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Assessment of the deterioration process of copper alloys: a case study of Central Lithuanian crossbow brooches with a triangular foot

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The deterioration and degree of preservation of copper alloy archaeological artefacts depends on several interacting factors that began when the artefacts were buried and continue in museum storage. Ageing and deterioration processes that have begun can be slowed, but not completely stopped. The influence of the type of copper alloy and museum environment storage conditions on deterioration processes was investigated. Crossbow brooches with a triangular foot were examined using non-destructive techniques such as portable XRF and radiography, as well as the data from excavation reports. The collected data on museum storage environment was analysed using the software program *Eclimatenotebook*. Based on the results of this analysis, the future preservation level was calculated using the risk assessment method. Most of the brooches examined were made of brass and were in a fairly good condition. The foot and pin were the most damaged parts. Future storage conditions with a high relative humidity (up to 80%) pose a great risk to the treated and untreated brooches.

Keywords: brooches, deterioration, Central Lithuania, X-ray fluorescence, relative humidity

INTRODUCTION

Archaeological copper alloys are usually found in a corroded state with or without preservation of a metal core. The degree of preservation depends on a whole series of interacting processes that began when the artefacts were placed in the ground and continue in museum storage. In other words, the objective ageing and deterioration processes that have begun can be slowed down, but not stopped. In evaluating the processes of embedding in the ground, the main focus is on geochemical processes (the grave or any deposition may contain not only objects produced of copper alloys, but also iron and silver, textiles, and other materials; the decaying remains of the deceased; the effects of soil; temperature fluctuations; other factors such as underground water), on biological (such as vegetation and micro-organisms) and on anthropogenic factors (intensive agriculture and land development). The survival of artefacts after excavation can be affected by conservation treatment and storage conditions in museums.

The aim of the research is to investigate the deterioration processes and the influence of the type of copper alloy on these processes. Other factors were chosen to evaluate the deterioration processes, namely, the time elapsed between the discovery of an archaeological artefact and its preservation, and the conditions of storage in museums in terms of the influence of relative humidity. Crossbow brooches with a triangular foot dated the 5–6th centuries AD were selected for the evaluation of the degree of preservation. Outside Lithuania, the crossbow brooches with a triangular foot are almost unknown. As Fig. 1 shows, the highest concentration of brooches is found in the central

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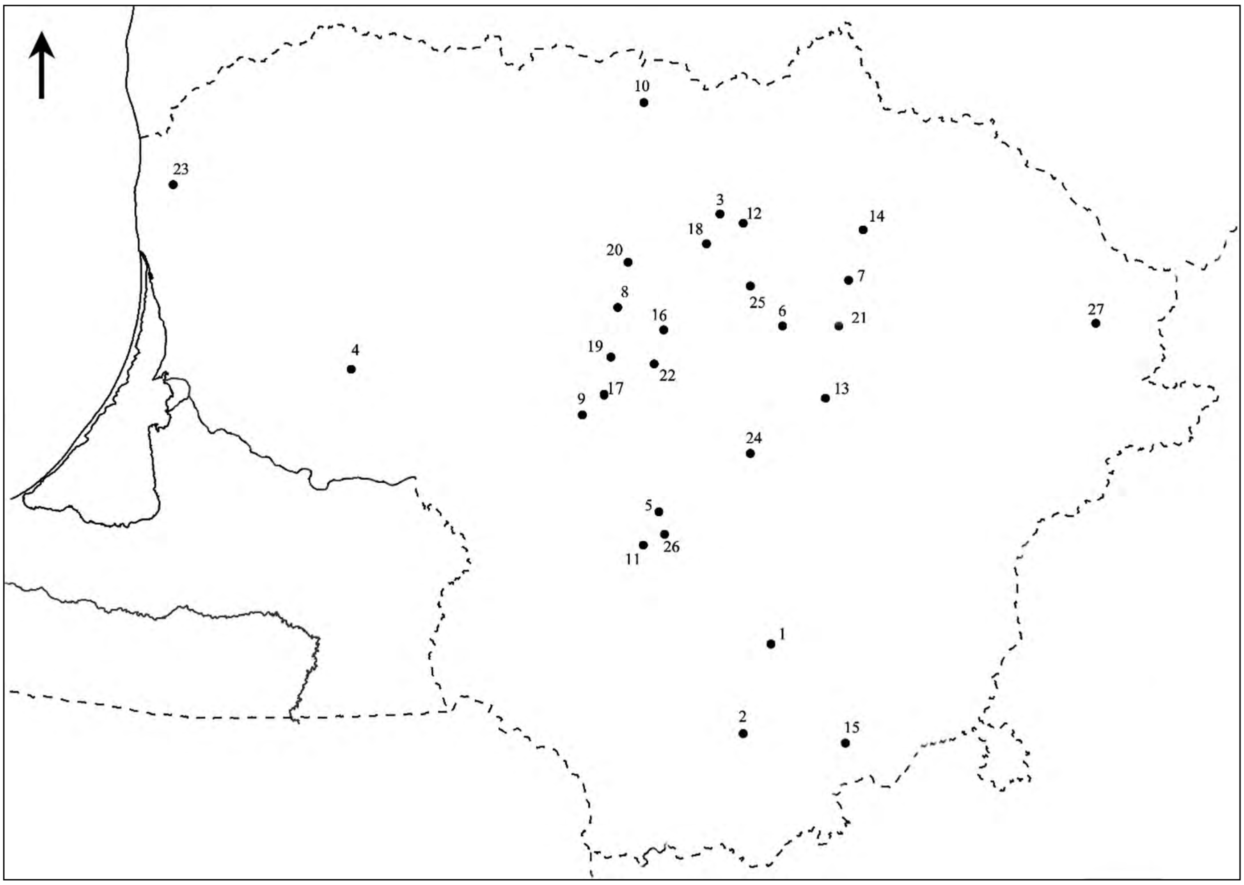

Fig. 1. Distribution of crossbow brooches with triangular feet: Aukštadvaris (1), Alytus (2), Berčiūnai (3), Dauglaukis (4), Eiguliai (5), Griniūnai (6), Juostininkai (7), Kairėnėliai (8), Kalniškiai–Bažavalė (9), Linksmėnai (10), Marvelė (11), Meldiniai (12), Obeliai (13), Pamarnakis (14), Pamušiai (15), Pašušvys (16), Pernarava (17), Plauciškiai (18), Plinkaigalis (19), Raginėnai (20), Riklikai (21), Rinkšeliai (22), Tūbausiai (23), Ukmergė (24), Upytė (25), Veršvai (26) and Vosgėliai (27) (by A. Tautavičius and U. Budvydas, updated by A. Vasiliauskaitė and drawn by A. Vasiliauskaitė)

part of Lithuania, single sites with these brooches are also known from Southeastern Lithuania. This means that these brooches were buried together with unburnt dead at about the same time, and thus remained in the ground for almost the same length of time, about 1500–1600 years.

