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An elemental exploration of the metal contents of an early 13th-century craft box from Lõhavere, using pXRF

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ABSTRACT

The craft box recovered from a 13th-century hillfort at Lõhavere, Estonia, contained a well-preserved selection of copper-alloy objects. The limited corrosion on these objects allowed a more accurate estimation of their compositions through non-destructive surface measurements. Using the resulting pXRF database, this study explored a possible correlation between the types of objects and their material composition. By comparing the most common contaminants with the alloying metals, a qualitative estimation of the material quality was conducted. The results showed that despite a considerable overlap between object types, the material composition differed based on the items' appearance and function. A shift from brass to bronze and tinned objects coincided with a greater availability of tin at the hillfort, as well as a rise in silversmithing. Moreover, objects with a silver appearance seemed to be more desirable in this period, apart from some high-status personal ornaments and traditional spiral tube decorations. The results possibly reflect different metalworking practices compared to earlier periods and contemporary sites. Some evidence of recycling is present among the spiral tubes, suggesting that they originated from different raw material sources, possibly removed from obsolete clothing. Alternatively, this could indicate a varying quality of imported copper-alloy, including wire, along the Hansa trade routes.

KEYWORDS

Final Iron Age, Livonia, pXRF, Hansa, archaeometry.

Introduction

The analysis of ancient metals and their alloys is a valuable pursuit in better understanding past technologies and crafts (e.g., Göbel 1842; Martinón-Torres et al. 2012; Pollard et al. 2015). However, this pursuit is often hindered by variations in the material properties of metals, especially on corroded objects recovered from archaeological contexts (Huisman et al. 2023). Nevertheless, a more comprehensive understanding of ancient metal composition can grant new insights into various aspects of metal use. The initial choice of raw materials by craftsmen can be better understood through an assessment of an object's properties, both in terms of production value to the maker and the popularity of the finished object with the end user. These choices can be further comprehended by exploring the nature of the ore sources and the contaminants present within ancient metals, especially copper-alloy objects. However, copper-alloy corrodes quite readily once buried, and corrosion often obscures the original alloy composition (Roxburgh et al. 2019, 56–58). In contrast, the craft box found at Lõhavere (Fig. 1: a; Rammo & Ratas 2018) contained a range of well-preserved metal objects, providing an opportunity to investigate alloy composition in metals with minor corrosion.

In ancient times, copper-alloy was initially produced by mixing copper with tin, resulting in a mixture we know as bronze. Some bronze alloys are known to be rich in arsenical copper, including numerous Bronze Age objects found in the Northern Caucasus and Lower Volga areas of Russia (Tylecoat 2002, 14). During the Roman period, a different copper-alloy, which we know today as brass, was introduced on an industrial scale (Craddock 1978; Unglick 1991; Morton 2019). This brass was manufactured using a different technique than for bronze (cementation, more specifically, zincification) and was made of copper metal combined with zinc. While brass seems to have diminished in popularity in Late Roman western Europe, evidence of the use of cementation to produce brass has been reported from Carolingian Dorestad (van Os 2012) and pre-1200 AD Dortmund (Rehren et al. 1993). Furthermore, mixtures of bronze and brass could also be produced (either deliberately or through recycling unsorted copper-alloy scrap), broadly referred to as gunmetal (Bayley & Butcher 2004, 14–16).

Pure copper is a soft material, with a low tensile strength. It is, however, highly malleable and ductile, which also makes it highly workable. Yet, trace level impurities, such as lead, antimony and copper oxide, would negatively affect its working properties. Tin was originally added to copper to improve its mechanical properties. Brass, on the other hand, was much easier to cast and cold work than bronze. A gunmetal mixture would have properties of both brass and bronze. Lead was also deliberately added to copper-alloy from Roman times onward. While the addition of lead had benefits in the casting and machining stages, its presence in quantities of over a few percent greatly reduces its strength and ductility (Staniaszek & Northover 1983). This is because lead is not soluble in copper-alloy, resulting in intergranular fractures when worked. This would, for

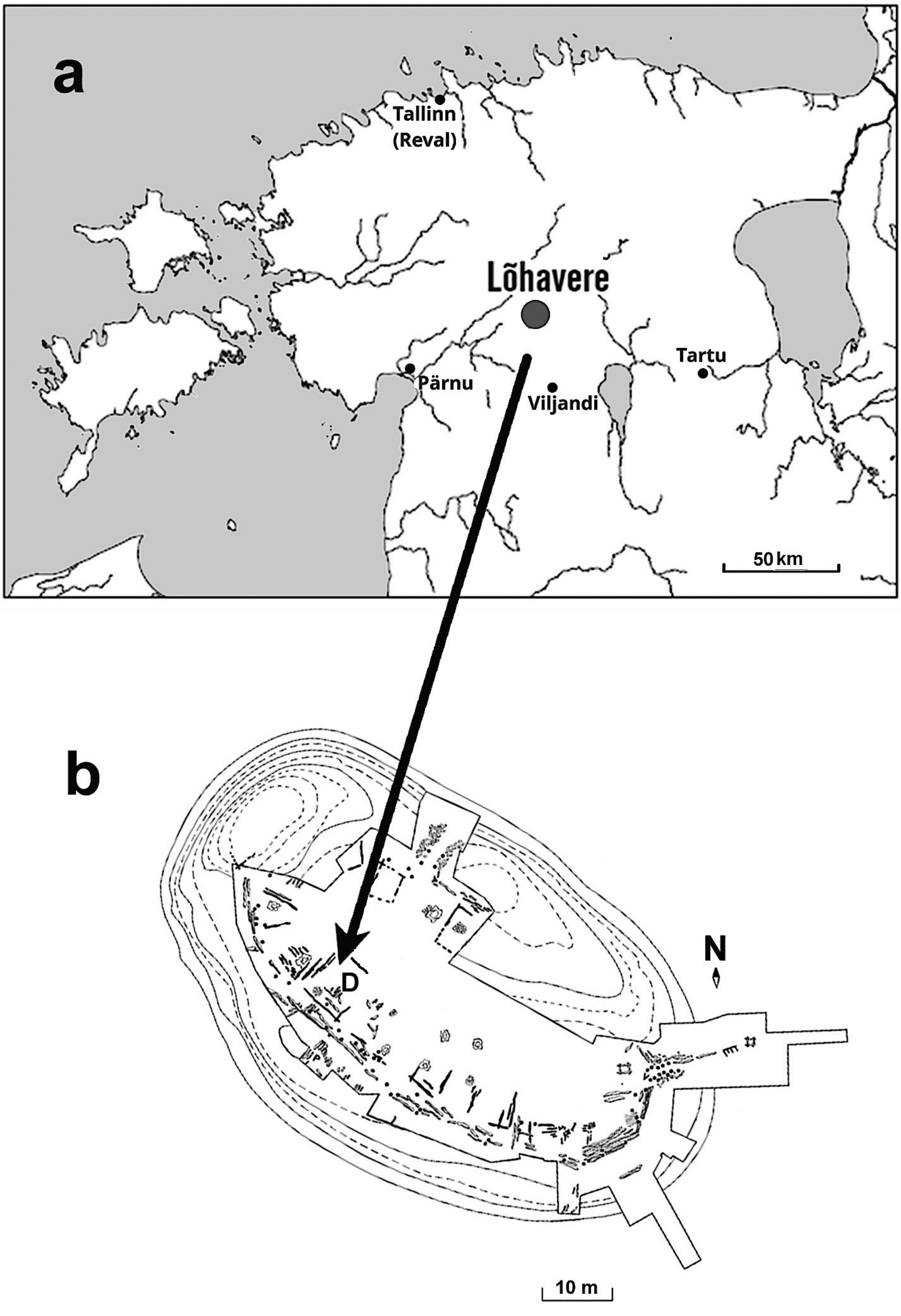

FIG. 1. Location of Lõhavere hillfort (a) and craft box in hillfort (b). The craft box was discovered inside the ruins referred to as House D (after Laul & Tamla 2014, 15, fig. 6; 11, fig. 1; 12, fig. 3). Map by Marcus Adrian Roxburgh.

example, reduce the ability to draw copper-alloy into wire form, as wire is prone to snapping at unwanted intervals. Dungworth (1997, 902) states that wire almost never contains more than 1% lead, while Bayley & Butcher (2004, 14) suggest that a few percent may be admissible.

