no filter, air atmosphere. A second experimental setup (40 kV, 10.60 μA, 60 s analysis time, 12 mil Al + 1 mil Ti filter, air atmosphere) was used on some areas, with higher sensitivity for elements above Ca. This setup allowed a semi-quantitative interpretation of the data using specific calibration libraries. In both cases, peak identification was achieved with the ARTAX software. Post-processing and graphic visualization of data was performed using the normalized net count rates, with respect to the Rh Kα line, for each acquired spectrum, so as to eliminate


**FIGURE 2 |** Images illustrating the selected bronze adornment objects and their preservation state.

**TABLE 2 |** Short description of the investigated objects.

| Object | Description |
|---|---|
| 2972 | Decorated spiral bracelet<br>*L* = 42.5 cm; *D* = 7 cm; *W* = 145.57 g<br>Analogies: other three decorated spiral bracelets of the bronze and iron objects hoard Tărtăria I (unpublished)/references: (Borş and Rădvan 2019) |
| 2971 | "Spectacles" type brooch (*Brillenfibeln*)<br>Artifact part of the Tărtăria I bronze and iron objects hoard<br>$L_{total}$ = 18.0 cm; $L_{pin}$ = 11.5 cm; $L_{loop}$ = 2.7 cm; *D* = 8 cm; *W* = 317.26 g<br>Bronze; casting, smoothen, modeled/good state of preservation, restored<br>"Spectacles" type brooch (*Brillenfibeln*), made of a single thick bronze wire, with circular section; each flat side has a multispiral shape–9 coils, twisted concentrically from right to left. In the middle part is modeled an "8"-shape double loop, the wire having rhombic section. On the back is completely preserved the pin and the catching support. Traces of "noble" (ancient) patina, thin and uniform<br>Middle period of the first iron age (middle Hallstatt period), Bîlvăneşti–Vinţ horizon (series) of bronze hoards, 9th–8th/7th c. BC ($HaB_3$–C/DFS VI)<br>Analogies: Three brooches of the bronze hoard from Alba Iulia-Partoş (Petrescu-Dîmboviţa 1977); five brooches of the bronze hoard from Blandiana (Petrescu-Dîmboviţa 1977); two brooches of the bronze hoard from Bîlvăneşti (Petrescu-Dîmboviţa 1977); one brooch of the bronze hoard from Badacsonytomaj (Kemenczei 2005); one brooch of the bronze hoard from Kecel (Kemenczei 2005); three brooches of the bronze hoard from Šarengrad (Kemenczei 2005); six brooches of the bronze hoard from Vinţu III (Kemenczei 2005)/references: (Borş and Rădvan 2019) |
| 2951 | Torque with circular perforated ends<br>Artifact part of the Tărtăria I bronze and iron objects hoard<br>*L* = 52.4 cm; *D* = 17 cm; *W* = 158.67 g<br>Bronze; casting, smoothen/good state of preservation, restored<br>Torque with circular ends, perforated, made of bronze bar with rhombic section (on one third of the diameter) toward the end, while on the other part having circular section and pseudo-twisted decor. Traces of "noble" (ancient) patina, thin and uniform<br>Middle period of the first iron age (middle Hallstatt period), Bîlvăneşti–Vinţ horizon (series) of bronze hoards, 9th–8th/7th c. BC ($HaB_3$–C/DFS VI)<br>Analogies: One torque of the bronze hoard from Alba Iulia–Partoş (Petrescu-Dîmboviţa 1977); at least two torques from the bronze hoard from Coldău II (Petrescu-Dîmboviţa 1977)/references: (Borş and Rădvan 2019) |
| 2952 | Torque with "T"-shape ends<br>Artifact part of the Tărtăria I bronze and iron objects hoard<br>*L* = 60.5 cm; *D* = 20 cm; $h_{end}$ = 2.0 cm; *W* = 438.36 g<br>Bronze; casting, smoothen/good state of preservation, restored<br>Torque with "T"-shape ends, made of bronze bar with rhombic section (on one third of the diameter) toward the ends, while the other part with circular section. Pseudo-twisted décor on 2/3 of the diameter, while on the parts toward the ends an incised décor–5 groups of hatched triangles, situated antithetical, with the points toward the interior. Traces of "noble" (ancient) patina, thin and uniform<br>Middle period of the first iron age (middle Hallstatt period), Bîlvăneşti–Vinţ horizon (series) of bronze hoards, 9th–8th/7th c. BC ($HaB_3$–C/DFS VI)<br>Analogies: two torques of the bronze hoard from Kecel (Kemenczei 2005); one torque of the bronze hoard from Šarengrad (Kemenczei 2005)/references: (Borş and Rădvan 2019) |
| 2941 | Simple torque<br>Artifact part of the Tărtăria I bronze and iron objects hoard<br>*L* = 42.0 cm; *D* = 15.5 cm; *W* = 84.46 g<br>Bronze; casting, smoothen/good state of preservation, restored<br>Simple torque made of a bronze bar with circular section. Decorated, on the entire length, with groups of short incisions, oblique and in vertical "V" shapes (oriented alternatively toward left and toward right). Light traces of deterioration on the object's surface. Traces of "noble" (ancient) patina, thin and uniform<br>Middle period of the first iron age (middle Hallstatt period), Bîlvăneşti–Vinţ horizon (series) of bronze hoards, 9th–8th/7th c. BC ($HaB_3$–C/DFS VI)<br>Analogies: other two simple torques of the bronze and iron objects hoard Tărtăria I (unpublished)/references: (Borş and Rădvan 2019) |

(Continued in next column)

some of the uncertainty coming from the experimental setup and the inhomogeneous nature of the objects (Pollard and Heron 2008).