The deterioration processes of the crossbow brooches with a triangular foot were studied using non-destructive techniques of X-ray fluorescence spectrometry (further XRF) and radiography (further X-ray), as well as using the valuable information from excavation reports such as drawings made during the excavations.

ARCHAEOLOGICAL BACKGROUND

Three cemeteries (Plinkaigalis, Marvelė and Kalniškiai–Bažavalė) with the highest concentration (over 30 items) of crossbow brooches with a triangular foot were selected for analysis.

Crossbow brooches were distinguished as a type by O. Almgren in his study of brooches from the Roman period in Northern Europe [1]. Later they were described by E. Blume, N. Aberg, H. Mooros and M. Schulce [2–6]. The brooches originated from the Germanic tribes living in the Elbe River Basin in the 1st – 4th centuries AD and later spread to the rest of Europe [7].

Lithuanian archeologists also studied crossbow brooches with a triangular foot. J. Puzinas, in his review of archaeological excavations in Lithuania in 1918–1938, distinguished this type of brooches and dated them to the 5–7th centuries AD. He also emphasised that brooches made of iron were quite rare in Lithuania [8]. The most comprehensive typology and chronological survey of crossbow brooches with a triangular foot were made by A. Tautavičius and U. Budvydas [9–11]. Based on the shape, the bow, the length of the axis and other features of the foot, Budvydas highlighted three subtypes which are not described in detail here, as the typology is not relevant for this paper. The brooches examined here were found in the inhumation graves of males, females and children (Fig. 2).

METHODS

Visual examination

First, the brooches were assessed by visual inspection in museums where they are stored. The preservation of copper alloy and the general integrity were visually assessed. The current visual integrity was compared with the drawings of brooches from the archaeological excavation reports, noting missing or broken parts. Some details (mainly corrosion areas) were examined with a digital microscope (Q-scope 9.0 MP, 200×). The digital microscope also helped to identify the technology and decorations used to produce these brooches.

Radiography

Other non-destructive analysis technique was used to examine the internal structure of the brooches. They were examined with a portable diagnostic X-ray machine GIERTH TR 90X30. Taking into account the different metal thickness, degree of corrosion and technological characteristics, three X-ray imaging modes were used: I (voltage 90 kV and exposure 1.0 mAs), II (voltage 80 kV and exposure 0.8 mAs) and III (voltage 70 kV and exposure 0.6 mAs).

X-ray fluorescence (pXRF) analysis

XRF analysis was carried out to clarify the main elements of the composition of brooch alloys and to classify the alloys into types. This non-destructive technique of surface analysis of archaeological copper alloy objects has been widely used for several decades [12–14]. The analysis of the brooches was performed using a portable Niton XL3t XRF spectrometer (power 2 W, voltage 50 kV, detector area ~50 mm^2 and manufacturer Thermo Fisher in the 'General Metals' mode). The cultural heritage alloy reference material set with 5 CHARM standards (bronze alloy, leaded bronze, brass alloy, leaded brass and gunmetal) was used for the analysis [15–17]. Each find was irradiated in at least two locations (for 30 s). The elemental composition was measured on the surface of the artefact. In most cases, the axis, the bow and foot were measured. The classification of alloy types is based on the methodology of J. Bayley and S. Butcher [18, Table 5]. According to the authors, the names given to the copper alloys reflect the different amounts of zinc, tin and lead contained in them. Qualitative analyses cannot provide a specific composition but only an indication of a more general type of alloy.

Sixty-one brooches were analysed. Data of 14 brooches were obtained from the open-access archaeometric database of copper alloys finds from the 1st to the 14th centuries [19]. Untreated brooches represent only a small percentage of the total, only 8 out of 101. Most of the examined

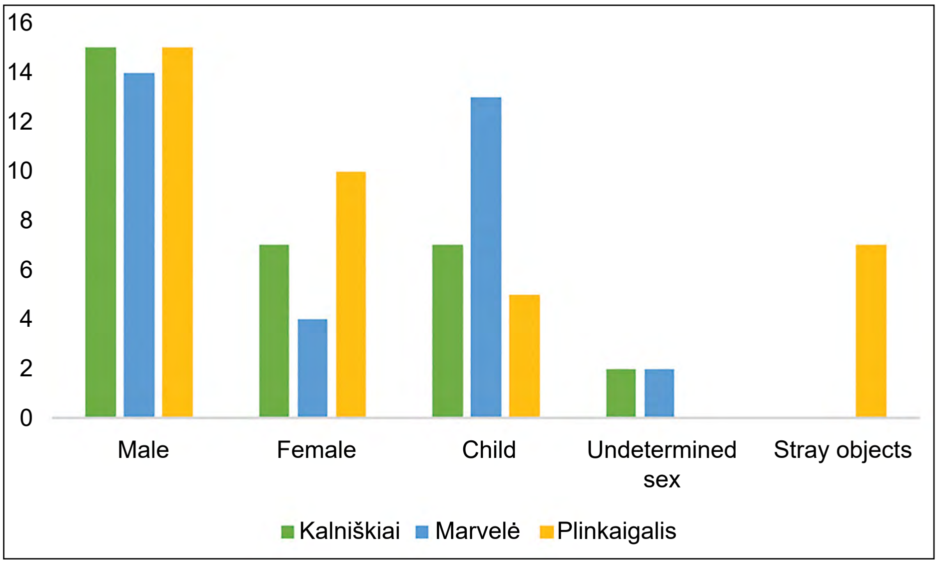

Fig. 2. The brooches distribution by gender in the studied cemeteries

brooches were treated according to the standard procedures for the conservation of archaeological metals. These included cleaning, drying, consolidation and coating. Polybutyl methacrylate (PBMA) was used as the consolidation material.