Early craftsmen lacked the capability to measure the elemental composition of copper-alloy as we can today. Instead, they relied on assessing properties such as malleability, ductility, hardness and color, which, to a trained eye, gave a good understanding of what they were working with (ibid., 13). Pure copper was pinkish in color, while bronze exhibited a brownish tone that became paler the higher the tin content. Brass, characterized by a yellow color, took on a more gold-like tone with increased zinc content. The presence of lead in either alloy did not significantly affect the color.

It is also necessary to consider lost surface treatments in the form of tin or pewter (tin and lead) coatings (Oddy 1980; Meeks 1986; Tylecote 1986; Giumlia-Mair 2020). The popularity of such treatments first emerged in the Baltic region during the Roman Iron Age, being used to change the outward-facing color of objects from a yellowy gold to a silvery white (Bayley & Butcher 2004, 43; Bliujienė 2013, 360; Olli & Roxburgh 2018, 54–59). Application methods included rubbing the surface of a hot object with a tin or pewter rod, or dipping the object into a bath of molten tin or pewter. Treated surface is the first part of an object to corrode when it enters the ground, and while the residual tin or lead may remain within the corroded outer surface, it is no longer visible. This artificially elevated level of tin or lead can be detected by portable X-ray fluorescence (pXRF), potentially leading to an incorrect interpretation as bronze or high-tin gunmetal rather than the actual bulk metal. Another technique of using tin to create a more silver-like surface is deliberately forming tin "sweat" on the outside of an object during casting (Meeks 1986). This occurs because added tin above 12% is not soluble in copper-alloys, causing the excess tin to migrate to the surface, as the molten alloy cools. These techniques would change the surface color to a metallic white or grey, possibly in an attempt to mimic the color of silver.

The purity of copper ore is also relevant to the broader discussion of the value of copper-alloy objects, as demonstrated, for instance, in a study by Radivojević et al. (2018). Ore purity was determined based on the amount of arsenic and antimony present. At a cumulative level of >2% contamination of these elements, the ore would be considered less pure. These levels were comparable to the Fahlore type, known for its high impurities and overall lower quality (ibid., 28, 30). A cumulative minimum of 10% was set by Dardeniz (2020, 3–12) to account for possible intentional usage of these elements.

Previous research has shown that the corrosion process mainly involves the leaching of copper (decuprification) and zinc (dezincification), which can significantly impede quantitative measurement of an object's original composition (Robbiola et al. 1998, 2108; Chiavari et al. 2007). However, modern technology, such as X-ray fluorescence spectrometry (XRF), is now successfully employed using qualitative/semiquantitative methods on corroded outer surfaces (e.g., Martinón-Torres et al. 2012; Orfanou & Rehren 2015; Roxburgh 2023). This non-destructive technique is particularly effective for sorting large quantities of corroded objects broadly into brass, bronze and gunmetal categories, as well as providing insights into original lead levels and the presence of past surface treatments (Lillak & Roxburgh 2021). Therefore, the aim of this article is to investigate possible correlations between object type and composition in the personal decorations and tools found within a craft box from Lõhavere. Given the good condition and closed context of the large assemblage of metal objects in this craft box, we ask the following questions:

- What can be determined regarding the original choice of metals?
- What evidence exists for the use of tin-based surface treatments?
- What conclusions can be drawn regarding the types of ore contaminants present?

The craft box (Fig. 2: a) has been dated to the early 13th century, corresponding to the end of Estonia's Final Iron Age (1050–1225 CE; Rammo & Ratas 2018, 135). This era in Estonia was characterized by a new political power structure governed by kinship-based power centers that were based at hillforts (Lang & Laneman 2006, 127–130; Valk 2014, 334, 362). The end of this age witnessed conquest and an intensification of overseas trade. The region comprising present-day Estonia and Latvia, known as Livonia, was the last part of Europe to be Christianized through a series of religious crusades. Livonia quickly became a target for political and economic expansion by both German and Danish military orders (Kouzelis 2020, 34–37). In the same period, the Hansa or Hanseatic League started to dominate in Baltic trade. By the 12th century, it had expanded to include trading posts in Russia and the Baltic States, such as Novgorod, Riga and Reval (Tallinn), establishing connections with trade and production centers in northern and western Europe (Kuipers 2019, 16–25).

One of the Hanseatic League's member nations was the Germans, based at the newly formed Hanseatic trading post at Riga. They crusaded north, led by Albert, the Prince-Bishop of Livonia. This expansion brought southern Estonia, including the hillfort at Lõhavere, under Germanic Christian control. Danish crusaders under King Valdemar II defeated the northern Estonians in 1219 CE. This victory led to the establishment of Tallinn (which was already a busy commercial port) as the capital city (Kouzelis 2020, 28). Both conquests brought an intensification of trade with Christian Europe.

Estonia never had its own copper-alloy resources, so all new supplies had to be imported (Lang 2007, 115). During the Viking Age, Estonia sat along the East Way (*Austrvegr*), a vast long-distance trade route connecting the Baltic Sea region with eastern Europe, including the Russian and Ukrainian river systems (Tvauri 2012, 220). It is also known that Islamic states were a major supplier of silver along this route at that time (Saage 2020, 89). By the 13th century, the Hanseatic League dominated trade between the Baltic and North Sea regions

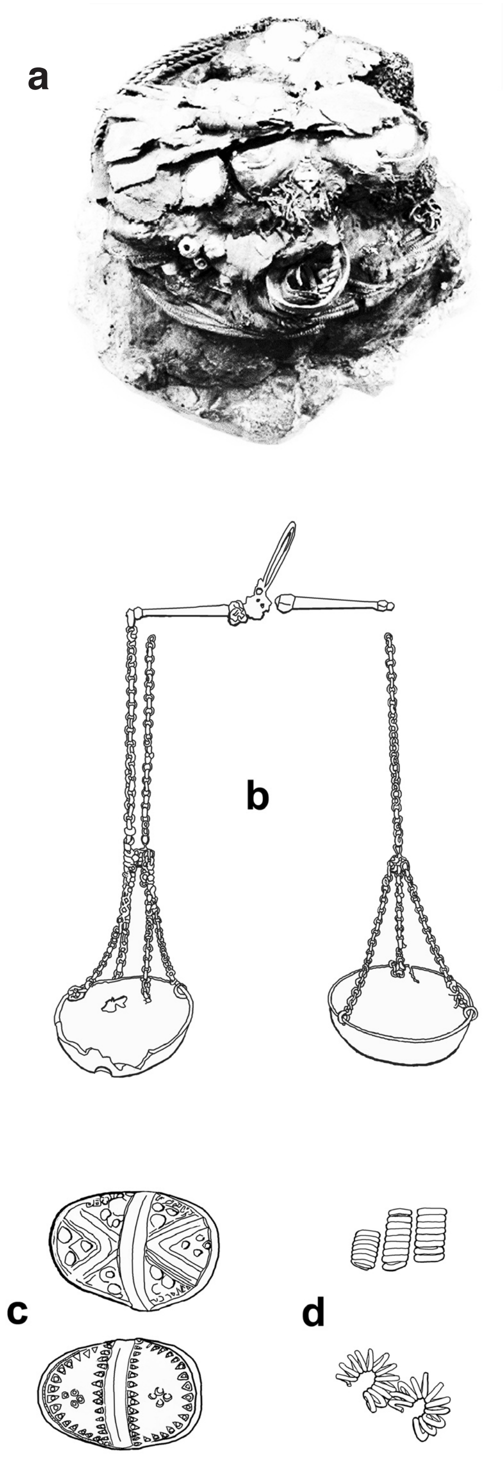

FIG. 2. a – craft box as it appeared upon recovery (after Laul & Tamla 2014, 15, fig. 6), b – scales, c – shield finger rings, d – straight and U-shaped spiral tubes. Drawn by Marcus Adrian Roxburgh.

