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Chemical compositional data of the corrosion products on Late Roman military crossbow brooches. A comparative study

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ABSTRACT

This paper presents an original dataset of 155 non-destructive surface pXRF analyses on 52 Late Roman crossbow brooches from the military cemetery at Krefeld-Gellep (Germany). These were gathered with the aim to characterise Late Roman military metallurgy, in particular where it concerns the role of state-controlled production, potential evidence for standardisation of manufacturing and the extent of recycling that took place of copper alloys at the time. It was found that although brass is often touted as an alloy particularly closely associated with the Roman army, it played a very limited role in the production of the crossbow brooch from Krefeld-Gellep, which instead were characterised by heavily leaded gunmetals and bronzes. Despite the prevalence of these complex alloys and the likelihood that these were arrived at through (prolonged) recycling and mixing, this paper concludes that Late Roman smiths were still able to make informed decisions about which materials to use. This is demonstrated by the preference of high-lead copper alloys for military dress accessories, while contemporary civilian dress accessories appear to have been predominantly made of a lower leaded, high-tin copper alloy.

1. Introduction

The last decade has seen a resurgence of research interest in the social history of the Late Roman Empire, moving beyond narratives of decline and fall towards paradigms of transformation and social change (Dodd, 2021; Heeren, 2017). A combination of archaeometry and social interpretations has already been applied successfully to a number of Roman brooch types (Bayley and Butcher, 2004; Roxburgh et al., 2017; Van Thienen and Lycke, 2017; also Teegen, 1997) to map changes in metal use and technology over time. Specific areas of interest have included the exchange in metallurgical knowledge and technology between the Roman Empire and Free Germany (Voß et al., 1998) and the potential for state or military interference in manufacturing (Van Thienen and Lycke, 2017). For Late Roman crossbow brooches specifically, previous works have highlighted the potential evidence for state control over their production (Swift, 2000; Van Thienen and Lycke, 2017), based on a combination of stylistic, metric and chemical analysis.

Production of military crossbow brooches was long assumed to have taken place in large-scale state-run workshops or fabricae in Pannonia in the 4th century (Riha, 1979, 171), although this was mostly based on assumptions rather than hard evidence (Van Thienen, 2021, 48; Swift, 2000, 3). Swift's detailed distribution study of various stylistic and decorative details suggested the presence of some workshops in Gaul and the Danubian provinces in the earlier 4th century as well (see Swift, 2000 for her composite typology incorporating Keller, 1971 and later adjustments by Pröttel, 1988), while based on the brooches from Lauriacum, Austria, Jobst (1975) argued for regional production. Some evidence for small-scale production has recently been found in Italy in the form of lead models (Giumlia-Mair et al., 2007).

A rigorous data-led approach to question of state control for Late Roman crossbow brooches was most recently undertaken by Van Thienen and Lycke (2017), who set out to identify measures of standardisation or regionality in the chemical composition of crossbow brooches found in Belgium and the Netherlands. They recognised that the earlier types showed a wide alloy variety, indicating regionality, especially in some Swift type 2 brooches (Heeren and Van der Feijst type 68b; Van Thienen and Lycke, 2017, 57). Furthermore, they found zinc and lead to have had the most pronounced influence on the distribution of Swift 3/4 brooches (Heeren and Van der Feijst type 68c) in a PCA biplot of zinc, tin and lead (Van Thienen and Lycke, 2017, 54), with variation declining steeply compared to earlier types (Van Thienen and Lycke, 2017, 57). The distribution of later brooch types, on the other hand, was found to be more influenced by lead and tin in their PCA analysis, despite showing the same degree of uniformity as earlier types.

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This was taken by the authors as a sign of a more regionalised organisation of production (Van Thienen and Lycke, 2017, 58).

However, the tacit assumption in their argument is that standardisation equals state control and, vice versa, variation equals regionality. This does not necessarily have to be the case. For instance, the involvement of the Roman state in procuring scrap and raw materials and its recycling may also have resulted in an increased variation in local, regional and wider patterns of metal chemistry compared to dress accessories that were produced locally on a smaller scale (by craftspeople who relied on much more limited streams of resources). Furthermore, there is evidence that in the Late Roman period, mining was increasingly privatised and relied increasingly on small-scale units of production (Edmondson, 1989, 98). The effects of state control over supply of resources and how these are reflected in the composition of the eventual objects made from them may be much more complex.

A second point raised by Van Thienen and Lycke is the potential identification of workshops in the metallurgical data (building on Swift's work recreating potential workshop sites from stylistic characteristics; Swift, 2000). In a ternary diagram of Swift type 3/4 brooches, Van Thienen and Lycke noticed several distinct groupings, which they suggested reflected individual workshops (Van Thienen and Lycke, 2017, 58, Fig. 5). The term "workshop" needs further defining in this context. Very little archaeological evidence is available on the organisation of crossbow brooch production, or on where different parts of the *chaîne operatoire* took place. Activities such as primary metal smelting, primary alloying, scrapping and recycling would influence the chemical signature of a workshop much more than casting, finishing and repairing (Bray and Pollard, 2012; Bray et al., 2015; Pernicka, 2014). It has been suggested that Late Roman crossbow brooches were made by itinerant smiths or personally issued by the Emperor, possibly while travelling with the armies from fort to fort (Van Buchem, 1966; Heeren and Van, 2017, 333), while Swift's typological work indicated a network of both larger and smaller supra-regional production sites (Swift, 2000).

The amount of control and independence that production sites had at a local level was very likely quite limited. Production at the state or provincial level (the *fabricae*) likely had higher amounts of control over the resources they could use, but even in that scenario, each workshop having a distinct metal chemistry seems unlikely considering all the factors around supply and manufacturing as well as potential variation over time.

This paper addresses these questions in two ways. First, an original dataset of corrosion composition of crossbow brooches from the Late Roman cemetery at Krefeld-Gellep, Germany is presented. This dataset was acquired using non-invasive surface pXRF as part of a larger project investigating Late Roman copper-alloy dress accessories in Germania Secunda (Van der Meulen-van der Veen, in prep.). Secondly, these new data are put into a wider framework of other compositional studies of crossbow brooches and other Roman copper alloys to investigate the possible indicators of state control over various parts of the production process. This broader comparative approach is also used to explore themes of recycling and the availability of raw material in the Late Roman West (in which recycling is often presumed to have played a significant role; Pollard et al., 2015; Bray et al., 2015). Finally, the comparison of compositional data taken from the corroded surface to data from core samples may provide a springboard for an evaluation of surface pXRF as a method for addressing archaeological research questions.