Evaluation of storage conditions in museums and their impact on future preservation

Among the ten agents of deterioration in museum environment incorrect relative humidity and temperature play a key role [20–23]. For this reason, these two factors were analysed in this study. The environment of storage areas was monitored with Hobo data loggers (H08-003-01 at the Lithuanian National Museum (further LNM) and HOBO UX100-003 at Vytautas the Great War Museum (further VDKM)). Relative humidity and temperature in the rooms were recorded hourly. The collected data from two years of monitoring (2021–2022) were analysed using the software program *Eclimatenotebook* [24]. The analysis of this program is based on four types of decay metrics. For this study, only one of the metrics was relevant. The metal corrosion metric represented the risk of environmental corrosion of metals and the analysis of temperature and relative humidity data was based on the moving average of humidity levels. The maximum equilibrium moisture content (% EMC Max) was used which indicates the maximum amount of moisture in the environment. The metal corrosion metric was divided into three zones: good (Max EMC ≤ 7.0), ok and risk (Max EMC > 10.5). A lower % EMC Max was a better corrosion prevention. Based on the results of metal corrosion metrics, the future preservation level was calculated using the risk assessment method [25–26]. This method was based on the probability of events and changes in the current values of an object or collection. A usual equation used in measuring risks in cultural collections is the following: magnitude of risk (MR) = P (probability) × FS (fraction susceptible) × LV(loss of value) × E (the extent of the risk), where MR is the extent or effect of a particular risk on a collection, P is the estimated change of occurrence of an event in 100 years, FS is the part of a collection considered vulnerable to a particular risk, and LV is the reduction in the value of the collection for its intended purposes. All indices were calculated between 0 and 1.

RESULTS AND DISCUSSION

Visual and X-ray assessment

The visual examination revealed that most of the crossbow brooches with a triangular foot were made of multi-component copper alloy, but there were also some of them made of silver and iron (Table 1). The axis of these brooches was made of copper alloy, silver or iron.

Table 1. **Results of the visual evaluation of materials used to make crossbow brooches with a triangular foot**

Site name	Cu alloy	Ag alloy	Fe alloy	Cu alloy with Ag plate
Kalniškiai	27	4	–	–
Marvelė	27	3	2	1
Plinkaigalis	32	1	4	–

The visual examination also revealed that most of the brooches were technologically forged. The wire was used to turn over the iron or copper alloy axis to make the brooch spring, and the knobs were also forged. Most of the fully preserved brooches come from the Plinkaigalis Cemetery. Almost completely preserved brooches with only one missing knob were found in all three cemeteries. In most cases, the knob was preserved on the left side of the brooch (17 out of 26). Most of the brooches came from male graves, as the majority of the brooches were found in the graves of this gender. The degree of preservation of the brooches from Marvelė and Kalniškiai cemeteries was quite similar. A visual comparison of the present condition with the images of the brooches in the excavation reports revealed a very small number of damaged objects which occurred after excavation [27–58]. In most cases, the degree of preservation before and after excavation was the same. That was also confirmed by X-ray. However, most of the treated brooches showed microspots of active corrosion, mostly visible only under a magnifying microscope. Adhesions were noted on some brooches but their presence could not be evaluated after the excavation, as no records were made at that time. The evaluation of X-ray images confirmed that some objects were broken and adhered at some point (Fig. 3).

The sides of the booch foot currently look damaged in many cases. X-rays have confirmed that

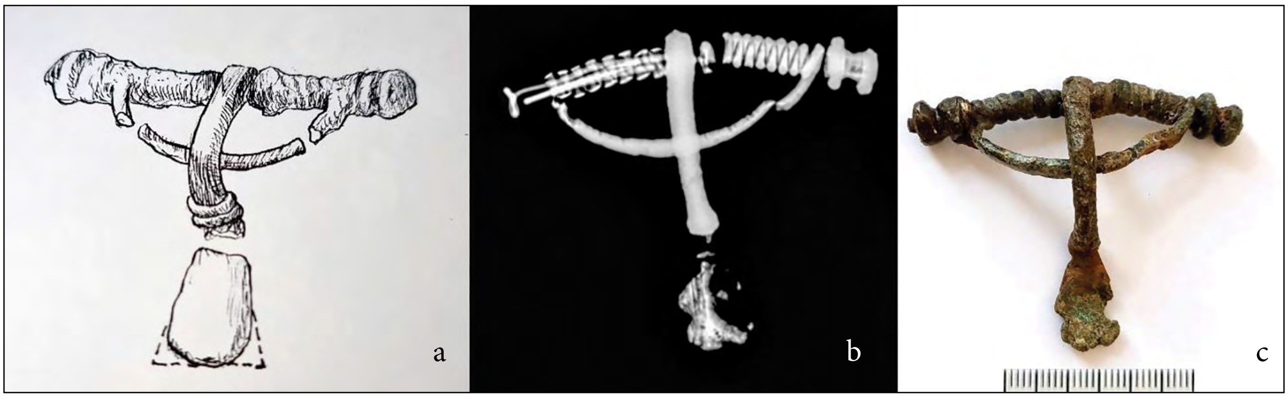

Fig. 3. Example of the preservation level of the brooch from the Kalniškiai Cemetery: (a) images from the excavation report, (b) X-ray image and (c) current view. VDKM AR 2436/45. Radiograph by R. Vedrickas. Photo by A. Vasiliauskaitė

the metal layer of the foot was much thinner compared to that of the brooch bow. And the triangular foot or its edges seems to melt on the X-ray images because of the thinner metal layer. This part of the brooch is more susceptible to corrosion, the metal core can be easily damaged, and even a small corrosion damage can affect the shape of the foot (Fig. 5). The same applies to the thin pins used to fasten the brooches. X-rays showed that the metal core was damaged in most cases. Untreated brooches represent only a small percentage of the total, only 8 out of 101, and they come only from the Marvelė Cemetery. X-rays confirm that their degree of preservation was very similar to that of treated brooches (Figs 4–5).