(Kouzelis 2020, 49), suggesting that central European and Scandinavian non-ferrous metal sources (Harz in Germany, Falun in Sweden, and the Carpathian Gylnitz and Smolnik mines; Jahnke 2010, 56–57) as well as the Dinant copper and brass production centers (van Os 2012) were prominent. Many metallic trade goods, including wire, were documented (Kouzelis 2020, 65). Tin casting boomed across Europe at this time, due to increased tin mining. Evidence of a greater variety of tin items being produced in Estonia is also apparent during this period (Saage 2020, 114). The incorporation of Estonia into the Hanseatic world marked a shift in metalworking from hillforts to newly founded towns. The immigration of western craftsmen to these towns also introduced new metal casting techniques, witnessed by changing crucible shapes (ibid.).

The hillfort at Lõhavere is considered one of the more powerful centers in southwestern Estonia, as narrated in the Chronicle of Henry of Livonia (HCL; Lang & Laneman 2006, 133–134). Lõhavere hillfort came into use in the 11th century, and in the 12th century, it became one of the strongest fortresses in Sakala County (Rammo & Ratas 2018, 135). According to Henry, the castle was burned down three times: in 1211, 1215, and 1223 CE (HCL XV: 7, XVIII: 7, XXVII: 2).

The craft box was discovered during excavations by Harri Moora in 1958, concealed in the rubble of house D (Fig. 1: b; Laul & Tamla 2014, 100; Rammo & Ratas 2018, 135–136). House D is thought to have belonged to a high-status family, possibly of nobility (Laul & Tamla 2014, 100). The contents of the birch bark box consisted of a careful arrangement of jewelry items, ready-made decorations, patches of fabric, sewing tools, and a pair of scales (ibid., 100–102).

Amid this era of political strife, one begs the question who owned this box and which processes were involved in crafting its contents. To approach these questions, the material properties of the metal items are an important concern. Which metal compositions were preferred for specific types of objects, and why? Hence, in this paper, we aim to investigate whether a correlation exists between the types of objects and their material composition, the choice and quality of ores, and subsequently relate these factors to the social status of the owner.

Materials

The craft box yielded well over 1000 metal objects, which were subsequently narrowed down to 878 (Table 1) according to the criteria mentioned below. This selection includes hangers, neck rings, pendants, bracelets, beads, bell buttons, ringlets, links, a catch, a dismantled set of weigh scales (Fig. 2: b), finger rings (Fig. 2: c) and spiral tubes (Fig. 2: d), the latter being by far the most numerous objects present. Upon opening the box, the topmost layer mainly contained pieces of braided fabric bands and balls of yarn. Beneath this was a second layer of carefully arranged metal decorations, consisting primarily of ready-made spiral tubes (Rammo & Ratas 2016). The bottom layer contained most of the jewelry, along with a set of scales (Rammo & Ratas 2018, 137–140). A large number of

TABLE 1. Objects in the craft box discovered at Lõhavere hillfort by type and functional category

<table>
<tr><th>Object type</th><th>Count</th><th>Category</th><th>Count</th></tr>
<tr><td>Hangers</td><td>5</td><td rowspan="3">Single decorations</td><td rowspan="3">40</td></tr>
<tr><td>Neck rings</td><td>3</td></tr>
<tr><td>Pendants</td><td>32</td></tr>
<tr><td>Bracelets</td><td>8</td><td rowspan="2">High-stress single decorations</td><td rowspan="2">19</td></tr>
<tr><td>Finger rings</td><td>11</td></tr>
<tr><td>Beads</td><td>14</td><td rowspan="6">Mass-produced decorations</td><td rowspan="6">208</td></tr>
<tr><td>Bell buttons</td><td>2</td></tr>
<tr><td>Catch</td><td>1</td></tr>
<tr><td>Links</td><td>5</td></tr>
<tr><td>Ringlets</td><td>185</td></tr>
<tr><td>Rumble bell</td><td>1</td></tr>
<tr><td>Scales</td><td>7</td><td rowspan="2">Tools</td><td rowspan="2">8</td></tr>
<tr><td>Rod</td><td>1</td></tr>
<tr><td>Spiral tubes</td><td>603</td><td>Spiral tubes</td><td>603</td></tr>
<tr><td></td><td>Total 878</td><td></td><td></td></tr>
</table>

various textile tools, particularly weaving tablets, were also scattered throughout the box (ibid., 137–138).

When studied for our present research, all the objects appeared well-preserved, with many having undergone surface corrosion removal during the conservation process. Nevertheless, a visible surface patina persisted on numerous items. The assemblage contained several types of personal jewelry, including decorations to be sewn onto fabric, as well as textile- and trading tools. For the analyses, the objects were sorted into functional categories (see Table 1): single decorations, defined as jewelry meant to be worn independently; high-stress single decorations, sharing a similar definition as other single decorations but typically subjected to more stress due to their manner of wear; mass-produced decorations, comprising smaller ornaments designed to be attached or woven together; tools, representing devices intended for specific functions; and spiral tubes, treated as a distinct category due to their sheer amount.

The category of single decorations consisted of hangers, neck rings, and pendants. While their interpretation remains speculative and is based on analogy, it is suggested that hangers and pendants could have been worn as earrings, necklaces, or other accessories suspended typically from a string or a catch (Mägi 2002, 27). These items could exhibit triangular shapes or elaborate decorations in cross or zoomorphic shapes (Laul & Tamla 2014, 71–73). Neck rings were likely meant to be worn independently and usually featured twisted or braided metal wires (ibid., 65–66). High-stress single decorations included bracelets and finger rings, which were likely subjected to more stress and corrosion while being worn around the hands. The bracelets were diverse in shape, as they could be braided using a similar technique as for the neck rings, fashioned from flat metal strips, or coiled around the wrist in spiral shapes (ibid., 83–87). The finger rings also exhibited diverse shapes and patterns (ibid., 87–88).

The category of mass-produced decorations contained objects designed either to be grouped together (beads, buttons) or to fasten other decorations (catches, links, ringlets). These items were often simpler in shape, except for the rumble bell and the beads, which were intricately decorated (ibid., 77–81). Spiral tubes were also classified under this category. They typically appeared in two functional shapes: common "straight" spiral tubes, and U-shaped spiral tubes. The latter were commonly attached to the corners of a decorative sequence of straight spiral tubes, frequently stitched to the hem of an apron or other garments (ibid., 56–64).

The category of tools contained two types of objects: various pieces of a set of trading scales found in the bottom of the box (ibid., 38–39; Rammo & Ratas 2018, 137–138), and a single rod, which was probably used for sewing.