LIBS data were recorded with a custom-made system, including a Nd:YAG Q-switched laser (Quanta Systems), with iStar ICCD camera and Mechelle spectrometer (Andor). The operating parameters were set to 355 nm wavelength, 3 μs delay, 9 μs gate width, 240 gain, 350–400 att. Multiple pulse stratigraphy was recorded in each case, considering the features of object, between 50–150 pulses. Collected data were post-processed using the principal component analysis tool (OriginLab OriginPro v2020b).

## RESULTS AND DISCUSSION

The digital radiographs (**Figure 3**) showed that all pieces were in a fairly good conservation status. The analysis of the acquired images highlighted the manufacturing technique of the objects and the problems arising from the corrosion of the metal. Although it can be noticed that the halo effect appears in the radiographs, the selected working regime allowed obtaining information regarding the metal core, while still accurately preserving the shape of the objects, including the surface decorative incisions. Although for some of them there are areas with visible surface corrosion layer, of various thickness and color, and in some points, even rusted areas, the inner metal core appears to be in a pretty good status, in all cases. The "spectacles" brooch shows some minor cracks through the metal wire, most probably due to the manufacturing technique, as well as mechanical defects, surface accidents, and, possibly, corrosion deposits between spires. Incipient corrosion processes are highlighted in objects 2952 (at the torques' heads) and 2951 (near the head and in the middle of the torques).

Although the depositional environment had a high degree of humidity due to the multiple underground springs, the DR results indicated that the objects investigated in this study and their metal cores were in a fairly good state of preservation. A


**FIGURE 3 |** DR images of the bronze adornments.

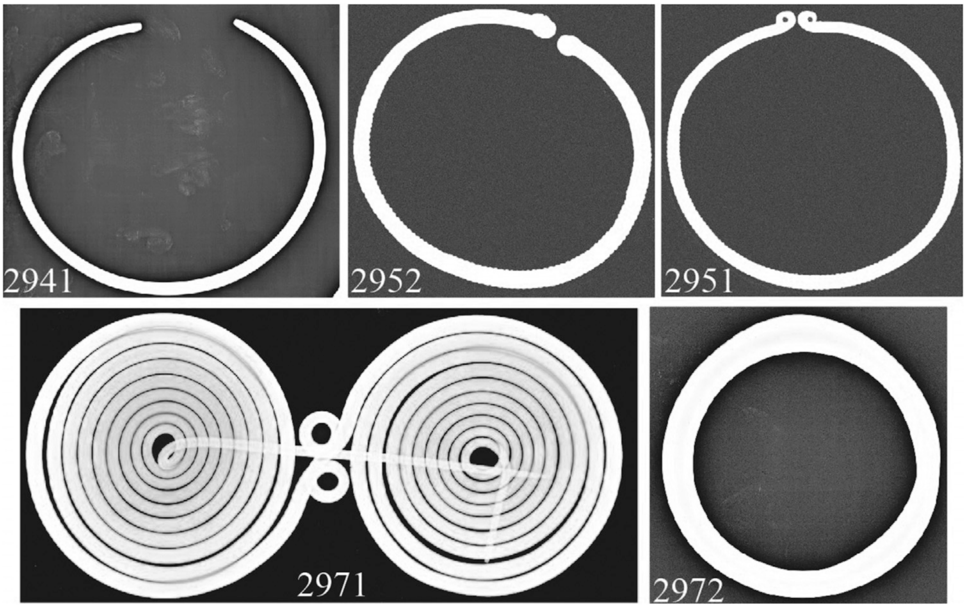


**FIGURE 4 | (A)** photograph of the metal hoard Cx116; **(B)** detail.

possible explanation would be the fact that they were not found as singular objects, but as a nucleus, an amalgam of soil with bronze objects in a ceramic vessel (see **Figure 4**), acting as a protective shield.

The XRF and LIBS analyses were only limited by the shape and dimensions of the objects, resulting in a total of 21 areas for XRF and 12 areas for LIBS, as illustrated in **Figure 5**, showing XRF point locations in white dots, and LIBS point locations in yellow dots.

A short description of each analysis area is included in **Table 3**. Analysis areas were chosen so as to cover the entire range of corroded, rusted, and exposed metal (most representative for the bulk material) parts of the objects.

Upon visual examination, it is obvious that the surface layer of the objects has variable thickness and composition. The objects are mostly covered with surface patina, of varying color, with small areas where the core metal can be seen, some of them also showing rust. In case of objects buried for such a long time, there is a two-way shift of elements, from the burial environment to the object, and the other way around, promoting several degradation processes, which lead to the formation of the so-called secondary and tertiary patina layers (Di Turo 2020). Thus, information can