2. Materials and methods

2.1. Materials

The crossbow brooch is firmly associated with military dress in the Roman West and is seen as part of a soldier's manner and dress (James, 2001), at least in the 4th century. Their association with the Late Roman army is further based on their ubiquity in frontier regions and in military complexes (Swift, 2000). At the turn of the 5th century, some have argued that the brooch became more associated with administrative and governmental positions and members of the civilian elite (Heeren and Van der Feijst, 2017, 182; Swift, 2000, 81; see Van Thienen, 2017 for a more in-depth discussion). However, the extensive amalgamation of governmental and military power in the Late Roman frontier zones (Van Thienen, 2017, 120) makes such a distinction largely academic.

The crossbow brooch is a cast brooch with a tubular hinge. It can be found throughout the entire Roman Empire, yet it is generally rare in Free Germany (Riha, 1979, 171). Their ubiquity has resulted in several typo-chronologies (see Table 1 and Fig. 2; cf. (Heeren and Van der Feijst, 2017, 178–182, type 68 and Swift, 2000, chapter 2 for an in-depth literature review of previous typologies), highlighting their uniformity across the Empire as well as regional patterns of style and distribution (see especially Swift, 2000, chapter 2).

Against this background, this paper presents the crossbow brooches from Krefeld-Gellep (Fig. 1). The Late Roman military complex at Krefeld-Gellep (*Gelduba*) consisted of a fortification (Reichmann, 1987) and cemetery (see for catalogues of the grave inventories Pirling, 1966; Pirling, 1974; Pirling, 1979; Pirling, 1989; Pirling, 1997; Pirling and Siepen, 2000; Pirling and Siepen, 2003; Pirling and Siepen, 2006), which was in use from the Early Roman period to the Frankish period. The cemetery at Krefeld was excavated between 1934 and 2002 (Pirling and Siepen, 2006, xi). The site, and especially its cemetery, has become famous for the large number of Late Roman finds from both the 4th and 5th centuries, which until the introduction of commercially led rescue archaeology had been rare at other sites, especially for the 5th century. Many of the burials at Krefeld reflect a military identity. At least 164 Late Roman graves contain some combination of weaponry, military belt accoutrements or military brooches.

In total, 67 Late Roman crossbow brooches were found in the cemetery at Krefeld-Gellep, 52 of which were available and/or suitable for pXRF analysis (see Table 1). The majority of crossbow brooches found in

Table 1
Crossbow brooch typology and count of analysed brooches in Krefeld-Gellep.

Type		Count	Readings	Date
Swift 2000	Heeren and Van der Feijst, 2017	1	3	
Swift 1	68a	1	3	AD 270-300
Swift 2	68b	2	6	AD 300-360
Swift 2i	68b1	2	6	AD 300-360
Swift 2ii	68b2			AD 300-360
Swift 2iii	68b3	5	15	AD 300-360
Swift 3/4	68c	6	18	AD 340-400
Swift 3/4A	68c1	10	28	AD 340-400
Swift 3/4B	68c2	20	59	AD 340-400
Swift 3/4C	68c3			AD 340-400
Swift 3/4D	68c4	1	3	AD 340-400
	68c5			AD 340-400
Swift 5i	68d1	1	3	AD 390-450
Swift 5ii	68d2	2	6	AD 390-450
Swift 6i	68e1			AD 400-500
Swift 6ii	68e2	1	3	AD 390-450
Total		52	155	

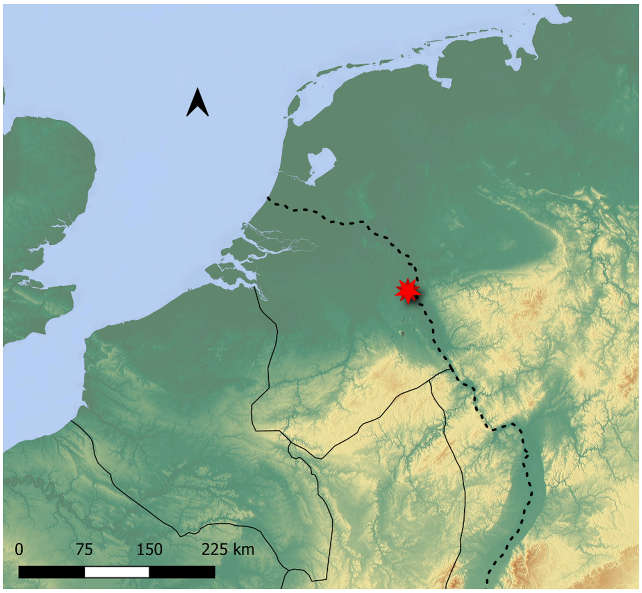

Fig. 1. The location of the Late Roman cemetery of Krefeld-Gellep (*Gelduba*). Map produced with QGIS software; base map taken from Maps for Free (https://maps-for-free.com/).

Krefeld are of the Keller 3/4 group, a brooch characterised by a relatively long foot and onion-shaped knobs. This pattern is repeated across the Lower Rhine frontier zone, with this mid-4th-century type outnumbering other types of crossbow brooch in many fortifications and associated cemeteries (for instance Cologne; Swift, 2000; Friedhoff, 1991; Von Boeselager, 2012, Jülich; Pöppelmann, 2010; Gottschalk, 2015; Maastricht and Heerlen; Haalebos, 1986; Nijmegen-Kelfkensbos (Heeren and Van der Feijst, 2017) and Oudenburg (Mertens and Van Impe, 1971).

After excavation, all brooches were cleaned, but not stabilized or treated. This means that the surface XRF was taken from a completely corroded surface (descriptions of each corrosion product are provided in the appendix). A detailed catalogue of the Krefeld-Gellep crossbow brooches, their decoration and find context will be published elsewhere (Van der Meulen-van der Veen, in prep.; all brooches collected in the first five volumes on Krefeld compiled by Renate Pirling are already presented in Swift, 2000; cf. Pirling, 1966; Pirling, 1974; Pirling, 1979; Pirling, 1989; Pirling, 1997). Several brooches showed signs of treated surfaces. These are discussed in section 3.3.

2.2. Methodology

The equipment used was a Niton Xl3t GOLDD XRF scanner equipped with a silicon drift detector, capable of analysing a surface area of 8mm^2 (also used by Roxburgh, 2019 and associated papers by that author), using the factory-calibrated "Electronic metals" setting. To improve precision and safety during the measuring sessions, the XRF unit was mounted into a protective chamber and connected to a laptop allowing the unit to be operated remotely. The "Electronic metals" setting was further modified to run on different tube voltages. Each analysis was run for 40 s in real time: 30 s on the main range filter using a tube voltage of 50 kV (targeting the copper-barium and gold-lead spectra) and 10 s on the low range filter at 20 Kv (targeting aluminium-copper). Previous studies using this same pXRF scanner indicated that the beam signal stabilises around the 30 s mark for the bulk materials (copper, tin, zinc and lead; Roxburgh et al. 2017, 248). The unit was calibrated on the CHARM reference set to ensure consistency and reproducibility of the results, as well as optimising the pXRF unit for analysing archaeological metals (Heginbotham et al. 2015).