Methods

The data for this study was acquired using methods published in Roxburgh et al. (2019) and subsequent articles (e.g., Roxburgh & Olli 2019; Roxburgh 2023). The dataset was gathered using a portable X-ray fluorescence spectrometer, specifically the Bruker tracer III-SD handheld XRF model. The elements measured for this study were Mn, Fe, Co, Ni, Cu, Zn, As, Pb, Bi, Zr, Nb, Ag, Sn, and Sb. These elements were subsequently narrowed down to alloying metals Cu, Zn, Sn, Pb, and Ag, and common contaminants Fe, As, Sb, and Bi, as these commonly scored above at least 0.5%. Elements As and Sb were further considered due to their potential use as alloying metals with copper, albeit this occurred primarily in the Early Bronze Age (Kienlin et al. 2006, 453–454; Dardeniz 2020, 1–2). Each unique metal object was measured once on a relatively flat surface. However, for the large quantities of spiral tubes, only selections of around ten were taken from each of the archive storage trays. The collected data was then normalized in Microsoft Excel to correct for contamination from soil and attached fabric patches on a light element-free basis (Roxburgh & Olli 2019, 217).

The resulting database consisted of 914 records. After detecting inaccuracies in the measured totals of some artifacts, the database was filtered with an error threshold of $70\% < x < 115\%$. The lower threshold encompassed a greater range before considering outliers, given that copper, the main alloying metal, is often under-detected using pXRF (Ferretti 2014; Orfanou & Rehren 2015). The final dataset thus comprised 878 records. These objects were then filtered into functional categories, as shown in Table 1.

These filtered measurements were visualized using scatterplots and ternary diagrams. The latter specifically present the ratios of tin, lead and zinc, cumulatively normalized to 100%, based on the analysis conducted by Roxburgh et al. (2019) and the calculation methodology outlined by Scheibe (2021). The normalized results were then assessed qualitatively in terms of three common alloying groups: brasses containing copper and zinc, bronzes containing copper and tin, and gunmetals containing varying mixtures of copper, zinc and tin (Roxburgh

2023, 10). To assess the presence or otherwise of past surface treatments, a threshold value of 13% tin or greater was adopted to identify measurements with values outside the usual range for tin in copper-alloy solutions, guided by the copper-tin phase diagram presented in Meeks (1986, 134, fig. 1). To assess ore purity, a cumulative minimum of 10% was adopted in line with the approach described by Dardeniz (2020).

Silver, despite being an alloying metal, was excluded from these graphs due to its notable presence in only two objects. These specific instances are discussed in the Results and Discussion sections. In the majority of the graphs, the results were divided based on their functional categories as shown in Table 1, except for those where the differences between object types were emphasized.

Results

ALLOYING METALS

Figure 3 presents the normalized spread of alloying metals of all artifacts, sorted by functional category. Overall, most objects exhibit a higher zinc range, which allows to classify them as brasses and gunmetals. Objects with high tin levels closest to bronze (but still containing some zinc) are mostly limited to spiral tubes and mass-produced accessories, while single decorations with higher tin levels appear to fall within the tinning range. High zinc levels, on the other hand, are prevalent in all categories, with items most likely originally made of brass or at least zinc-rich gunmetal (Fig. 3: a), although they are in far smaller numbers in the category of mass-produced decorations. Lead levels are generally low, except for a distinct group of spiral tubes with higher lead and tin levels (circled in Fig. 3: b). This group mostly comprises U-shaped spiral tubes. Finally, two shield-type finger rings contain a large percentage of silver, ranging between 75–78%.

Figure 4 depicts the initial range of copper, compared to the cumulative percentages of tin, lead, and zinc levels. This graph shows that most objects linger around 10–20% alloying metal. Only three single decorations, approximately 20 mass-produced decorations, and around 60 spiral tubes significantly exceed this range. For objects subjected to higher mechanical stress, all but one outlier sit around or below the average range. The majority of initial outliers appear to have a high tin percentage. This may reflect the application of a tin layer on the object's surface, a practice known as tinning, which is further explored in the Discussion section.

ALLOY CLASSIFICATION

The results are first presented by object type and then by preservation condition, as illustrated in Fig. 3. Objects with high tin content (13%+) are also presented. (Additionally, an Excel craft box report is available online as Supplementary Material: https://www.researchgate.net/publication/373256029_Supplementary_Material_-_Craft_Box.)

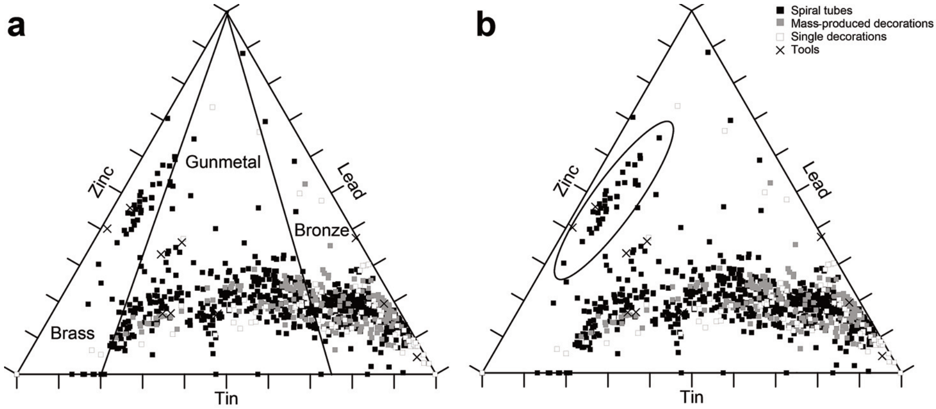

FIG. 3. Ternary diagrams of lead, tin and zinc levels by functional category. a – corroded brass, gunmetal and bronze division lines; b – zinc-rich group highlighted in the circle.

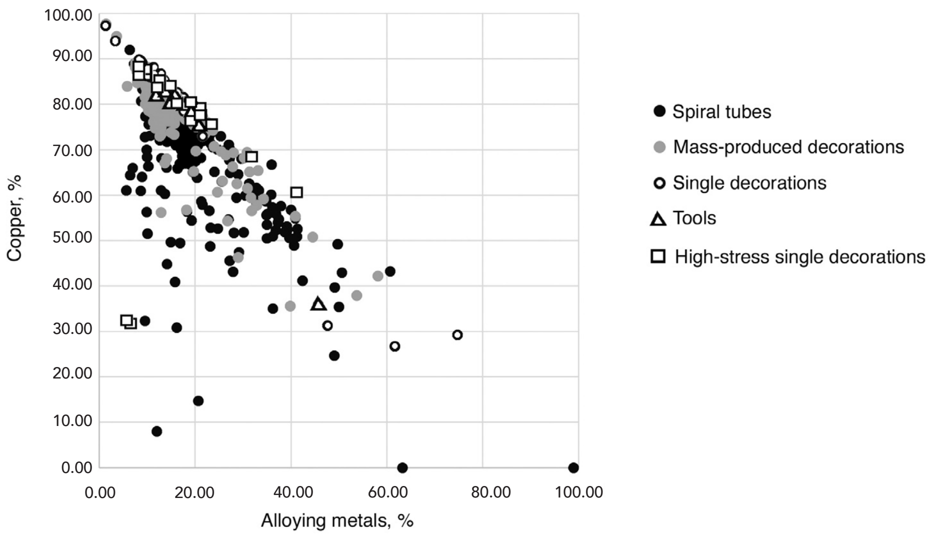

FIG. 4. Overview of all alloying metals compared to copper percentages, sorted by functional category.