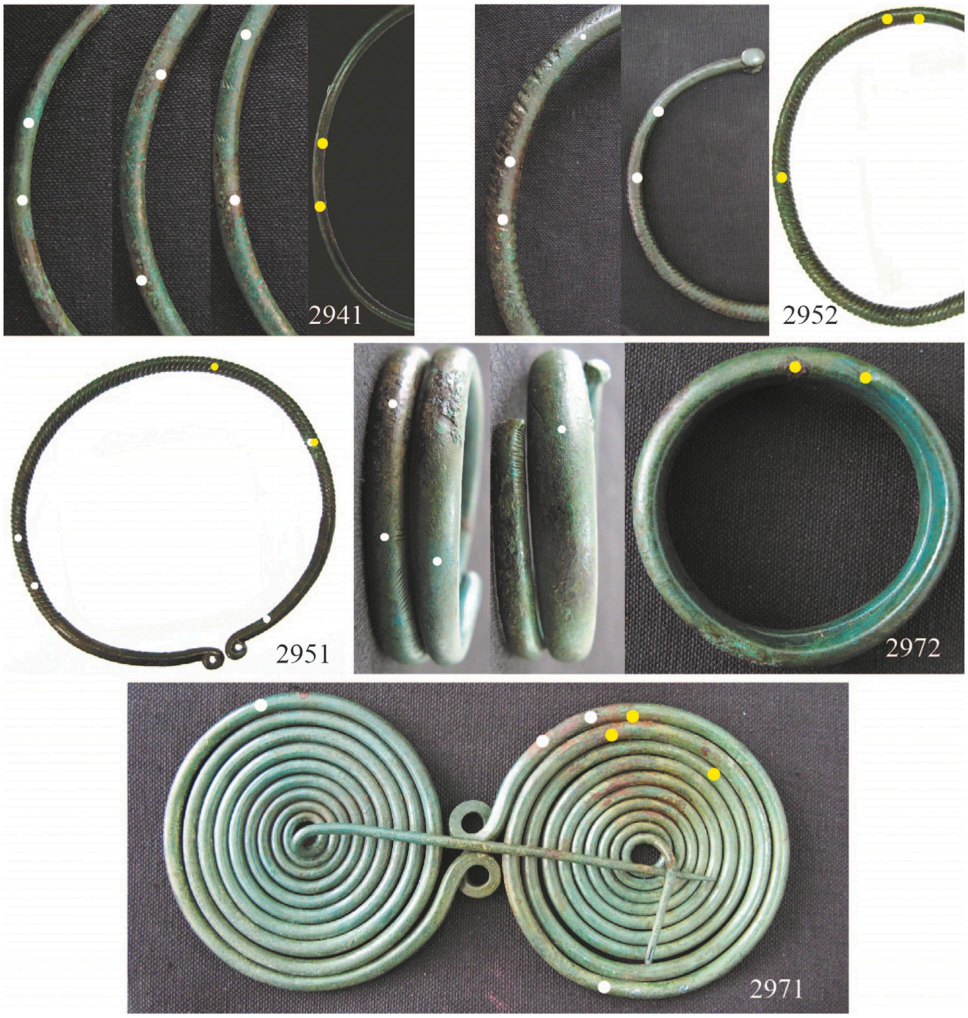


**FIGURE 5 |** Location of the analysis areas. XRF areas are marked with white circles and LIBS areas are marked with yellow circles.

be retrieved not only about the metal itself, but about the deposition ground also. Furthermore, until recently it was believed that the corrosion processes are only active while the object is buried in the soil. However, it was recently evidenced that the characteristics of the burial soil, together with the storage conditions after excavation, can play an important role in the reactivation of these corrosion processes (Rémazeilles et al., 2020). The compactness of the patina suggests the lack of carbon compounds (Petean and Arghir 2012), while the diversity of corrosion products can be the result of higher concentration of soil elements, such as chlorine, phosphorous or oxygen (Graziani et al., 2020; Ingo et al., 2020). The range of colors at the surface suggests the presence of several degradation and soil-derived products, such as: cuprite ($C_{u2}O$), tenorite (CuO), cassiterite ($SnO_2$), spertiniite (Cu(OH)), mushistonite ($CuSn(OH)_6$), goethite (FeO(OH)) (Petean and Arghir 2012; Manso et al., 2015). XRF results are consistent with these assumptions. Several elements were identified in the spectra, some of which can be linked to the bronze, others to depositional inputs. The weight percent of the identified elements was calculated using custom calibrations of the XRF equipment and are listed in **Table 4**, after eliminating outliers given by the higher inhomogeneity in some of the analysis spots. Although some of the copper concentration values might seem strangely small, the complete mineralization of copper into by-products and the amount of non-detectable elements can drastically reduce the copper concentration of the original material (Bonizzoni 2015). Elements, such as Cu or Sn, can also migrate from the metal core to the surface of the objects, in certain conditions, leading to a depletion in the original metal and selective increase at the surface (Schweizer 2007; Di Turo 2020).

The major element found in all spectra was copper, followed by tin and variable amounts of iron and lead. Similar composition was found for other objects of this hoard, as well, but which showed a thick corrosion layer (Radvan et al., 2016). Given that lead does not usually occur with copper ores more than in trace amounts, its identification may point toward a deliberate

**TABLE 3 |** Short description of the analysis areas.

| | | 2941 | 2952 | 2951 | 2971 | 2972 |
|---|---|---|---|---|---|---|
| XRF | 1 | Green, light green | Dark green | Brown, blue-green | Rust | Brown, black, small areas of exposed metal |
| | 2 | Brown, rust, small areas of exposed metal | Brown | Brown, dark green | Dark green, black, rust | Dark green |
| | 3 | Green-yellow | Brown | Brown, dark green | Light green | Intense green |
| | 4 | Green | Brown, small areas of exposed metal | Brown, dark green, light green | Intense green | Intense green, black, green-yellow |
| | 5 | Brown-green | Green | — | — | — |
| | 6 | Brown, small areas of exposed metal | — | — | — | — |
| LIBS | 1 | Brown, small areas of exposed metal | Crater | Brown, dark green | Rust | Rust |
| | 2 | Brown-green | Green | Brown, dark green, light green, near XRF-4 | Rust, green | Intense green |
| | 3 | — | Brown | — | Light green | — |