Metal composition

The results of the elemental composition analysis are shown in Table 2. The values obtained were averaged and used as data in % for further analysis. The analysis revealed that most of the brooches were made of brass and brass/gunmetal (Figs 6–7).

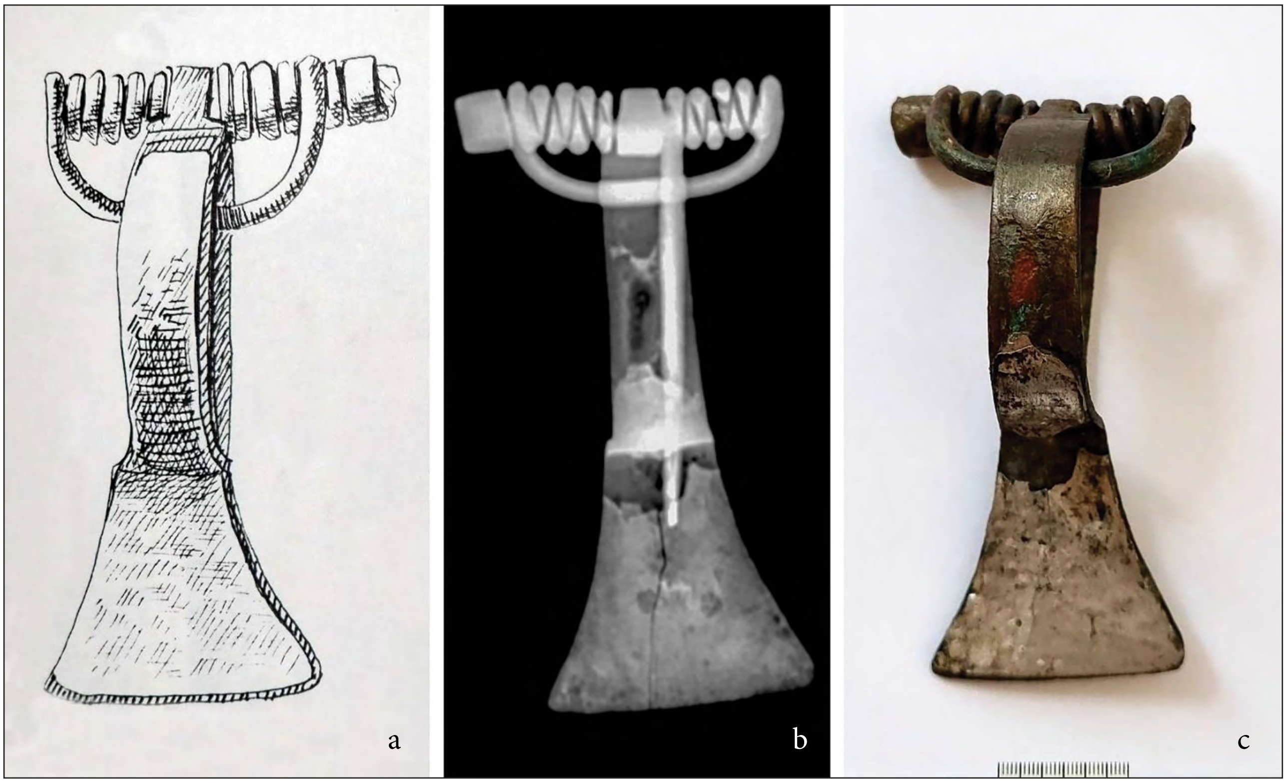

Fig. 4. Example of the preservation level of the brooch from the Marvelė Cemetery: (a) images from the excavation report, (b) X-ray image and (c) current view. VDKM AR 2509/200. Radiograph by R. Vedrickas. Photo by A. Vasiliauskaitė

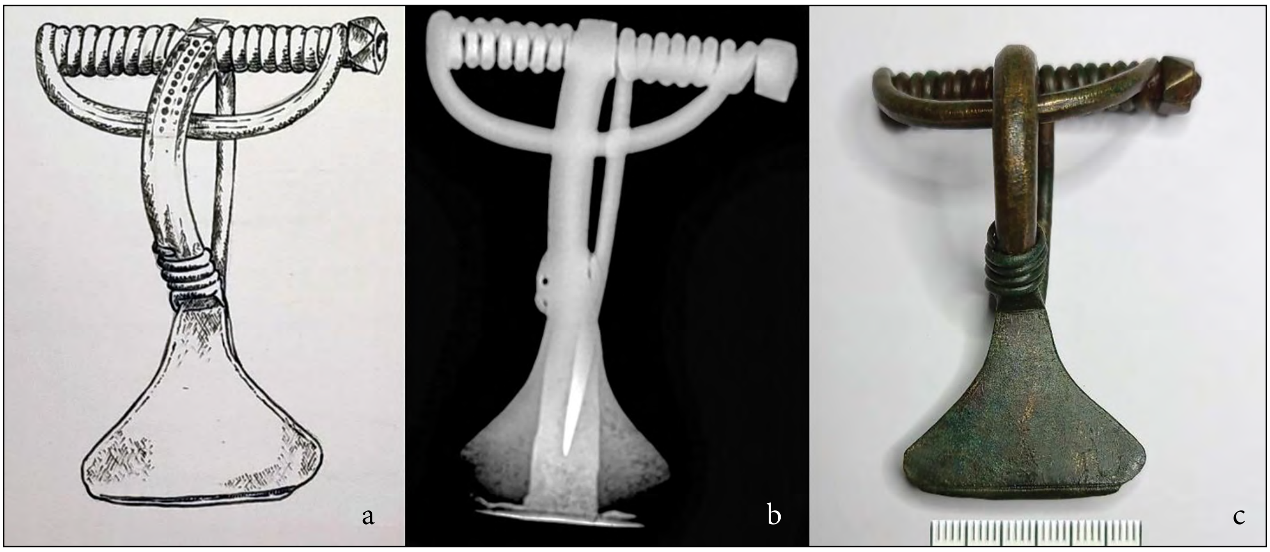

Fig. 5. Example of the preservation level of the brooch from the Plinkaigalis Cemetery: (a) images from the excavation report, (b) X-ray image and (c) current view. LNM AR 700:26. Radiograph by R. Vedrickas. Photo by A. Vasiliauskaitė