For each brooch, flat surfaces on the foot, bow and axis support were analysed so that the internal consistency of the data could be established and more accurate information about the composition of the entire object could be gathered. Conservation and corrosion processes were recorded using the scale as defined by Fernandes et al. (2013, Table 1).

11 elements were extracted from the raw pXRF data (Cu, Sn, Zn, Pb, As, Sb, Hg, Ag, Au, Ni and Fe; accounting for between 97 and 99 % of the raw output) and recalculated to make up 100 %. Most of the elements commonly associated with soil contamination, namely manganese, aluminium, silicon, chlorine, sulphur, calcium and phosphorus did not reach the limit of detection in the unmodified spectra. Bismuth was occasionally found as a trace element, with a maximum identified value of 0.6 %. Iron was included in the normalised spectrum as its presence might stem from soil contamination and corrosion, but also from impurities in the copper ore and the smelting process (Craddock and Meeks, 1987). Absent values or "zeros" in the dataset were replaced by the limit of detection value as calculated by factory settings of the pXRF unit for each individual matrix.

Each reading was given an alloy label using the definitions for copper alloys as set out by the Oxford FLAME project (Bray et al. 2015; Pollard et al., 2015; Bray, 2020), in which alloys are defined by the presence of tin, zinc and lead above 1 % as a significant amount. Although this method is seen by some as unsuitable to analyses taken from corroded surfaces (Roxburgh et al., 2019, 63), it has the benefits of not imposing complicated or modern definitions of alloys (Bayley and Butcher, 2004; Dungworth, 1997; Mortimer, 1991; Hammer et al., 1998) on archaeological objects, instead allowing the visualisation of complex chemical structures in the data with minimal assumptions about craft or intentionality (Bray, 2020, 243–245). A low threshold presence or absence of major alloying elements at 1 % allows us to study the character of different combinations, rather than setting higher, modern thresholds for "true" alloying. Below it will be argued that the metal compositions found in the Krefeld brooches can be sorted into a number of groups that transcend these alloy definitions. In this paper, the FLAME copper alloy definitions will be used to describe individual or groups of artefacts that fall within those categorisations to ensure that a consistent and shared nomenclature is used upon which further dissection and discussion can be built.

With surface pXRF, the influence of corrosion processes on the data is of course a major factor that needs to be addressed (Hall, 1961; Nørgaard, 2017). Previous studies comparing the chemical data obtained of destructive measurements and non-invasive surface techniques have noted the selective depletion of copper and zinc and relative enrichment of tin and lead in the surface spectra (Fernandes et al., 2013; Roxburgh et al., 2019; Constantinides et al., 2002; Orfanou and Rehren, 2015). Further challenges may be presented by the inherent heterogeneity of the corrosion product, (Gigante et al., 2003, 294; Nicholas and Manti, 2014), uneven surfaces (Liritzis and Zacharias, 2011, 123; Frahm and Doonan, 2013, 1426), original decoration and surface treatment such as gilding or tinning (Hall, 1961; Martinón-Torres et al., 2012, 545) as well as surface depletion and enrichment of elements in the corrosion phases. Multiple readings per brooch were taken to ensure the inherent heterogeneity could be adequately mapped. Averages are only used to present data when explicitly mentioned, as the representation of zinc would be negatively impacted by averaging the compositional data.

3. Results

The protocol used for this paper was also able to reliably detect trace elements at the 0.1 % level (Pollard et al., 2015), although there are many factors that influence this (Heginbotham and Solé, 2017; Heginbotham et al., 2019) and different methodological decisions made by different projects have a much more pronounced effect on the ability to detect elements at the 0.1 % level than on the 1 % level. The detection of trace elements remains largely unaddressed in this paper, because that is an area in which many compositional studies differ too greatly in terms of detection limits, spectrum width and analytical difficulties to make