**TABLE 4 |** Concentrations of the main XRF-identified elements.

| | Concentration (wt%) | | | |
|---|---|---|---|---|
| | **Cu** | **Sn** | **Pb** | **Fe** |
| 2941-1 | 71.63 | 16.83 | 1.00 | 2.40 |
| 2941-3 | 60.90 | 8.86 | 0.92 | 15.46 |
| 2941-4 | 76.40 | 13.35 | 0.46 | 3.24 |
| 2951-1 | 47.76 | 23.99 | 3.57 | 13.91 |
| 2951-3 | 75.37 | 16.47 | 3.22 | 1.86 |
| 2951-4 | 80.24 | 9.63 | 2.67 | 2.77 |
| 2952-1 | 80.27 | 10.73 | 2.27 | 1.39 |
| 2952-2 | 54.77 | 19.65 | — | 6.29 |
| 2952-3 | 23.68 | 37.93 | — | 12.15 |
| 2952-4 | 67.56 | 15.11 | 2.49 | 5.77 |
| 2952-5 | 81.65 | 10.61 | 2.17 | 1.61 |
| 2971-1 | 58.14 | 18.76 | — | 2.52 |
| 2971-2 | 60.85 | 17.37 | — | 3.00 |
| 2971-3 | 63.68 | 15.65 | — | 3.14 |
| 2971-4 | 62.66 | 15.46 | — | 4.06 |
| 2972-1 | 25.24 | 5.44 | 2.60 | 48.71 |
| 2972-2 | 58.53 | 7.47 | 4.17 | 14.17 |
| 2972-3 | 67.86 | 9.32 | 1.47 | 8.34 |

Additionally, trace amounts of Co, Zn, As, Bi, Ag, Sb, S, Si, Ti have been identified in the spectra, which may be linked to the copper ores used (Carcea et al., 2006), and help identify the source of the objects, if compared to other similar objects, from different hoards/locations.

From the XRF data which were normalized to the corresponding Rh Kα line, some ratios were calculated, between the main identified elements, shown in **Figure 6**. The Pb:Cu ratio varies highly from point to point. Object 2971 shows a consistently higher Pb content as compared to Cu, contrasting to object 2952, for example, which shows the highest variability of this ratio, and also of the Sn:Cu ratio, indicating important surface morphological changes. On the other hand, tin appears rather constant as compared to lead, with the exception of two analysis areas on object 2972, which have much more lead as compared to tin, in this case.

Most of the areas showed small amounts of Fe, as compared to the main element, copper, but there were some areas in which the iron content was higher. While most Fe:Cu ratios were generally below 0.01, considerably higher ratios were calculated for some of the spectra acquired from objects 2941, 2951, and 2972, consistent with a darker, brown aspect. Iron provenance may be explained in several ways. It can either be linked to the type of copper ore used as raw material (calcopirite and bornite are