The dataset for spiral tubes, the largest category with 526 objects, was classified as follows: 42% gunmetal, 25.3% bronze, 19.6% high-tin bronze (Sn 13%+), 4% high-tin gunmetal (Sn 13%+), and 3.4% brass. One outlier in this category contained no copper. U-shaped spiral tubes (77 objects) were classified as 30% gunmetal, 27.3% brass, 26% bronze, 14.3% high-tin bronze, and 2.6% high-tin gunmetal. Ringlets (185 objects) were classified as 40.5% bronze, 37.8% gunmetal, 19% high-tin bronze, 2.2% high-tin gunmetal, and 0.5% brass. Beads (14 objects) were classified as 93% high-tin bronze and 7% gunmetal. Bracelets (8 objects) were evenly split between 50% bronze and 50% gunmetal. Finger rings (11 objects) were classified as 33.3% high-tin bronze, 33.3% gunmetal, and 25%

silver. Pendants (32 objects) were classified as 61.3% bronze, 25.8% gunmetal, and 3.2% brass, with one additional pendant being copper and one being silver. Pendant hangers (5 objects) were classified as bronze. The scales (7 pieces) were classified as 71.4% gunmetal and 28.6% brass. The chatelaine links (5 objects) consisted of four gunmetal items and one bronze item. The neck rings (3 objects) included two gunmetal and one bronze item. The catch was classified as gunmetal, the rod as high-tin bronze, and the rumble bell as bronze. The two bell buttons were classified as bronze and gunmetal, both being gilded.

Two preservation conditions were observed: the first being where the objects appeared to have retained their original (green-brown-black) patina, and the second being where the objects had no patina, appearing clean, shiny and metallic, presumably having been cleaned during the conservation process. A pXRF analysis of variation between the cleaned and the patina groups was conducted. For spiral tubes, 215 measurements on clean objects were compared against 217 on patina. In the clean group, 31.2% were classified as bronze, 22.3% high-tin bronze, 36.3% gunmetal, 6% high-tin gunmetal, and 4% brass. In the patina group, 25.3% were bronze, 10.1% high-tin bronze, 58.9% gunmetal, 1.8% high-tin gunmetal, and 3.7% brass. For U-shaped spiral tubes, a group of 24 cleaned objects was compared against the 32 items with patina. The clean group contained 16.7% bronze, 20.8% high-tin bronze, 50% gunmetal, and 12.5% brass. The patina group included 28.1% bronze, 6.3% high-tin bronze, 28.1% gunmetal, and 37.5% brass. For ringlets, a group of 107 cleaned objects was compared against the 39 items with patina. In the clean group, 49.5% were bronze, 6.5% high-tin bronze, 43% gunmetal, and 1% was high-tin gunmetal. In the patina group, 38.5% were bronze, 46.2% high-tin bronze, and 15.4% gunmetal.

High tin content (13%+) was observed in the following objects: 19.6% out of the 526 spiral tubes exhibited high-tin bronze and 4% high-tin gunmetal; 14.3% out of the 77 U-shaped spiral tubes exhibited high-tin bronze and 2.6% high-tin gunmetal; 19% out of the 185 ringlets contained high-tin bronze and 2.2% high-tin gunmetal; 93% out of the 14 beads exhibited high-tin bronze; and 33.3% out of the 11 finger rings contained high-tin bronze. One of the three cross-shaped pendants included high-tin bronze, and the leaded side of two other pendants showed high-tin bronze. Two out of the seven braided neck rings exhibited high-tin bronze, and so did the single rod. A total of 204 high-tin measurements (177 bronze, 27 gunmetal) out of the 883 measurements were observed. No significant variation in lead level was noted on these objects.

ALLOY CLASSIFICATION

Apart from copper and the alloying elements tin, lead and zinc, other components may be present in the alloys. These components may be potential contaminants or trace components from the ores of each alloying metal. Differences in the concentration of contaminants may indicate differences in alloy composition, ore provenance, or the level of refining of metals or alloys.

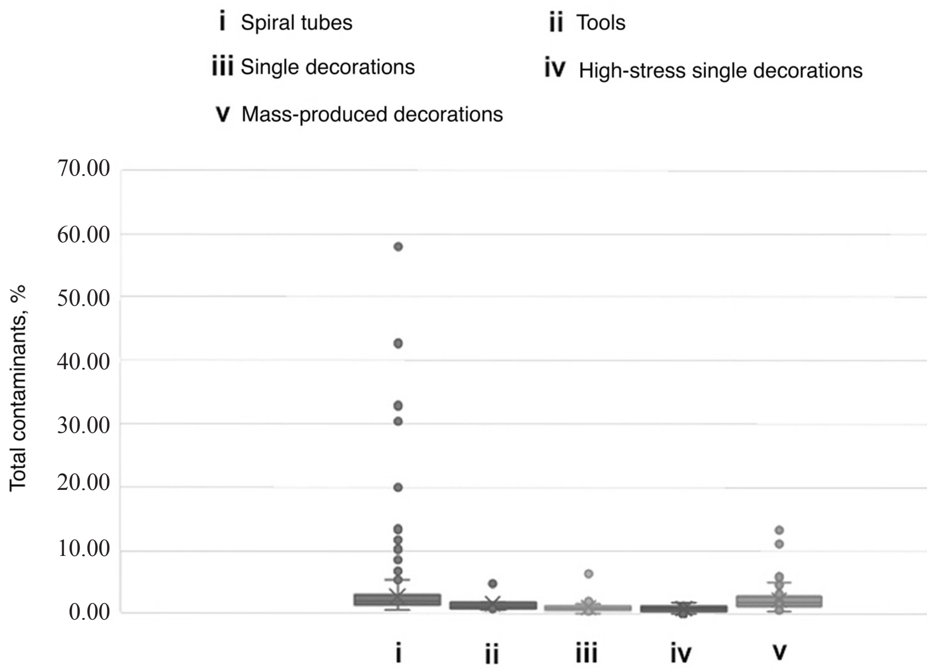

FIG. 5. Total major contaminants, sorted by functional category.

To track potential differences in the choice of raw materials by type of object, Fig. 5 presents the total major contaminants per functional category, with 50 out of the 878 records falling in the high-impurity range. Figure 6 shows the spread of arsenic vs antimony per functional category. Although arsenic and antimony concentrations are too low (below 10%) to be regarded as alloying elements in their own right, high levels of arsenic and antimony ores are present in the mass-produced accessories and non-decorative objects (such as tools), with a neck ring being the only exception. This may indicate the use of lower-quality ores or less severe refining and quality control in mass-produced items. In contrast to arsenic and antimony, elevated concentrations of iron are probably not related to the original ore. As described by Huisman et al. (2023), iron can become incorporated into the corrosion layers of copper alloy objects when the burial environment alternates between anaerobic and aerobic. The silver shield-type finger rings featured a distinct lack of contaminants.