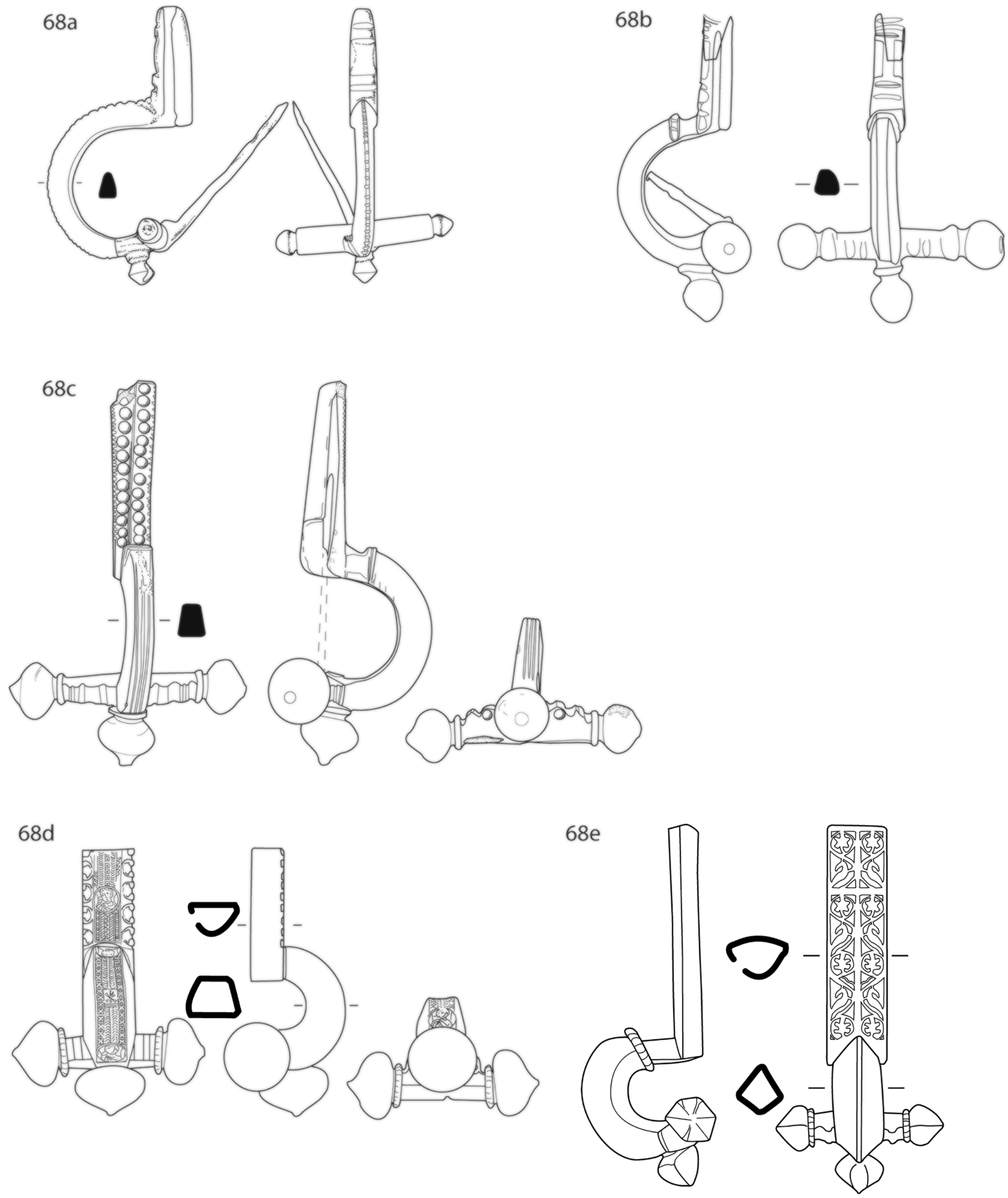

Fig. 2. Typo-chronology of Late Roman crossbow brooches, reproduced with permission of the authors after Heeren and Van der Feijst, 2017, Plate 65-67. Scale: 2:3. For concordance with 'Swift 2000, see Table 1.

any sort of comparison worthwhile in smaller-sized datasets. In the Krefeld data, arsenic, antimony and silver were all reliably and repeatedly detected at the 0.1 % mark as trace elements. In a small number of samples, mercury and nickel were also detected, and their absence in the majority of samples is interpreted as a true absence rather than a failure to detect. Unless otherwise mentioned, the presentation below is based on the individual readings, not averages per brooch. The impact of this is discussed below in section 3.1.

3.1. General metal use

On average, the Krefeld brooches contain just over 40 % in alloying ingredients (tin, zinc, lead). Although this number will be slightly elevated due to the selective surface depletion of copper (in Bayley and Butcher's core AAS data alloy ingredients add up to 20 % on average), it may also be an indication of a scarcity of raw copper circulating in the Late Roman period, with the majority of objects made from recycled material from the Early and Middle Roman period (Bray, 2020, 248). A large amount of alloying material could make the copper go a long way, a development also seen in the debasement of contemporary copper-based coins (Butcher, 2015, 194-198), potentially related to a decline in copper mining activity in the Late Roman period (Edmondson, 1989, 97–98).

All bar one of the crossbow brooches contained more than 1% lead (Table 2), with an average of 25 % and some outliers recording over 60 % lead. The preference for a high lead content is clearly shown in a bar plot of all readings (Fig. 3), with half of the brooches falling between 20 and 45 % mark.

The main alloy types identified in the Krefeld finds based on the corrosion material were leaded bronze and leaded gunmetal (Table 2), again reflective of broader alloy patterns in Late Roman metal use for dress accessories, vessels tools and other objects (Roxburgh, 2019; Van

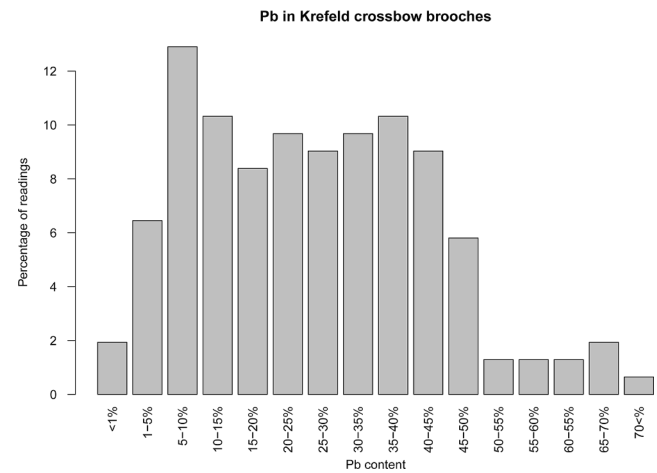

Fig. 3. Bar chart of lead content found in the Krefeld crossbow brooches. Y-axis expresses numbers of readings recalculated to percentages of the dataset.

der Meulen-van der Veen, in prep.; Van der Meulen, 2021; Dungworth, 1997; Voß et al., 1998). Brass and leaded brass were not found to be important alloys in the Krefeld dataset and were similarly rare in other studies including Late Roman copper alloys (Dungworth, 1997; Roxburgh, 2019; Roxburgh et al., 2017; Voß et al., 1998). Although the pXRF returned the same alloy label for most brooches across multiple readings, seven brooches recorded as different alloy types in different readings (graves 1117, 1222, 2711, 2896, 3025, 3974, 6110).

In most of these cases, this was caused by low levels of zinc, hovering around the 1 % mark, resulting in a single aberrant measurement per brooch. Rather than indicate issues with the equipment, this shows the limits of classifying alloys in general: every threshold creates problematic cases that fall just within or without those boundaries. As stated above, the FLAME alloy labels are not used here as analytical categories, but rather to establish terminology. Surface depletion of zinc will also have played a role in this, as evidenced by the occasional spike in zinc detection in some brooches. To counterbalance this, averages per brooch are used for some plots.

The overlap in actual corrosion composition between different alloy labels is most clear for leaded bronze and leaded gunmetal. Most of the crossbow brooches recorded highly mixed alloys, namely leaded gunmetal (just over half of the brooches measured) and leaded bronze (40 % of brooches measured). Most of the corrosion products of the Krefeld crossbow brooches categorised as a leaded gunmetal contained very little zinc, on average around 4 %. The relatively low zinc content in mixed leaded gunmetal alloys is a first indication that these alloys were arrived at through mixing zinc-containing alloys with leaded alloys rather than producing new zinc-containing alloys from primary materials.

This is further supported by how similar these two alloys were found to be in terms of their tin and lead content. Both alloys overlap significantly in a ternary diagram of relative tin, zinc and lead percentages (Fig. 4), suggesting that the zinc content of most leaded gunmetals was so low that it was not actively considered as a factor in the alloy choice. In other words, for many of these objects it seems that the method by which the alloy is defined is making the distinction rather than the actual composition of the alloy, as the bulk of the copper alloys used looks fairly homogenous: a preference is expressed for high-lead, medium-tin alloys which may or may not contain a small amount of zinc.