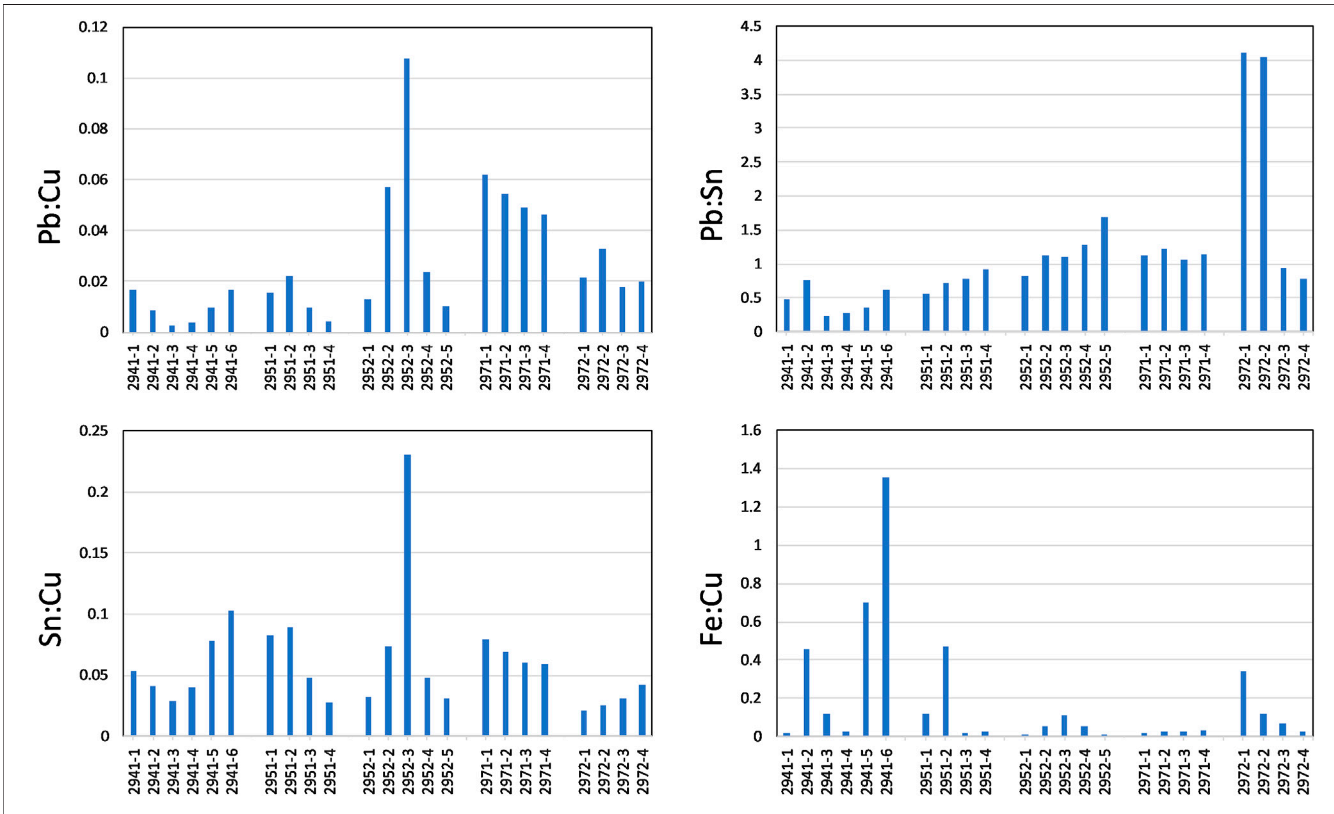


**FIGURE 6 |** Elemental ratios.

addition, a practice of the Late Bronze Age in the European area (Scott and Schwab 2019). However, such small lead concentrations as those identified here are more consistent with impurities of the copper ores (Scott and Schwab 2019).