Table 2. **Classification of the analysed brooches according to alloy type**

Site name	Object ID	Grave No.	Gender	Cu	Sn	Pb	Zn	Fe	Ag	Alloy type
Plinkaigalis	LNM AR 700:260	56	Female	72.87	0.49	3.22	16.34	6.31	0.12	Brass
Plinkaigalis	LNM AR 700:550	124	Female	75.52	4.43	5.52	8.11	5.27	0.65	Brass/gunmetal
Plinkaigalis	LNM AR 700:619	148	Male	84.17	1.11	2.36	8.64	3.28	0.14	Brass
Plinkaigalis	LNM AR 700:150	42	Male	74.97	0.79	2.96	20.11	0.59	0.06	Brass
Plinkaigalis	LNM AR 700:867	244	Child	71.42	7.24	6.52	6.63	7.47	0.13	Brass/gunmetal
Plinkaigalis	LNM AR 700:26	4	Female	75.24	1.36	4.15	13.1	5.51	0.05	Brass
Plinkaigalis	LNM AR 700:935	279	Male	93.08	0.45	3.48	0.21	2.23	0.17	Brass/gunmetal
Plinkaigalis	LNM AR 700:151	42	Male	65.56	1.18	6.12	17.64	8.61	0.09	Brass
Plinkaigalis	LNM AR 700:1212	Stray	–	84.3	0.86	2.34	10.35	1.57	0.19	Brass
Plinkaigalis	LNM AR 700:525	122	Female	71.56	0.17	1.02	22.21	2.8	0.13	Brass
Plinkaigalis	LNM AR 700:1272	Stray	–	82.6	0.04	0.46	15.6	0.54	0.09	Brass
Plinkaigalis	LNM AR 700:6	2	Male	79.95	0.01	0.18	15.13	3.82	0.15	Brass
Plinkaigalis	LNM AR 700:563	126	Female	82.17	1.6	2.78	12.92	2.78	0.18	Brass
Plinkaigalis	LNM AR 700:563 (axis)	126	Female	30.99	1.04	1.81	7.01	59	0	Brass
Plinkaigalis	LNM AR 700:1181	Stray	–	77.74	1.49	1.1	19.04	0.21	0	Brass
Plinkaigalis	LNM AR 700:657	163	Female	78.84	1.4	6.44	10.34	2.41	0.24	Brass
Plinkaigalis	LNM AR 700:301	64	Male	76.21	1.27	4.53	10.85	6.57	0.2	Brass
Plinkaigalis	LNM AR 700:1186	Stray	–	79.05	0.01	2.52	16.77	0.95	0.08	Brass
Plinkaigalis	LNM AR 700:1036	329	Male	74.39	2.01	4.2	13.34	5.07	0.39	Brass
Plinkaigalis	LNM AR 700:421	101	Female	77.37	4.28	5.11	9.69	3.08	0.26	Brass
Plinkaigalis	LNM AR 700:516	121	Female	72.23	0.02	0.23	26.07	0.26	0.11	Brass
Kalniškiai	VDKM AR 2460/17	179	Male	82.2	3.02	7.42	5.91	0.61	0.14	Brass/gunmetal
Kalniškiai	VDKM AR 2460/17 (axis)	179	Male	42.61	1.63	2.32	6.42	43.71	0	Brass/gunmetal
Kalniškiai	VDKM AR 2406/77	38	Male	80.09	1.11	0.75	16.06	1.42	0.07	Brass
Kalniškiai	VDKM AR 2483/11	246	Male	78.15	1.1	4.89	3.58	4.89	0.82	Brass/gunmetal

Table 2. **(Continued)**

Site name	Object ID	Grave No.	Gender	Cu	Sn	Pb	Zn	Fe	Ag	Alloy type
Kalniškiai	VDKM AR 2483/11 (axis)	246	Male	29.52	3.11	1.55	2.13	63.26	0.34	Brass/gunmetal
Kalniškiai	VDKM AR 2406/78	38	Male	77.17	6.29	4.99	10.18	0.42	0.42	Brass/gunmetal
Kalniškiai	VDKM AR 2406/78 (axis)	38	Male	32.32	0.98	1.67	3.71	60.21	0	Brass/gunmetal
Kalniškiai	VDKM AR 2461/28	208	Male	65.96	4.96	4.16	8.57	15.37	0.09	Brass/gunmetal
Kalniškiai	VDKM AR 2461/28 (axis)	208	Male	49.08	0.65	5.02	3.37	41.48	0.1	Brass
Kalniškiai	VDKM AR 2406/54	29	Male	81.72	8.55	2.67	1.08	0.94	4.64	Bronze
Kalniškiai	VDKM AR 2406/54 (axis)	29	Male	46.75	3.12	1.8	1	45.49	1.65	Bronze
Kalniškiai	VDKM AR 2468/44	240	Child	61.07	19.87	8.43	2.13	5.77	2.12	Leaded bronze
Kalniškiai	VDKM AR 2461/35	209	Child	66.76	10.57	5.19	2.55	14.44	0.16	Bronze
Kalniškiai	VDKM AR 2461/35 (axis)	209	Child	39.12	2.9	3.88	2.6	51.01	0.13	Brass/gunmetal
Kalniškiai	VDKM AR 2453/52	76	Male	92.42	0.01	0.89	5.81	0.49	0.14	Brass
Kalniškiai	VDKM AR 2404/16 (axis)	5	Male	36.96	0.82	0.41	0.68	45.29	15.75	Brass/gunmetal
Kalniškiai	VDKM AR 2422/41	54	Male	71.75	0.81	20.4	5.2	0.75	0.2	Leaded brass
Kalniškiai	VDKM AR 2449/72	126	Child	79.2	8.9	4.24	4.32	1.7	1.32	Brass/gunmetal
Kalniškiai	VDKM AR 2451/2	141	Male	62.41	12.61	11.76	3.31	8.59	0.92	Leaded bronze
Kalniškiai	AR 2451/10 (1 of 2) (axis)	144	Female	31.51	1.88	5.76	1.84	58.12	0.12	Brass/gunmetal
Kalniškiai	AR 2451/10 (1 of 2)	144	Female	81.00	4.08	9.58	3.09	1.20	0.24	Leaded brass/ gunmetal
Kalniškiai	AR 2451/10 (2 of 2) (axis)	144	Female	60.66	1.77	4.37	6.50	25.83	0.14	Brass/gunmetal
Kalniškiai	AR 2451/10 (2 of 2)	144	Female	70.83	2.93	6.97	4.79	13.51	0.19	Brass/gunmetal
Kalniškiai	VDKM AR 2460/59	189	Female	70.67	13.4	11.49	1.65	2.13	0.2	Leaded bronze
Kalniškiai	VDKM AR 2461/2	201	Female	70.63	7.14	14.35	3.74	1.86	1.87	Leaded brass/ gunmetal
Kalniškiai	VDKM AR 2505/1	253	Male	77.93	1.05	3.84	2.54	3.35	0	Brass/gunmetal
Kalniškiai	VDKM AR 2461/21	207	Male	79.86	3.06	4.93	2.72	8.99	0.08	Brass/gunmetal
Kalniškiai	VDKM AR 2436/45	97	Male	57.5	10.22	16.5	5.8	9.33	0.19	Leaded brass/ gunmetal
Kalniškiai	VDKM AR 2442/5	42	Female	88.22	1.75	4.66	4.66	0.5	0	Brass/gunmetal
Kalniškiai	VDKM AR 2442/5 (axis)	42	Female	55.81	1.93	3.26	5.51	33.4	0	Brass/gunmetal
Kalniškiai	VDKM AR 2449/68	125	Child	85.96	1.17	1.04	3.8	7.88	0	Brass/gunmetal
Kalniškiai	VDKM AR 2460/58	189	Male	84.23	2.03	9.46	2.65	1.01	0.2	Leaded brass/ gunmetal
Kalniškiai	VDKM AR 2460/58 (axis)	189	Male	25.43	0.59	5.53	2.33	66.01	0	Brass/gunmetal
Kalniškiai	VDKM AR 2406/42	24	Male	74.46	2.36	6.13	12.25	4.49	0.15	Brass
Marvelė	VDKM Mv 1479/69	1255	Male	86.29	0.03	2.9	9.19	1.26	0.06	Brass
Marvelė	VDKM Mv 1479/69 (axis)	1255	Male	55.23	0.24	3.62	7.39	32.86	0.28	Brass