In absolute terms, the corrosion products on leaded gunmetal and leaded bronze crossbow brooches in Krefeld contained on average 44 % alloying ingredients (total of tin, zinc and lead) and an average total of 2.5–3 % in trace elements (arsenic, antimony, silver, gold, nickel, iron). Boxplots of tin and lead content in both alloy types (Fig. 5) indicate that there was considerable uniformity between the distribution of leaded gunmetal and leaded bronze. Both were found to contain on average around 15 % tin and around 25 % lead with similar distributions across the 1st and 4th percentile.

Most of this material seems to be best described as a homogenous, heavily recycled, low-zinc, low-tin and high-lead mixed alloy. In most other alloy categorisation systems based on destructive sampling (which maintain higher zinc thresholds; e.g., Dungworth, 1997, fig. 6.4; Mortimer, 1991; Bayley and Butcher, 2004; Hammer et al., 1998), these low-zinc alloys would have been classified as leaded bronze instead. This signals that there may in fact have been little difference between low-zinc leaded gunmetals and leaded bronzes in terms of composition and in how they were used, both being the result of intensive mixing and recycling. The Krefeld data show a consistent main sequence of material

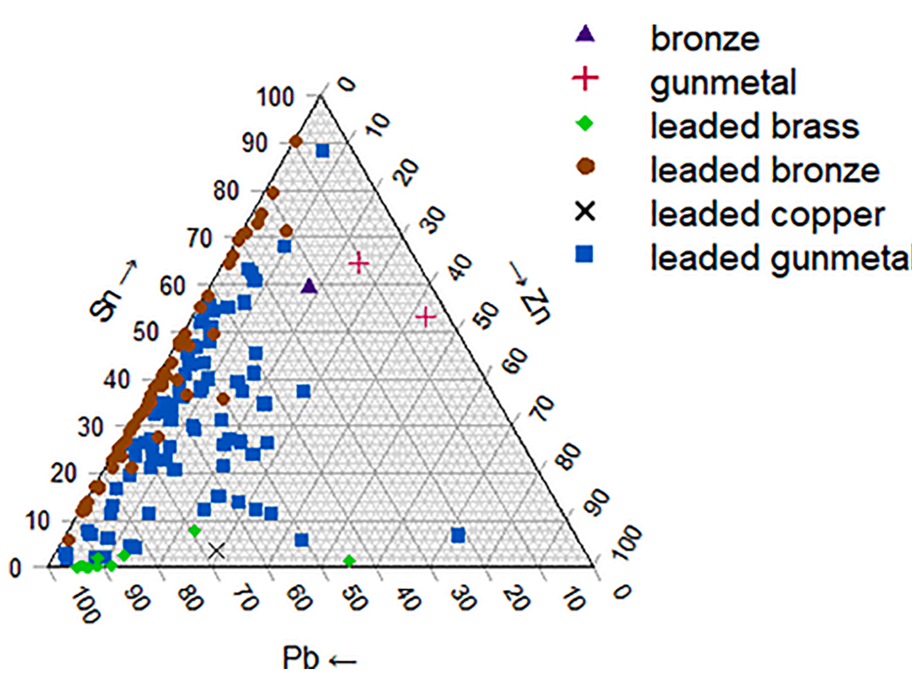

Fig. 4. Ternary diagram (Sn-Zn-Pb) of individual readings on crossbow brooches. Colour-coded for FLAME alloy label.

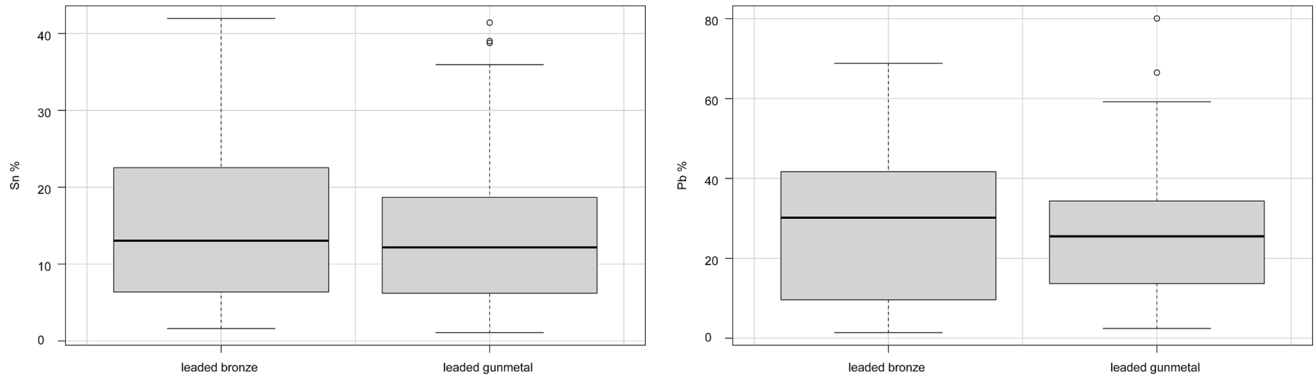

Fig. 5. Boxplots of tin and lead content in leaded bronze and leaded gunmetal brooches from Krefeld-Gellep.

with similar histories. However, splitting the data out along chronological and typological variables shows that some meaningful differences between the leaded bronze and leaded gunmetal alloys can be identified (section 3.2).

3.2. *Typological patterns*

Van Thienen and Lycke (2017) already showed that some crossbow brooch types cluster well along typological groupings in PCA biplots. A biplot of a single value decomposition principal component analysis of the main alloying and trace elements in all individual readings shows this to be broadly the case for the Krefeld-Gellep brooches as well.

Fig. 6 shows a largely chronologically informed distribution along the x-axis. The earliest types 1 and 2 cluster towards tin and silver. On average, these early brooches contained around 23 % tin, compared to 11 % in later 3/4, 5 and 6 type brooches. All groups overlap to some degree with type 3/4, which is the largest typological group in the dataset and consequently displays the most variation. A wide range of metal compositions was found in this group, including a number of relatively high-lead leaded gunmetals and some relatively high-tin leaded bronzes (both also visible as separate groups in Fig. 4). Measurements on Swift 3/4 type brooches also yielded a small number of leaded brass brooches (see below). Swift groups 5 and 6, the latest brooches in the typology, also cluster reasonably close together. These appear to be characterised by a comparatively high copper content (absolute wt% for copper in these brooches from graves 5590, 3031 and 1222 range from 75-95 %).