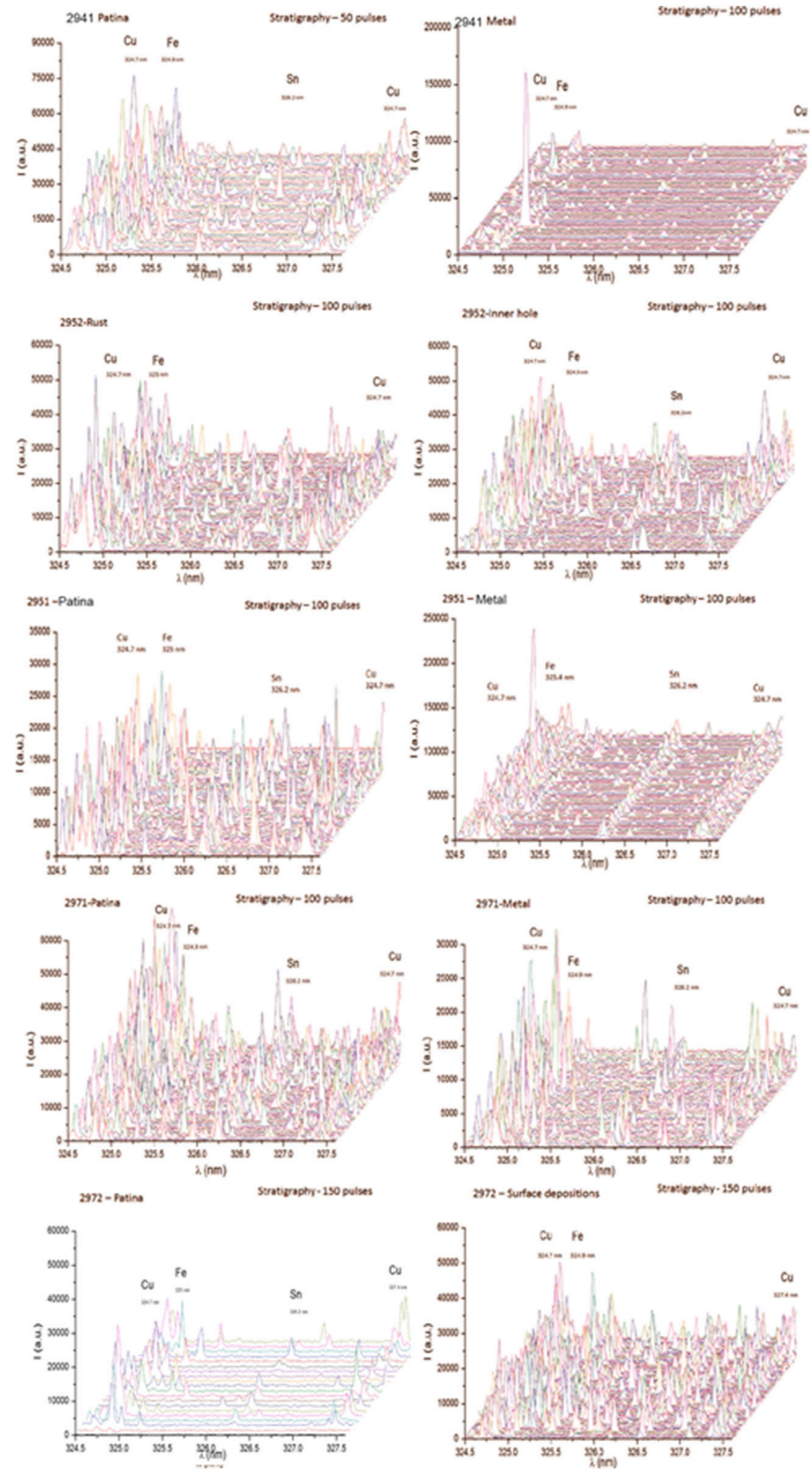


**FIGURE 7 |** LIBS spectra of the bronze adornments.

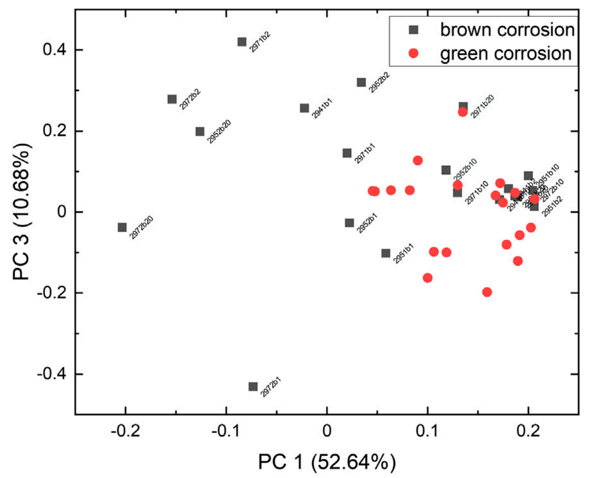


**FIGURE 8 |** PCA loadings plot of PC1 vs. PC3.

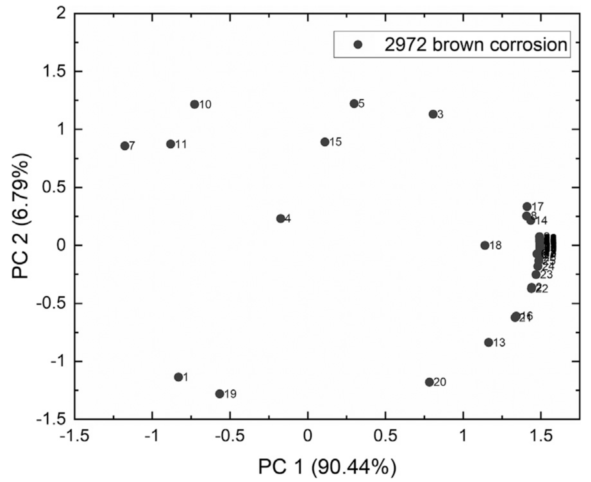


**FIGURE 9 |** Loadings plot of PC1 vs PC2 for the brown corrosion on object 2,972, 100 pulses.

copper ores rich in iron (Carcea et al., 2006)), or to the specific manufacturing process (the Dacian craftsmen worked with both bronze and iron in the same workshop (Rustoiu 1996)), or to the migration processes occurring between bronze and iron objects buried together and post-depositional processes in the soil matrix (Fernandes et al., 2013).

The trace elements all had small ratios as compared to the main element, Cu, typically below 0.03, with the exception of sulfur, which showed ratio values ranging from 0.2 to a minimum of 0.02 (**Supplementary Material**).

The LIBS spectra revealed a more homogeneous elemental distribution inside the object, in the metal core, as compared to the surface layer, which appears more heterogeneous. This is reflected by the noisier spectra, bearing the mark of the depositional environment's features and the chemical transformations having occurred during the conservation of the objects in the soil matrix (**Figure** 7). The LIBS distributions indicate a higher Cu:Fe ratio in depth as compared to the surface layer. This might sustain the idea inferred by the XRF results that the major iron input is from the environment and not from the original material. Tin also shows higher concentration on the outer layers as compared to the bulk metal, indicating metal depletion.

Following the collection of the LIBS data, post-processing was performed using Principal Component Analysis (PCA), in order to discriminate the kinetic series and to inspect the most prominent variables that will allow low-scaling the numerous data acquired and a deeper visualization of the two main areas of interest: uniform green patina and brown corrosion.

Firstly, PCA was performed for all the objects using the data from 1, 2, 10, and 20 kinetic series, in order to evaluate the stratigraphic disposure. **Figure 8** illustrates the loading plot of PC1 vs. PC3, for brown (b) and green (g) corrosion areas from all objects, after 1, 2, 10, and 20 pulses. As can be observed, the data corresponding to the green areas (g) tend to cluster, as the data coming from the brown areas present a quite irregular display, mostly for the first pulses. The most distant objects from the cluster appear to be 2971 and 2972 (for the brown corrosion point of view).

Thus, in **Figure 9** is depicted the loading plot for the first two principal components PC1 and PC2, for the complete stratigraphic data collected on the brown corrosion area of object 2792, namely 100 kinetic series. Greater inhomogeneity is revealed within the first 20 pulses. After the 21st pulse, the data appear more homogenous, probably a result of the fact that the laser pulse has gone through the brown corrosion layer and reached the core of the object. This can be correlated to the higher Pb ratio that was determined using XRF analysis, and we can conclude that the elemental matrix for 2792 and, probably for 2791 also, differs from the other pieces, thus they may have been manufactured in a different batch from the other objects.

The PCA indicates a fairly good differentiation between the brown and green corrosion areas which have been analyzed. Overall, as indicated by the XRF analysis, the green areas are characterized by higher copper input, while the brownish areas show more iron. Moreover, given the fact that the points collected in-depth (after 10 and 20 pulses) for the brown areas are grouped together with the green-looking areas, it is obvious that for the brown areas, copper concentration is higher deeper in the stratigraphy than at the surface of the object.

Overall, elemental characterization proved valuable, since burial of metal objects for such a long period of time yields complex effects on the objects, which cannot be fully understood by taking into account just the features of the burial environment (Scott 2002).

## CONCLUSION

Five adornment objects from the Tărtăria I hoard, Romania, belonging to the Middle period of the First Iron Age, have been investigated with imagistic and elemental characterization methods: digital radiography, X-ray fluorescence spectroscopy, and laser-induced breakdown spectroscopy. Digital radiography showed a fairly good preservation status, with incipient corrosion processes of the core of some of the objects, and traces of the manufacturing process and subsequent mechanical defects in others. The good preservation state of the objects was an interesting aspect, and, probably the result of the depositional peculiarities—the amalgam of soil, iron and bronze objects within a ceramic vessel, acting as a protective shield, against accelerated degradation which could have been caused by the humid environment sustained by the multiple underground water sources.