Table 2. **(Continued)**

Site name	Object ID	Grave No.	Gender	Cu	Sn	Pb	Zn	Fe	Ag	Alloy type
Marvelė	VDKM Mv 1479/84	1257	Female	75.01	1.78	11.69	3.84	5.42	1.54	Leaded brass/ gunmetal
Marvelė	VDKM Mv 1479/32	1244	Female	79.72	5	11.62	2.07	0.48	0.72	Leaded brass/ gunmetal
Marvelė	VDKM Mv 1479/32 (axis)	1244	Child	54.04	1.54	4.28	1.76	37.75	0.32	Brass/gunmetal
Marvelė	VDKM Mv 1796/174	1411	Male	86.54	0.13	1.72	2.85	6.87	0.42	Brass
Marvelė	VDKM Mv 1796/174 (axis)	1411	Male	62.9	0.06	2.68	4.89	27.79	0.2	Brass
Marvelė	VDKM Mv 1796/146	1404	–	76.3	4.93	2.75	5.47	9.46	0.36	Brass/gunmetal
Marvelė	VDKM Mv 1796/355	1466	Child	75.61	3.95	8.46	7.45	3.79	0.22	Leaded brass/ gunmetal
Marvelė	VDKM Mv 1796/355 (axis)	1466	Child	34.85	0.78	4.48	3.43	54.97	0	Brass
Marvelė	VDKM Mv 1796/366	1467	Child	76.86	4.22	9.06	7.97	1.12	0.21	Leaded brass/ gunmetal
Marvelė	VDKM Mv 1796/366 (axis)	1467	Child	17.81	1.88	4.06	1.76	72.97	0.17	Brass/gunmetal
Marvelė	VDKM Mv 1796/189	1414	Male	81.07	11.28	3.2	3	0.75	0.19	Bronze
Marvelė	VDKM Mv 1796/189 (axis)	1414	Male	17.8	1.24	0.92	1.15	78.57	0	Brass/gunmetal
Marvelė	VDKM AR 2500/156	407	Male	78.6	10.2	4.52	2.17	3.37	0.79	Bronze
Marvelė	VDKM AR 2531/115	721	Male	72.41	0.92	10.2	8.35	7.04	0.17	Leaded brass
Marvelė	VDKM AR 2478/277	210	Male	79.7	4.62	5.43	8.53	1.23	0.23	Brass/gunmetal
Marvelė	VDKM AR 2478/277 (axis)	210	Male	32.25	4.78	13.17	4.81	44.48	0.31	Leaded brass/ gunmetal
Marvelė	VDKM AR 2509/245	556	Male	73.75	3.87	9.33	4.35	7.98	0.44	Leaded brass/ gunmetal
Marvelė	VDKM AR 2479/53	277	Male	84.73	1.43	4.37	9.07	0.17	0	Brass
Marvelė	VDKM AR 2479/53 (axis)	277	Male	23.02	0.9	4.36	3.13	68.17	0	Brass/gunmetal
Marvelė	VDKM AR 2531/34	693	Male	70.08	8.27	6.86	5.73	8.04	0.18	Brass/gunmetal
Marvelė	VDKM AR 2479/192	693	Male	50.26	29.17	12.16	1.39	5.94	0.42	Leaded bronze
Marvelė	VDKM AR 2479/144	299	Child	84.53	0.91	5.53	4.89	2.79	0.22	Brass
Marvelė	VDKM AR 2479/144 (axis)	299	Child	62.84	0.6	4.93	5.81	24.93	0.15	Brass
Marvelė	VDKM AR 2479/91	284	Female	84.92	1.09	2.26	11.21	0.21	0.03	Brass
Marvelė	VDKM AR 2479/91 (axis)	284	Female	25.52	0.73	3.71	2.75	67.42	0	Brass/gunmetal
Marvelė	VDKM AR 2479/278	328	Child	77.49	1.19	4.2	9.46	7.3	0.09	Brass
Marvelė	VDKM AR 2479/134	298	Male	76.95	2.42	5.08	14.33	0.59	0.29	Brass
Marvelė	VDKM AR 2479/170	304	Male	75.85	8.5	3.45	7.51	4.06	0.19	Brass/gunmetal
Marvelė	VDKM AR 2479/276	328	Child	77.94	3.9	6.85	9.82	1.18	0.16	Brass/gunmetal
Marvelė	VDKM AR 2509//26	535	Male	47.41	17.94	15.06	2.5	15.94	1.07	Leaded bronze
Marvelė	VDKM AR 2509/200 (plate)	535	Male	10.97	1.95	1.9	0.43	0	83.93	Silver