In terms of alloy types, differences between typological groups can also be identified (see Fig. 7; indeterminate brooch excluded). As noted in section 3.1, there is an undercurrent of heavily recycled leaded gunmetal/leaded bronze that was found across each crossbow brooch type. Whereas both Swift groups 2 and 5 were predominantly made of leaded gunmetal, the Swift 3/4 group showed the most variation. Three Swift 3/4 brooches returned consistent results recording more than 1 % lead and zinc (leaded brass), namely graves 1216, 2992 and 3093. On average, these contained very low amounts of zinc (up to 3 %). It is noteworthy that the corrosion processes of the leaded brass brooches in Krefeld did not contain significantly more zinc than those of the leaded gunmetal brooches from the same site. Detected lead contents in leaded brasses varied widely (averages of 12, 41 and 31 % respectively), although it is difficult to make any clear assessment of this based on just three brooches. In the ternary diagram (Fig. 4), these three leaded brass brooches group closely to graves 1041, 1493, 2942 and 4661. These are all leaded gunmetal brooches with low absolute amounts of tin and the ternary presentation skews them towards leaded brasses.

There are no indications that the lack of tin in these four brooches

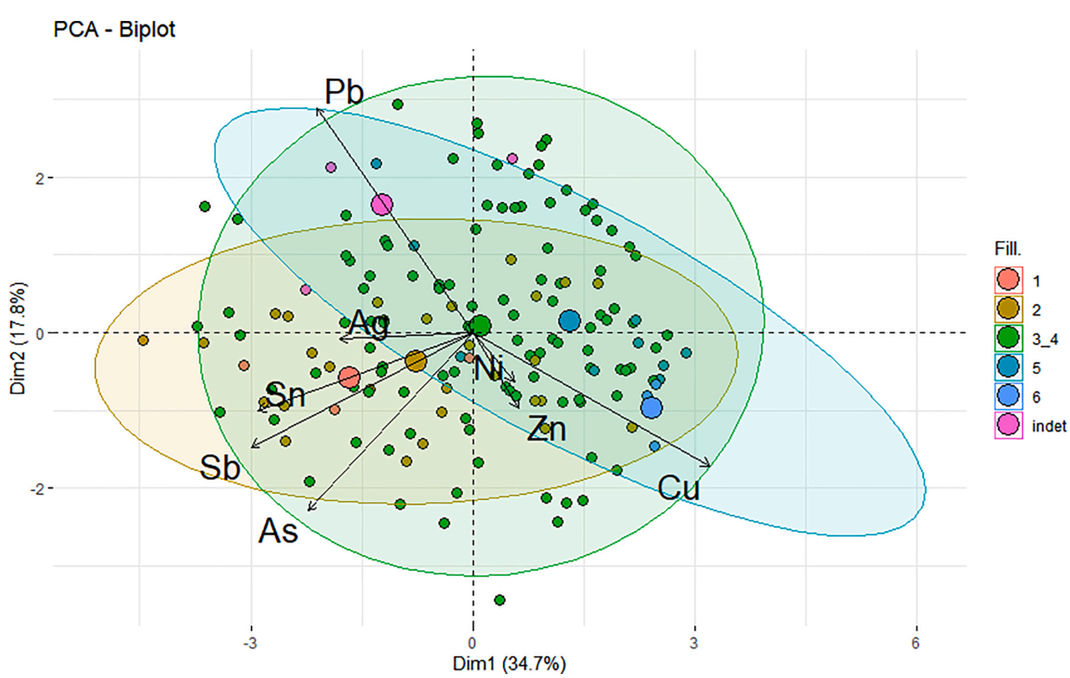

Fig. 6. Biplot of single value decomposition principal component analysis. Spectrum: Cu, Sn, Zn, Pb, As, Sn, Ag and Ni.

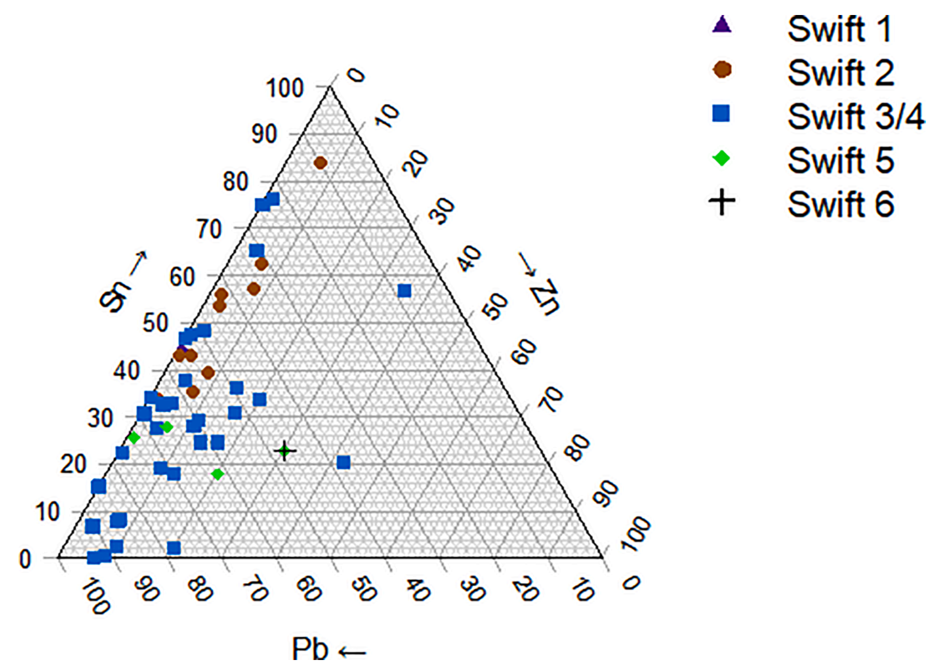

Fig. 7. Ternary diagram of Late Roman crossbow brooches from Krefeld (averages per brooch of 152 readings on 51 brooches). Colour-coded for typology.

can be related to the design of the analysis or to the corrosion. Leaded brass objects were consistently recorded as such throughout the project, also on materials not covered in this paper (Van der Meulen-van der Veen, in prep.). In a corrosion layer, tin would be expected to enrich rather than deplete (Fernandes et al., 2013; Roxburgh et al., 2019; Constantinides et al., 2002; Orfanou and Rehren, 2015) and the detection of low tin levels hovering around the 1 % threshold is consistent within objects, despite the potential for variation within corrosion products on different parts of the same object.

3.3. Evidence for surface treatment

Some data may also be presented on decorative surface treatments found on Late Roman crossbow brooches. Although none of the brooches give a visual indication that they had decorative surfaces, some measurements may be taken as an indication of deliberate surface enhancement. Four of the 52 Krefeld brooches yielded readings of more than 30 % tin, far more than may be explained by a combination of surface enrichment through corrosion and an originally high tin content. These high tin levels were found on both leaded bronze brooches (graves 1609 and 3043) and leaded gunmetal brooches (graves 3511 and 3521) and consistently on all parts of the brooch. This seems indicative of tinning through dipping, rather than wiping, which would also be more suitable to these complex three-dimensional objects (Meeks, 1986).