Discussion

Spiral tubes formed the largest dataset, encompassing all copper-alloy classifications in the results. However, no particular alloy groups were discernable. Neither did the samples, taken from various archive trays, nor the sizes or shapes show any grouping. It is likely, in this well-preserved collection, that some copper

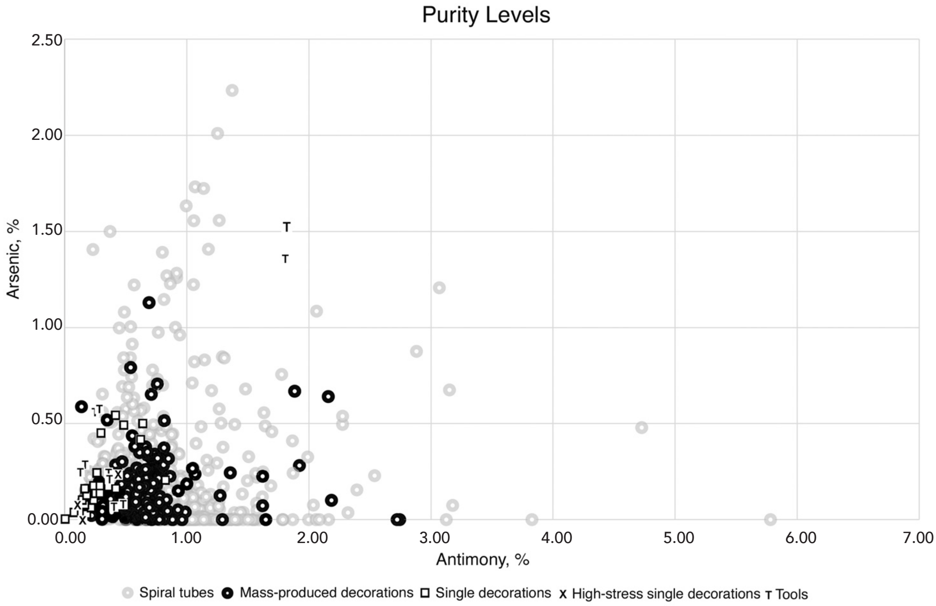

FIG. 6. Spread of arsenic vs antimony, sorted by functional category.

and zinc depletion still took place during the corrosion process. Therefore, the original metals would have had more gunmetal and brass present than was currently detectable in the corroded objects. Despite some visible signs of silvery surfaces, no convincing evidence of tinned surface treatment was apparent. Specifically, no groups of spiral tubes consistently contained high tin (13%+) measurements. A small group of long spiral tubes was found in such good condition that they needed only little cleaning. However, many other tubes had been cleaned more thoroughly in a past conservation event. Although these objects now appear shiny and clean, the surfaces represent an outer depletion layer (as opposed to the inner core where the original alloy could be measured), from which copper and zinc have leached. Therefore, the measurements on these surfaces are artificially high in tin and lead. This was confirmed when comparing the measurements of cleaned vs original patina. A noticeable drop in high-tin bronze was observed, as well as an increase in the number of gunmetal objects in the patina group.

In conclusion, the craft box most likely contained spiral tubes produced in bronze, gunmetal and brass, with no convincing signs of tinning. If the craft box had contained many freshly produced spiral tubes, perhaps from a single resource or a small selection of raw materials, one might expect a more uniform set of measurements. However, this was not the case. It is more plausible that the spiral tubes were collected more or less indiscriminately, thus originating from many different sources. Alternatively, the results could reflect the nature of wire imported via the Hansa trade routes. Many copper-alloy sources, possibly in the form of scrap metal, could have been processed into wire commodities for

Hanseatic merchants and subsequently traded to Estonia. Future provenance studies on these interesting items may prove worthwhile.

The U-shaped spiral tubes tell a slightly different story. Many more brass measurements were noted compared to straight spiral tubes. The analysis of clean vs patina groups once again revealed tin and lead enrichment, suggesting that zinc and, hence, brass were even more common in U-shaped spiral tubes. Despite this, no evidence of surface treatment was found. Brass exhibits a more yellowy or gold-like color than the other alloys in this study. It is possible that these U-shaped spiral tubes were deliberately crafted using brass wire to stand out from the color of other spiral tubes. The raw materials, such as zinc ores, needed to manufacture brass, were likely unavailable in the region at that time. Therefore, the brass may have arrived through Hanseatic traders in the form of wire, ingots, or scrap items. Alternatively, the U-shaped spiral tubes could have been made of readily available brass wire, or perhaps they could have been removed from a single item of worn-out clothing for recycling.

The ringlets formed the final large dataset, suggesting production in bronze and gunmetal, based on measurements. However, this might not capture the full story. The analysis of the clean vs patina groups revealed a large rise in tin-rich bronze within the patina group. This contrasts with the results for the spiral tubes and is more indicative of tinned surface treatment absorbed by the patina during corrosion. This hypothesis is further supported by visible inspection, where silvery surfaces correlated with high tin measurements. It is possible that a white silvery color was a deliberate craft choice for at least some of these ringlets, applied through tin-based surface treatment.

The measurements for the beads consistently indicate high-tin bronze, suggesting that they were intentionally tinned to achieve a silvery-white color rather than a yellowy copper-alloy tone. Again, this seems to align with a fashion-related craft choice. The bracelets, in contrast, appear to have been made of bronze or gunmetal, without tin surface treatment, indicating a preference for the original yellowy copper-alloy color. Three of the finger rings were made of silver and one was made of brass, which, in contrast, would have been yellowy gold colored. Another three were made of gunmetal. The remaining four rings were high-tin bronze, which could again be evidence of intentional tinning. In this case, these four rings may have been deliberately tinned to mimic the color and perhaps the status of silver rings.

One pendant was made of silver, while the others were mainly crafted from bronze and gunmetal. No tin enrichment was detected, indicating no evidence of tinning. In contrast, there was some evidence of tinning on the pendant hangers, but only on one side. It is possible that it was desirable for the hangers to have a different metallic color than the pendants. Otherwise, the hangers appear to have been made of bronze. The components of the weighing scales seem to have been made of brass or gunmetal, but no evidence of tinning was detected. Similarly, no evidence of tinning was found among the measurements on the neck rings, which appear to have been made of bronze or gunmetal.

The rod, although probably made of bronze, could also have been tinned. The catch, the rumble bell, and the bell buttons all appear to have been made of bronze or gunmetal, with no evidence of tinning. However, the bell buttons also seem to have been gilded.

In answer to what can be determined regarding the original choice of metal, the analyses revealed a wide range of copper-alloy mixtures present in the craft box. It is likely that the spiral tubes came from many different sources, possibly having been removed from past costumes and then jumbled up when stored in the craft box, while waiting future reuse. Alternatively, the variation could have taken place during the wire production stage, providing an opportunity to recycle a variety of older objects. This variation might have entered the craft box assemblage when the owner acquired the wire or finished spiral tubes at a market. The U-shaped spiral tubes were predominantly made of brass, suggesting a deliberate choice of this more gold-like alloy to make them stand out from the color of the other spiral tubes. Alternatively, the U-shaped spiral tubes could have originated from a more singular manufacturing event, perhaps crafted from readily available brass wire or possibly removed from a single item of clothing for recycling.

In answer to what evidence exists for the use of tin-based surface treatments, it can be noted that a significant number of objects appear to have been tinned. It was determined that the ringlets were probably made of bronze and gunmetal; however, the analysis revealed a large proportion of tin-rich bronze measurements on the patina, indicative of tinned surface treatment. This hypothesis is further supported by visible inspection, where silvery surfaces correlated with high tin measurements. This suggests that the silvery white color of a tinned item was important in the clothing fashion of the time, perhaps serving as a decorative contrast to the yellowy gold-like color of brass and bronze copper-alloy. The measurements for the beads and four of the finger rings also suggest tinning. Once again, this appears to be a fashion-related craft choice, possibly imitating the color of silver.