Table 2. **(Continued)**

Site name	Object ID	Grave No.	Gender	Cu	Sn	Pb	Zn	Fe	Ag	Alloy type
Marvelė	VDKM AR 2478/302	333	Female	82.54	0.9	5.63	6.8	3.68	0.15	Brass
Marvelė	VDKM AR 2479/15	267	Child	75.9	1.31	5	8.74	8.85	0	Brass
Marvelė	VDKM AR 2479/40	273	Child	75.89	3.37	4.78	7.05	8.76	0	Brass/gunmetal
Marvelė	VDKM AR 2479/143	299	Child	80.53	2.15	6.82	5.84	4.27	0.08	Brass/gunmetal

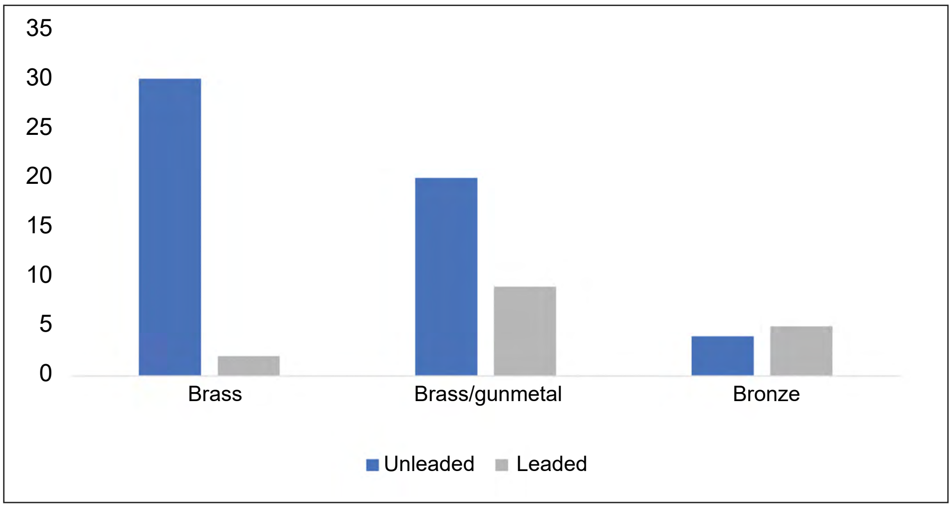

Fig. 6. General classification of the analysed brooches according to the alloy type

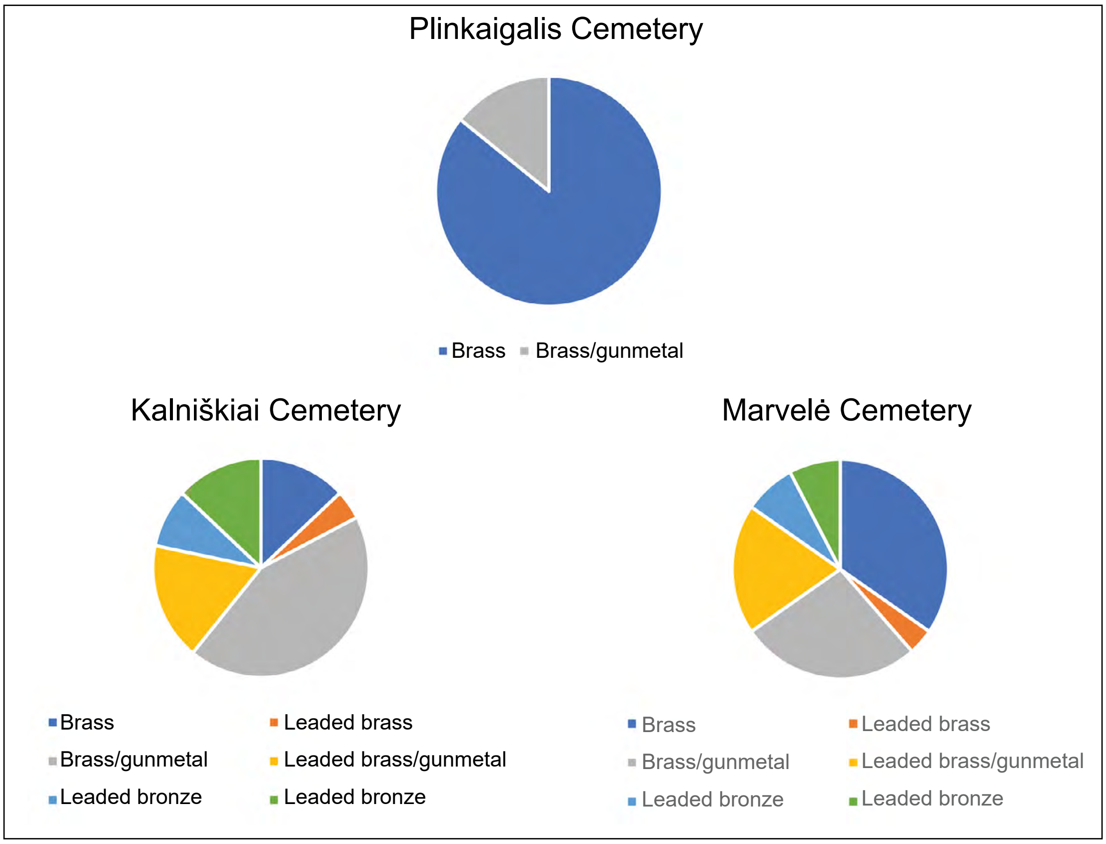

Fig. 7. Classification of the alloy types of the individual cemeteries

Brass was one of the most suitable copper alloys for making artefacts by forging. The elemental composition of artefacts had changed from bronze to brass since the middle of the 1st century AD. Brass was still the predominant copper alloy in the 5th – 6th centuries AD.