Low levels of silver (0.1–2 %) were found in most brooches (121 readings), but these levels are not high enough to indicate the presence of silver-plating, silver foil or silver-washing. Only 16 readings recorded gold above 0.1 % (across eight brooches), one of which was high enough to suggest gilding (6.83 % on the foot of a 5th-century leaded gunmetal HF 68e2 brooch). This same reading also recorded 0.37 % mercury, potentially indicative of mercury gilding rather than gold leaf or gold-plating (although mercury may be present in gilded layers that were not achieved through mercury gilding; Lins and Oddy, 1975).

These numbers of surface-decorated crossbow brooches fit well with the "hierarchy" of decorated surfaces identified in other studies. In the study by Van Thienen and Lycke, 17 brooches yielded evidence for gilding, three of which were mercury gilded. No tinning was identified, but one brooch was silvered (2017, Fig. 4). In the crossbow brooches from Britain, Bayley and Butcher identified four leaf or mercury gilded and five tinned brooches (2004) out of a total of 101 crossbow brooches analysed. The rarity of crossbow brooches treated with precious metals or other materials made to look like precious metals could indicate the use of surface enrichment to express military rank or status (see for an in-depth discussion of high-status crossbow brooches Deppert-Lippitz, 2000).

4. Discussion

Generally, despite the selective depletion and enrichment of some of the main elements, this study showed good reproducibility in repeatedly and consistently detecting the same alloy labels using surface pXRF. In six brooches, different readings recorded a different alloy, in almost all cases due to a lack of zinc detection in one of the three analyses. In larger datasets, where the aims are geared towards identifying larger trends, these minor differences will have less of an impact (Orfanou and Rehren, 2015, 396; Nicholas and Mantis, 2014, 2).

Surface enrichment may have played a part in the 15 % average tin content found in the Krefeld brooches and 13 % by Roxburgh et al. (2017) on crossbow brooches from the Netherlands, compared to the average of 6 % in Bayley and Butcher's (2004) dataset. However, the tin spectrum showed some stark outliers in individual readings where the tin content would spike 20 % or more above the levels recorded on other sections of the same brooch. This was almost always accompanied by a relative depletion of copper. In the cases where elevated tin levels were found across the entire brooch, decorative tinning may be suspected (see section 3.3), but in those cases where one individual reading stood out, accidental targeting of localised tin sweating or remains of soldering material may also have been a factor (Meeks, 1986).

Leaded gunmetal is generally the most common mixed copper alloy of the Late Roman period. Based on British evidence, notably Dungworth's work on the northern border areas (1997), Pollard et al., 2015 estimated up to 70 % of all copper alloys in the Roman and early Saxon period were leaded gunmetal alloys. In continental studies with sufficient samples, this number seems to have been lower, around 30–50 % in Germany and the Netherlands in the Roman period (Roxburgh, 2019; Voß et al., 1998).

Several comparative datasets of crossbow broach composition are available for comparison, some large enough to compare to the Krefeld dataset in more detail, despite the inevitable differences in methodology (see Table 2 for a summary). Unpublished numerical data, which beside crossbow brooches also included numerous other Roman brooches and objects from the Netherlands were kindly made available for comparison by Marcus Roxburgh (for the entire dataset Roxburgh, 2019 will be cited, for his discussion of the Roman brooches specifically Roxburgh et al., 2017). These data are of particular interest, as they were collected with the same pXRF scanner as used in this study (see Roxburgh et al., 2019 for methodology).

Bayley and Butcher (2004) presented quantitative data gathered using AAS on drillings taken from the core of the objects as well as a wider range of qualitative XRF analyses from crossbow brooches from Britain (some of which were already published in Bayley, 1992 and reproduced in Swift, 2000). Riederer (2001; Riederer, 2002) has published a number of AAS analyses of crossbow brooches from Germany and Switzerland. For a more thematic comparison, the recent paper by Van Thienen and Lycke, 2017 on compositional data of corrosion of crossbow brooches from Belgium and the Netherlands may also be used. As the data behind their paper only included the peak net intensities and not the recalculated wt% or ppm values, no direct comparisons could be drawn with their raw data and any comparison made here is therefore based solely on the interpretations presented in their paper. There are also some regional studies including other Late Roman copper alloys that can be used to embed the crossbow brooch data (northern Britain: Dungworth, 1997; Netherlands: Roxburgh, 2019; data from Germany previously published Open Access in Voß et al., 1998 kindly made available by Hans-Ulrich Voß).

4.1. General metal use

The relatively high amount of alloying ingredients in the Krefeld-Gellep crossbow brooches may have been partially caused by corrosion effects. However, destructive samples on contemporary crossbow brooches from Switzerland, Germany and Britain show that a relatively low copper content was fairly common in the Western Empire (on average 22–24 %, with outliers up to 37 %; Bayley and Butcher, 2004; Riederer, 2001; Riederer, 2002) and is indicative of an increased reliance on recycled and mixed materials.

Table 2 presents the FLAME alloy labels found in the comparative datasets. The preference for leaded alloys for crossbow brooches is clear, especially for leaded gunmetal. This overrepresentation in crossbow brooches is contrasted with data by Dungworth (1997) and Voß et al. (1998) on other dress accessories, vessels and assorted objects, which show a much stronger presence of non-leaded alloys as well as a more important role for leaded bronze.

Bayley (1992; reproduced in Swift, 2000) originally noted leaded bronze as the most common alloy type in their dataset (crossbow brooches of Hull types T190-192), although under the FLAME system these are largely labelled as leaded gunmetals here. Notably, Bayley and Butcher only noted leaded brass in the Hull T192 type, a type largely comparable to the Swift 3/4 (Bayley and Butcher, 2004, 159), the only type in the Krefeld dataset to yield this same alloy. Swift raised the possibility that crossbow brooches made outside of Britain may have been more likely to be made of brass than of bronze (Swift, 2000, 88). Although she may have maintained higher thresholds for lead and zinc to arrive at those labels, the lack of high-zinc alloys in Bayley and Butcher's dataset or any of the Continental studies cited here likely counters this.

Furthermore, leaded bronze was the most common alloy found for crossbow brooches analysed by Roxburgh et al. (2017). Most of these are again of the Swift 3/4 type and the majority come from the military fortification at Nijmegen, so possibly this is a local phenomenon. Leaded bronze or leaded brass did not play a significant role in crossbow brooches analysed by Riederer (2001, 2002), despite the lack of typological information was available for those analyses.