Lastly, what conclusions can be drawn regarding the types of ore contaminants present? The craft box from Lõhavere contained many items in line with the long-lasting material traditions of Estonia, but preferences for metal compositions may have changed. The first observation is the matter of quality control: it appears that mass-produced accessories, such as beads, spiral tubes and ringlets, were made of lower-quality ore, as evident from the higher percentages of arsenic and antimony. As copper-alloy objects are resmelted for reuse, particularly the arsenic levels may deplete. As mentioned by Radivojević et al. (2018, 157), this occurs through the evaporation of arsenic that is not incorporated into the base metal. Arsenic evaporation through resmelting may be reflected in objects with higher antimony levels, in contrast to lower arsenic levels. Primarily links, spiral tubes and ringlets fall into this category (Fig. 4), suggesting that these may have been made of recycled metals. On one hand, this may point to a greater priority of high-quality ores for more prominent, expensive ornaments, such as rings and bracelets. On the other hand, it may suggest that decorations crafted from high-contaminant ores were not made of resmelted metal. In agreement with Saage (2020, 76), this implies that there were fewer steps between ore acquisition and object shaping than for some low-contaminant objects. In fact, this would make these low-contaminant objects more prized, suggesting the direct usage of a newly shaped bar for small decorations, rather than being used for tools, weaponry, or more expensive jewelry.

The presence of iron, especially in higher amounts, is more challenging to explain. The high, outlying percentages may correlate with alloying metals, such as copper and zinc, but it is more likely attributed to soil contamination, as proposed by Huisman et al. (2023). The presence of iron in primarily mass-produced accessories suggests that high iron percentages mostly affected lower-quality ores, either during the smelting process or as a result of corrosion.

The choice of main alloying metals makes for an interesting second group of observations. While most objects linger around a period-typical average percentage of alloying metals, specifically lead, tin and zinc, mainly mass-produced decorations, such as beads, ringlets and spiral tubes, exceed this average. Until the 18th century, a higher percentage of alloying ores – specifically zinc – should have been impossible, considering the technological limitations at the time (Pollard & Heron 2008, 201–207). Conversely, the process of tinning may skew these numbers. The excess of alloying metals, primarily represented in the higher presence of tin, suggests a deliberate application to the object's surface to achieve an appealing silvery sheen. In the broader context of Final Iron Age Estonia, there seems to be a diminishing preference for brass, as fewer objects contain zinc over tin compared to earlier periods (Fig. 3). This shift may reflect a newfound greater availability of tin, which had been centralized with the advent of hillforts (Saage 2020, 91–92). Overall, this could indicate a desire for sturdier objects, as bronze is typically harder than brass, though also more brittle, as suggested by Morton (2019).

The shift towards tin was likely not simply a functional matter of availability. Compared to earlier periods, precious metals, primarily silver, were twice as prominent in Final Iron Age Estonia (Saage 2020, 94, 105–108). Silver was similarly attested in Lõhavere. Only one fragment of a crucible was found with traces of silver, zinc and lead (but no traces of copper). Therefore, there is no direct evidence of extensive casting of bronze and silverware at the hillfort. However, some items were cast from tin and pewter, as evidenced by Saage & Warmlander (2018, tables 1–2, 7). With the increase of local silversmithing, it is likely that the desire for social competition in owning precious metals also grew. However, as suggested by Rammo & Ratas (2016, 3), instead of focusing on brass to mimic a golden appearance, artisans may have preferred the color of silver. This is reflected in the presence of the two silver rings at Lõhavere and in the high number of tinned objects. The silver color produced by tinning may well have been a way to signal higher wealth or social status. To the untrained eye, a tinned bracelet may very well have suggested that the wearer had access to an expensive and fashionable metal.

Despite the increasing prominence of tin, the usage of brass persisted. Aside from mimicking gold, brass, in and of itself, was a valuable metal due to the limited availability of zinc and the overall quality of brass items (Pollard & Heron 2008, 207). It is thus unsurprising that brass was largely reserved for objects that played a more prominent role in social competition. One such item was the pair of scales (Fig. 2: b), which, after centuries of being buried, still shows the characteristic golden sheen of brass. More than simply a merchant's tool, the scales, in and of themselves, were likely a status symbol. Their presence in a craft box, typically owned by women, suggests that the owner was a female merchant in charge of selling her own crafted (or traded) goods (Rammo and Ratas 2018, 142). An impressive and flashy pair of scales may have been a way for the owner to assert her status in a typically male-dominated field.

For alloy choices, a notable observation is the presence of lead. Leaded alloys typically have a lower melting point, which makes them easier to cast and shape (Kearns et al. 2010, 54). The most distinct example of leaded alloys at Lõhavere is the group of leaded brass U-shaped spiral tubes (Fig. 2: d). The high level of lead implies that these shapes were challenging to forge, and craftspeople added lead to ease this process. Furthermore, the U-shaped spiral tubes suggest a hierarchy of spiral tube types. Most U-shaped spiral tubes were made of brass or gunmetal, and none appear to have been tinned. Consequently, spiral tube decorations featuring these shapes were likely more valuable than their bronze counterparts. Even so, there seems to have been a reluctance to adapt the long-traditional decoration to the preference for a silvery appearance that was becoming more common in other types of decoration.

Overall, the results only partially correlate with the changes in common metal alloys, as observed by Saage (2020, fig. 2). While Saage states that brass continued to be the most common metal (2020, 93–95), at Lõhavere, bronze objects are far more prominent. Brass persisted in luxury goods and traditional spiral tube decorations. While previously explained through the increased availability of tin and silver, leading to a changing preference in aesthetics, it is worth examining what may have caused this change. The severing of Scandinavian influence at the end of the Viking Age likely also caused renovations in the metal industry. The production of brass is a notably challenging affair. Acquiring pure zinc is difficult, as it often comes with undesirable compounds, and does not readily melt together with copper like tin does (Morton 2019, 4–7). During this time, metalworking in Estonia was largely associated with agricultural life, and specialization had become rarer (Saage 2020, 93). It is thus possible that Lõhavere had fewer blacksmiths knowledgeable in brassworking, focusing instead on silversmithing and imitations of silver. Nevertheless, any conclusive remarks would depend on evidence from local smitheries and provenance studies of metal artifacts to determine their origin. After all, the box likely belonged to a single person, and the findings do not necessarily reflect the entire settlement.

Finally, the contents of the craft box appear to have been period-typical, except for the prominence of bronze. From previous analyses of 9th–13th-century graveyards, it can be concluded that brass objects primarily link to personal ornaments worn by women and children, though bracelets, neck rings and finger rings were also worn by men in funerary contexts (Mägi 2002, 105–112; Rammo & Ratas 2016, 1–3). This glimpse into the daily usage of these items grants archaeology a way to reconstruct both the social and economic value of such objects. While many of the Lõhavere ornaments were made of copper-tin alloys, brass remained a prominent material. Thus, this study also underlines the importance of tradition: though bronzes became more readily available, the cultural importance of the golden appearance of spiral tubes appears to have overshadowed the convenience of more abundant tin resources.

Conclusions

This article explored the possible correlation between the types of objects and the composition of copper alloys in Estonian personal decorations and tools. The assemblage consisted of a unique find of a nearly intact and largely uncorroded collection of copper-alloy objects. The analysis revealed a general divide in metal composition between functional types, while retaining considerable overlap in the percentages of tin and zinc. The findings suggested that contamination from lower-quality ores largely occurred in mass-produced items, where the quality of individual smaller pieces was likely a lesser concern.

The most notable observation is the difference in copper alloys present in the Lõhavere craft box compared to pre-11th-century Estonia, when brass was preferred. The Lõhavere assemblage was primarily composed of copper-tin alloys, with several items possibly tinned. This development might coincide with a newfound popularity of silversmithing, as well as the centralization of tin smelting in hillforts. The craft box may represent a shift in metal availability, along with changing aesthetic preferences towards the end of the Final Iron Age. Despite this shift, for objects with longer traditions, such as spiral tubes, the golden appearance of copper-zinc alloys likely remained important.