The analysis of 22 axes of brooches showed a high percentage (over 10%) of iron on the surface. According to some researchers, the observed high iron contents are the result of post-depositional processes in which the applied surface treatment does not completely remove iron containing soil [59]. However, in the case of the crossbow brooches with a triangular foot the presence of a high iron content could indicate that the axis was made of iron and iron corrosion on the axis bar was so active at a particular time that its corrosion products adhered strongly to the surface of the copper alloy.

The variations in the metal composition of the brooches from the Plinkaigalis Cemetery differ from the others. They consisted of only two types of alloys. In the cemeteries of Kalniškiai and Marvelė the variations in the composition and the degree of preservation of the brooches are quite similar.

Other factors

All three cemeteries were located in a similar geographical position – on the river bank in Central Lithuania lowlands. Not far from Kalniškiai and Plinkaigalis cemeteries there were gravel quarries. The geological layers vary from clay to sandy to gravel. In addition, some of the cemeteries, such as Marvelė, may have been inundated by floods [60, 61]. Therefore, geochemical processes and mechanical damage to artefacts (e.g. deformation of finds under different circumstances in grave pits) may have occurred at different rates.

Most of the fully preserved brooches (20) come from the Plinkaigalis Cemetery, which was excavated earlier than the others. Kalniškiai and Marvelė cemeteries were excavated around the same time, and the degree of preservation of the brooches is quite similar (about 10 fully preserved brooches). Thus, they were taken in a quite good condition from the different depths of the burial environment. The brooches were found at different depths: in Kalniškiai from 20 to 110 cm, in Marvelė from 140 to 270 cm and in Plinkaigalis from 15 to 150 cm. The date of excavation, the number of brooches found, the date of acquisition and conservation treatment are listed in Tables 3–5.

Table. 3. **Plinkaigalis Cemetery excavation date, the number of brooches found, the date of acquisition and conservation treatment**

Type	Excavation date							
	1977	**1978**	**1979**	**1980**	**1981**	**1982**	**1983**	**1984**
No. of brooches found	5	9	7	6	3	1	1	5
Acquisition date	1981	1980	1980	1980	1988	1988	1988	1988
Conservation date	1987	1987	1987	1987	1989	1989	1989	1989

Table. 4. **Kalniškiai Cemetery excavation date, the number of brooches found, the date of acquisition and conservation treatment**

Type	Excavation date										
	1990	**1991**	**1992**	**1993**	**1995**	**1996**	**1997**	**1998**	**2000**	**2001**	**2003**
No. of brooches found	5	2	2	1	5	2	4	7	1	1	1
Acquisition date	1991	1992	1993	1995	1997	1997	1999	1999	2004	2005	2005
Conservation date	1997	1997	1997	1997	1998	1998	2000	2001	2004	2006	2006

Table. 5. **Marvelė Cemetery excavation date, the number of brooches found, the date of acquisition and conservation treatment**

Type	Excavation date					
	1991	**1992**	**1993**	**1994**	**2001**	**2006**
No. of brooches found	1	19	3	3	2	5
Acquisition date	1992	2002	2005	2009	2022	2022
Conservation date	1993	2005	2006	2012	–	–

A correlation between these characteristics and the degree of preservation of the brooches is not apparent.

Effect of storage environment conditions

80% of the brooches are kept in storage, the rest are on display. *Eclimatenotebook* calculated the metric of metal decay for LNM %EMC max = 8.9 (max 51% relative humidity) and for VDKM %EMC max = 13 (max 78% RH). Based on these results, the brooches in VDKM are at greater risk than in LNM due to a high relative humidity, taking into account that there is a probability that relative humidity will reach 78% at least once in next 100 years. A high humidity will increase metal corrosion and brooches with iron parts will be more susceptible (FS) to environmental damage than others and could lose half of its current condition (LV). The calculation of the future long-term preservation calculation MR = 1 × 0.7 × 0.5 × 1 = 0.35 shows the average degree of potential damage.

CONCLUSIONS

According to the XRF analysis, most of the examined crossbow brooches with a triangular foot from the 5–6th centuries AD were made of brass. This type of copper alloy may be the key factor in a good degree of preservation of the brooches. Both the treated and untreated brooches are in fairly good condition based on the visual and radiographic assessment. The foot and the pin are the most damaged parts. A correlation between the burial environment and depth, excavation time, conservation treatment and the degree of preservation of the brooches was not evident in this study. However, future long-term storage conditions with a high relative humidity (up to 80%) pose a major threat to both treated and untreated brooches. In particular, thin iron parts such as the foot and pin, as well as broken or damaged parts could increase corrosion processes, resulting in partial loss of value.

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Asta Vasiliauskaitė

VARIO LYDINIŲ IRIMO PROCESO ĮVERTINIMAS: LANKINIŲ SEGIŲ TRIKAMPE KOJELE IŠ VIDURIO LIETUVOS ATVEJO ANALIZĖ

Santrauka

Archeologinių vario lydinių dirbinių suirimas ir išlikimo laipsnis priklauso nuo kelių sąveikaujančių veiksnių, kurie prasideda užkasus dirbinius į žemę ir tęsiasi muziejaus saugyklose. Jau prasidėjusius senėjimo ir irimo procesus galima tik pristabdyti. Buvo tirta lankinių segių trikampe kojele metalo sudėties bei jas supusios aplinkos įtaka irimo procesams, naudojant neinvazinius metodus, tokius kaip rentgeno spindulių fluorescencinę analizę ir rentgenografiją, taip pat naudojant archeologinių tyrimų ataskaitų duomenis. Surinkti muziejų saugojimo aplinkos duomenys buvo analizuojami naudojant programą *Eclimatenotebook*. Remiantis šios analizės rezultatais, rizikų įvertinimo metodu buvo apskaičiuotas galimas segių išlikimo lygis ateityje. Dauguma tirtų segių pagamintos iš žalvario ir buvo gana geros būklės, išskyrus jų plonas kojeles ir adatas. Būsimos saugojimo sąlygos, esant aukštam santykiniam oro drėgniui (iki 80 %), kelia didelę riziką tiek konservuotoms, tiek nekonservuotoms segėms.