The combination of XRF with LIBS was useful in overcoming the intrinsic nature of the raw material and the inhomogeneity induced by the surface layers, offering a better understanding regarding the effects induced by long-term storage in the ground, reflected by the varying patina. Non-invasive X-ray fluorescence spectroscopy revealed elements related to both the raw material, and to the depositional environment of the objects (such as iron). The raw material was identified as a copper alloy with various amounts of tin and lead, along with traces of other elements, such as Co, As, Ag, Zn, or Bi. The results were consistent with those obtained for other pieces of these hoards which had been previously investigated. Although the high iron input could have been explained in several ways, the LIBS multi-pulse stratigraphy revealed higher copper content in depth as compared to the iron content, which sustained the idea that the major iron input was coming from the depositional environment.

Not surprisingly, all elements showed high variability, which was accounted by a combination of factors: the inhomogeneous nature of the original material, the migration of elements which lead to the depletion of the metal core and selective increase of some element's concentration at the surface of the objects, under the influence of the soil conditions.

## DATA AVAILABILITY STATEMENT

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

## AUTHOR CONTRIBUTIONS

LG designed the work; collected, processed and interpreted XRF data and led the writing of the manuscript; MD performed LIBS spectroscopy, helped with the interpretation of the results and writing of the paper; LMA performed the DR analysis; CB provided access to the investigated items and helped in writing of the paper from an archaeological point of view; RR coordinated the data collection and supervised the preparation of the manuscript; IMC helped in collecting and processing XRF data. All authors read and approved the final manuscript.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmats.2020.600913/full#supplementary-material.

## REFERENCES


Álvarez-Mon, J., Basello, G. P., and Wicks, Y. (2018). *The elamite world*. New York, NY: Taylor & Francis Group.

Arafat, A., Na'es, M., Kantarelou, V., Haddad, N., Giakoumaki, A., Argyropoulos, V., et al. (2013). Combined *in situ* micro-XRF, LIBS and SEM-EDS analysis of base metal and corrosion products for islamic copper alloyed artefacts from umm qais museum, Jordan. *J. Cult. Herit.* 14, 261. doi:10.1016/j.culher.2012.07.003

Awasthi, S., Kumar, R., Rai, G. K., and Rai, A. K. (2016). Study of archaeological coins of different dynasties using libs coupled with multivariate analysis. *Optic Laser. Eng.* 79, 29–38. doi:10.1016/j.optlaseng.2015.11.005

Bonizzoni, L. (2015). ED-XRF analysis for cultural heritage: is quantitative evaluation always essential?. *J. Phys.: Conf. Ser.* 630, 012001. doi:10.1088/1742-6596/630/1/012001

Borş, C., Irimuş, L., Rumega, V., Dobrotă, S., and Rişcuţa, C. (2013). Un nou sit de tip Basarabi. Raport preliminar asupra cercetărilor arheologice preventive la Tărtăria-Podu Tărtăriei vest (campania 2012). *Cercetări Arheologice* 20, 9–102. doi:10.46535/ca.20.01

Borş, C., and Rădvan, R. (Editors) (2019). Meşteşug şi prestigiu: depozitele hallstattiene de Obiecte din bronz şi fier de La Tărtăria. Documentarea unei colecţii (I)/craft and prestige: the Hallstatt period hoards of bronze and iron objects from Tărtăria. Documenting a collection (I). Brăila: . Editura Istros.

Caple, C., and Garlick, V. (2018). Identification and valuation of archaeological artefacts: developments using digital X-radiography. *J. Inst. Conserv.* 41, 128–141. doi:10.1080/19455224.2018.1464487

Carcea, I., Roman, C., and Chelariu, R. (2006). *Ingineria proceselor metalurgice (in Romanian)*. Iasi: Editura Performantica.

Chris, C., and Vicky, G. (2018). Identification and valuation of archaeological artefacts: developments using digital X-radiography. *J. Inst. Conserv.*

Denker, A., Bohne, W., Opitz-Coutureau, J., Rauschenberg, J., Röhrich, J., Strub, E. (2005). Influence of corrosion layers on quantitative analysis. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* 239, 65–70. doi:10.1016/j.nimb.2005.06.180

Di Turo, F. (2020). Limits and perspectives of archaeometric analysis of archaeological metals: a focus on the electrochemistry for studying ancient bronze coins. *J. Cult. Herit.* 43, 271–281. doi:10.1016/j.culher.2019.10.006

Fernandes, R., van Os, B. J. H., and Huisman, H. D. J. (2013). The use of hand-held XRF for investigating the composition and corrosion of roman copper-alloyed artefacts. *Herit. Sci.* 1, 30. doi:10.1186/2050-7445-1-3010.1186/2050-7445-1-30

Figueiredo, E., Araújo, M. F., Silva, R. J. C., Senna-Martinez, J. C., and Inês Vaz, J. L. (2011). Characterisation of late bronze Age large size shield nails by EDXRF, micro-EDXRF and X-ray digital radiography. *Appl. Radiat. Isot.* 69,1205–1211. doi:10.1016/j.apradiso.2011.04.027

Fulminante, F., and Unavane, M. (2020). "Community practices" and "communities of practice" in smelting technology by XRF analysis of

Archaic bronze votive figurines in central Italy (6th–5th centuries BC). *J. Archaeol. Sci.: Report* 31, 102266. doi:10.1016/j.jasrep.2020.102266

Graziani, V., Iorio, M., Albini, M., Riccucci, C., Di Carlo, G., Branchini, P., et al. (2020). Metals and environment: chemical outputs from the interaction between gilded copper-based objects and burial soil. *Front. Mater.* 7. doi:10.3389/fmats.2020.00032

Ingo, G. M., Albini, M., Bustamante, A. D., del Pilar Zambrano Alva, S., Fernandez, A., Giuliani, C., et al. (2020). Microchemical investigation of long-term buried gilded and silvered artifacts from ancient Peru. *Front. Mater.* 7. doi:10.3389/fmats.2020.00230

Kemenczei, T. (2005). *Funde ostkarpatenländischen Typs im Karpatenbecken*. Stuttgart, Germany: Franz Steiner Verlag.