Even so, these findings only represented the personal possessions of one household at most. The large variation in the copper-alloys present in the spiral tubes suggested diverse sources, either recycling activities by the craft box owner or prior purchases at a market. All in all, this study provided an incentive for further analysis at the Lõhavere site. The remnants of smithies and the funerary records specifically would assist in further contextualizing the craft box finds. Whether the preference for silvery items was an individual taste or reflected a broader socio-economic change at the settlement, remains to be seen.

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Lõhavere 13. sajandi alguse käsitöövaka metallesemete materjaliuuringud portatiivse röntgenfluorestsents-spektromeetriga

Esmee J. Hummel, Marcus Adrian Roxburgh ja Hans D. J. Huisman

RESÜMEE

Artiklis tutvustatakse 13. sajandi alguse käsitöövakas olnud erinevat tüüpi metallesemete materjaliuuringute tulemusi. 13. sajandi esimesel veerandil hävinud Lõhavere linnamäelt pärit kasetohust vakk leiti 1958. aastal professor Harri Moora juhitud arheoloogilistel kaevamistel. Peale arvukate tekstiilijäänuste ja puidust käsitöövahendite oli selles üle tuhande metalleseme, sealhulgas rikkalik valik ehteid ja pronkskaalud.

Hästi säilinud, erinevast materjalist esemetega peitleid tõstatas kohe palju küsimusi, nagu vaka omaniku staatus ning esemete funktsioon ja valmistusviis. Varasemates artiklites on neid küsimusi juba üksikasjalikult käsitletud, kuid röntgenfluorestsents-spektromeetria (pXRF) võimaldas olemasolevaid teadmisi täiendada, keskendudes esemete valmistamiseks kasutatud sulamite koostise uurimisele. Uue metoodikaga teostatud uuringud lisasid teavet mitut tüüpi esemete valmistamiseks kasutatud metallide valiku, pinnatöötluse ja sulamite üksikkomponentide toormest (maagist) lähtuvate saasteainete kohta. Peaaegu kõik esemed olid valmistatud vasepõhistest sulamitest, mis sisaldasid erineval hulgal pliid, tsinki ja tina, kuigi mõnes esemes esines ka hõbedat.

13. sajandi alguse Eestis oli väliste jõudude võimule pääsemisega kujunemas uus majanduslik-poliitiline võimustruktuur. Muutused ühiskondlik-poliitilises dünaamikas ilmnesid ka tolleaegses metallitöötlemise praktikas. Hilisrauaajal (1050–1225 pKr) metallitööstus elavnes ja muutusid ka ehtemetallide materjalieelistused: pronksi osatähtsus langes ning esile tõusid messing, relvametall (punapronks) ja hõbe. See uuesti leitud trend pidi eeldatavasti kajastuma ka käsitöövaka sisus, mistõttu pakkus esemetes kasutatud metallitüüp erilist huvi.

Uurimismaterjal jaotus viide objektikategooriasse. Kategooriasse „üksikehted" kuulusid esemed, mida sai kanda üksikult, nagu kaelarõngad ja keekandjad. Kategooriasse „tihti kasutatavad üksikehted" kuuluvad esemed (sõrmused ja käevõrud) sarnanesid eelmise kategooria omadega, kuid nende kulumine oli kandmisviisi tõttu suurem. Kategooria „masstoodetud ehted" hõlmas helmeid,

nööpe ja rõngaid-rõngakesi, mis olid mõeldud koos kandmiseks või kinnitati mõne muu rõivaosa külge. Kategooriasse „tööriistad“ kuulusid kaalukomplekt ja (õmblus)varras. Omaette kategooria moodustasid „spiraaltorud“ – traditsioonilistest spiraaltorukestest koostatud ja rõivaste külge õmblemiseks mõeldud võreornamentide ja võrgendite osad või toorikud. Kuna seda tüüpi üksikobjekte oli väga palju ja neil oli ühesugune kultuurilooline taust, funktsioon ja väärtus, liigitati need omaette esemerühmaks, mitte osaks kategooriast „masstoodetud ehted“.

Seejärel määrati portatiivse röntgenfluorestsents-spektromeetriga esemetes kasutatud sulamite põhikomponentide ja saasteainete sisaldus. Vaatamata üldkogumi elementide suurele hulgale otsustati uurimistöö huvides piirduda komponentmetallidest vase, tsingi, tina, plii ja hõbedaga ning saasteelementidest raua, arseeni, antimoni ja vismutiga.

Tulemused jagati kahte (põhi)rühma. Esimesse kuulusid sulamikompositsioonid, milles uuriti tina, tsingi ja plii sisaldust. Lisaks keemilisele koostisele võrreldi erinevate esemekategooriate komponentmetallide kvantitatiivset koostist. Suurem tsingisisaldus ilmnes kõigis viies kategoorias, samal ajal kui pliisisaldus oli üldiselt väike. Valdavalt sisaldas enamik vasesulamist esemeid umbes 10–20% komponentmetalle, kuigi mitmel masstoodetud ehtel ja spiraaltorul oli see sisaldus märksa suurem. Analüüsitulemuste põhjal jaotusid sulamid erineva koostisega pronksideks, relvametallideks ja messingiteks. Selgus, et relvametallist ja pronksist esemed olid ülekaalukalt levinuimad, samal ajal kui messingikasutus piirdus vaid kindla rühma spiraaltorude ja mõne kangkaalu detailiga.

Teise rühma puhul uuriti maagist lähtunud saastumist. Suure lisandisisaldusega sulamite hulka kuulus 878 uuritud objektist ligi 50, kusjuures kõik peale ühe pärinesid „masstoodangu“ kategooriast. Selgus, et erinevalt teistest saasteainetest ei lähtunud rauaga saastumine maagist, vaid võis tekkida pärast esemete matmist pinnasesse. Sellegipoolest ilmnevad masstoodetud tarvikutes võrreldes saasteainete üldise kõrge tasemega väiksemad kvaliteediprobleemid. Vaeti ka võimalust, et metall võis olla ümber sulatatud, sest suurem antimonisisaldus esines mõnikord koos väiksema arseenisisaldusega, ja arseen võib ümbersulatamise käigus aurustuda. See aga võib tähendada, et teatud maakidest saadud metalli kasutatigi sihilikult helmeste ja muu madalamat materjalikvaliteeti eeldavate n-ö pudi-padi-esemete valmistamiseks.

Lisaks võis tina ja plii sisalduse suurenemine võrreldes tsingiga olla seotud metallitöötluse arenguga. Messingit on tunduvalt keerulisem toota kui pronksi ja spetsialiseeritud sepikodade arvu vähenedes võis ka huvi leida vahendeid messingist esemete valmistamiseks jääda tagaplaanile. Kuna andmestik kohalike sepikodade kohta on napp, jääb see siiski vaid esialgseks oletuseks.

Messingist esemete vähenemine ja suurema tinasisaldusega sulamite kasvav levik võisid olla seotud nii majanduslike muutustega kui ka sotsiaalkultuuriliste väärtushinnangute teisenemisega. Eeldatavasti paranes tina kättesaadavus Lõhavere linnuse jaoks, mille tulemusel kasvas pronksist ja relvametallist esemete hulk. Samal ajal levis kõikjal hilisrauaagses Eestis ulatuslikult ka hõbe. Lisaks hõlpsale kättesaadavusele võis see olla seotud üldiste esteetiliste väärtushinnangute ja trendide muutumisega mõningate metallide suhtes. Kui kasutada pinnatöötluseks tinatamist, meenutab saadud tulemus vägagi hõbeda sära. Traditsioonilistes kaunistustes, eriti spiraaltorudest koostatud ornamentides, jätkati siiski ka messingi kasutamist. Seega ei kõigutanud mõne metalli kergem kättesaadavus ja moekuse ihalus traditsioonilisi väärtusi.