Krebs, R. E., and Krebs, C. A. (2003). *Groundbreaking scientific experiments, inventions, and discoveries of the ancient world*. Westport, CT: Greenwood Press.

Ložnjak Dizdar, D. (2009). *Grobovi uglednica mlađe faze culture polja sa žarama u sjevernoj Hrvatskoj. Prilog poznavanju ženske nošnje kasnog brončanog doba na prostoru južne Panonije,* VAMZ – Vjesnik Arheološkog Muzeja u Zagrebu, 3.s., XLII, 2009, 157–182.

Manso, M., Schiavon, N., Queralt, I., Arruda, A. M., Sampaio, J. M., and Brunetti, A. (2015). Alloy characterization of a 7th century BC archeological bronze vase—overcoming patina constraints using Monte Carlo simulations. *Spectrochim. Acta B Atom Spectrosc.* 107, 93–96. doi:10.1016/j.sab.2015.03.001

Metzner-Nebelsick, C. (2005). "Despre importanţa cronologică şi cultural-istorică a depozitelor din România în epoca târzie a bronzului şi în epoca timpurie a fierului," in *Bronzefunde aus Rumänien II./Descoperiri de bronzuri din România II, 2005*, Editor T. Soroceanu (Bistriţa, Cluj-Napoca, Romania: Editura Accent).

Noll, R. (2012). *Laser-induced breakdown spectroscopy, fundamentals and applications*. Berlin, Germany: Springer-Verlag Berlin.

Nørgaard, H. W. (2017). Portable XRF on prehistoric bronze artefacts: limitations and use for the detection of bronze Age metal workshops. *Open Archaeol.* 3 (1). doi:10.1515/opar-2017-0006

Pabst, S. (2012). *Die Brillenfibeln. Untersuchungen zu spätbronze- und ältereisenzeitlichen Frauentracht zwischen Ostsee und Mittelmeer: marburger Studien zur Vor- und Frühgeschite 25.* Rahden, Germany: Verlag Marie Leidorf GmbH.

Petean, I., and Arghir, G. (2012). "Aspects concerning the composition of some bronze roman coins patina", in *A XII-a conferinta nationala multidisciplinara "profesorul dorin pavel-fondatorul hidroenergeticii romanesti"*. Bcureşti, Romania: Editura Agir.

Petrescu-Dîmboviţa, M. (1977). *Depozitele de Bronzuri din România.* Este dublată informaţia

Pollard, M. A., and Heron, C. (2008). *Archaeological chemistry*. 2nd Edn. Cambridge, United Kingdom: RSC Publishing.

Popović, P., Vukmanović, M., Vasić, M., and Borić-Brešković, B. (1998). *Vajuga-Pesak: nekropola starijeg gvozdenog doba*. Beograd, Serbia: Arheoloski Institut.

Rădvan, R., Borş, C., and Ghervase, L. (2016). Portable X-ray fluorescence investigation of certain bronze beads of hoard Tărtăria I and their specific corrosion. *Rom. J. Phys.* 61, 9–10.

Rémazeilles, C., Langlet-Marzloff, V., Creus, J., Lotte, G., Deshayes, C., Baleux, F., et al. (2020). Remarkable corrosion resumption of archaeological bronzes, induced by the oxidation of ternary Cu-Sn-S phases in atmosphere, after long-term burial with sulfides. *Corrosion Sci.* 175, 108865. doi:10.1016/j.corsci.2020.108865

Rustoiu, A. (1996). *Metalurgia bronzului La daci (sec. II î.Chr.—sec. I d.Chr.). Tehnici, ateliere şi produse de bronz.* Bucureşti, România: Bibliotheca Thracologica XV.

Šatović, D., Desnica, V., and Fazinić, S. (2013). Use of portable X-ray fluorescence instrument for bulk low corroded indoor bronzes. *Spectrochim. Acta B.* 89, 7–13. doi:10.1016/j.sab.2013.08.007

Schweizer, F. (2007). "Bronze objects from lake sites: from patina to "biography"," in *Ancient & historic metals: conservation and scientific research: proceedings of a symposium organized by the J.-Paul Getty Museum and the Getty Conservation Institute, November 1991*. Editors D. A. Scott, J. Podany, and B. B. Considine (Singapore: The J. Paul Getty Trust), 33–50.

Scott, D. A. (2002). *Copper and bronze in art: corrosion, colorants, conservation*. Los Angeles, CA: The Getty Conservation Institute.

Scott, D. A., and Schwab, R. (2019). *Metallography in archaeology and art*. Cham, Switzerland: Springer Science + Business Media, LLC.

Simileanu, M. (2016). Libs quantitative analyses of bronze objects for cultural heritage applications. *Rom. Rep. Phys.* 68, 1.

**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.