Although care should be taken in comparing absolute wt% between studies carried out by different analysts with different equipment standards, some general patterns in zinc and lead contents can be reported on. Applying the 1 % threshold for a first categorisation of the data, the zinc-containing alloys in the Krefeld dataset only contained on average 4 % zinc, with only 18 readings out of 155 recording more than 5 % zinc. Zinc levels were found to be slightly lower in leaded brass brooches (3 %) compared to leaded gunmetal brooches (4 %), both well below Dungworth's thresholds for brasses and gunmetals (15 % and 5–15 % respectively; Dungworth, 1997, fig. 6.4). The destructive AAS sample data available from Britain show an average of 5.08 % zinc in leaded gunmetal crossbow brooches and 18.55 % for leaded brass (although only two of those were found). Riederer similarly recorded around 6 % zinc in destructive AAS samples on in leaded gunmetals, although these data are unevenly distributed: four brooches from Straubing scored above 10 %, the rest not above 2.5 % (Riederer, 2001; Riederer, 2002).

These data show that zinc levels were quite low in core samples too, although surface depletion of zinc must be suspected in the Krefeld data when compared to the AAS evidence. As experimental studies have shown, zinc in copper alloys may be expected to deplete on the surface with a factor of around 9 % in unleaded brasses (Roxburgh et al., 2019, 64), while in alloys with sufficient tin contents, zinc may survive better on the surface (Constantinides et al., 2002, 90; Robbiola, 1990). The low zinc contents of the corrosion products on leaded gunmetal found in Krefeld may in that light be interpreted as reflective of a genuine low-zinc leaded gunmetal alloy. High zinc contents and brass use were generally not identified in any great numbers in contemporary non-military copper alloys (Dungworth, 1997; Voß et al., 1998). The crossbow brooches from Krefeld, which showed a fairly consistent undercurrent of low zinc contents, fit well within this broader pattern of metal use in the Late Roman West.

Brass has often been flagged as an alloy particularly associated with the Roman military (Dungworth, 1997; Caley, 1964, 92; Bayley, 1998, 19), although for brooches in particular, this appears to have been largely an Early Roman phenomenon (Dungworth, 1997; see Müller, 2002 on the composition of Aucissa brooches from Haltern for example). Van Thienen and Lycke correlated their typological group 3/4 to a variety of zinc-containing alloys, noting that this correlation was absent for other groups such as the 2 and 6 (2017, 54). This pattern was not found

Table 2
Alloys identified using the FLAME system (Pollard et al., 2015) in various datasets presented in percentages.

	Crossbow brooch				Contemporary objects/dress acessories		
Alloy	This paper	Bayley and Butcher 2004	Roxburgh et al. 2017	Riederer 2001; Riederer 2002	Dungworth 1997	Voß et al. 1998	Roxburgh 2019
brass					2.01	1.32	1.68
bronze	0.65	3.03			12.85	14.91	1.68
copper						1.75	2.52
gunmetal	1.29	4.55			12.85	4.82	0.84
leaded brass	6.45	3.03	11.90	5.56	2.41	0.44	5.04
leaded bronze	38.06	33.33	52.38	27.78	29.32	43.42	37.82
leaded copper	0.65		2.38		0.80	0.88	0.84
leaded gunmetal	52.90	54.55	33.33	66.67	39.76	32.46	49.57
Total n of objects	52	66	42	18	252	49	119

in the Krefeld brooches, with Swift groups 2 and 5/6 yielding leaded gunmetals with similar zinc wt% as the Swift 3/4 brooches from the same site.

4.2. The role of lead in Late Roman crossbow brooches

Much more pronounced was the presence of lead as a contributing factor in the Krefeld crossbow brooches. The high lead contents of the corrosion product (average 26 %) were mirrored by similarly large amounts of lead found in crossbow brooches in other studies. (Roxburgh et al., 2017, 254 noted a significant component of lead in crossbow brooches from the Netherlands (on average 30 % lead on the surface; Roxburgh et al., 2017), while Bayley and Butcher, 2004 recorded on average 47 % in the core samples of British crossbow brooches. For northern Britain, Dungworth's data similarly showed a preference for leaded alloys for Late Roman military fittings (Dungworth, 1997). A recent study on copper-alloy corrosion processes identified that lead could both deplete or enrich selectively on the surface (Fernandes et al., 2013), so these widely different ranges of lead content are not unexpected.

Although leaded alloys made up the majority of all Late Roman copper alloys in the research area (Bayley and Butcher, 2004; Dungworth, 1997; Voß et al., 1998; Roxburgh, 2019), military copper alloys were found to contain higher amounts of lead and lower amounts of tin compared to contemporary civilian dress accessories. The most common non-military Late Roman brooch in the Lower Rhine frontier area is the simple two-piece Armbrust brooch, dated to the 4th and 5th century and worn by both men and women, predominantly in the civilian sphere (Schulze, 1977, namely types 35 and 36).

pXRF analysis on these Armbrust brooches consistently yielded 23-25% tin on average on the corrosion layer (Roxburgh et al., 2017, fig. 5.3.22; Van der Meulen-van der Veen, in prep). For contrast, the Krefeld crossbow brooches on average contained only 15 % tin.

Similarly, the high lead content of Late Roman crossbow brooches seems to be a uniquely military attribute. Not only are high lead values recorded in crossbow brooches across several studies (see above), but these values are also replicated in contemporary Late Roman military belt fittings, especially buckles (Van der Meulen, 2021). The civilian simple two-piece Armbrust brooches on the other hand, were found to contain on average only 6–7 % lead (Roxburgh et al., 2017, fig. 5.3.22; Van der Meulen-van der Veen, in prep.). Zinc levels tended to be even lower in civilian leaded gunmetal brooches: for the Armbrust brooch, around 2-3 % zinc was detected on the corroded surface in other studies using pXRF (Roxburgh et al., 2017; Van der Meulen-van der Veen, in prep.).

5. Conclusion

The aims of this paper were threefold: present the crossbow brooches from Krefeld-Gellep and use them to assess the evidence for Roman state control over production and embed these data in a wider discussion about copper alloy use in the Late Roman period. Finally, this section presents some comments on the use of corrosion data in discussions on archaeometallurgy.

5.1. State control and a "military metal signal"

All studies for which the underlying chemical data on crossbow brooches was available for comparison (Bayley and Butcher, 2004; Roxburgh, 2019; Riederer, 2001; Riederer, 2002), show the same trends in metal use. Each of these regional studies identified a clear preference for highly leaded alloys in the production of crossbow brooches, occasionally with a low level of zinc (rarely rising above 3-4 % in corrosion data and 6 % for destructive samples). This was even noted in studies relying on corrosion data, including the original data presented in this paper.

Rather than the zinc content, this paper identified lead as the most important signifier for a "military" alloy, in this case in Late Roman crossbow brooches. Although it has long been recognised that the majority of copper alloys in the Late Roman period contained some lead (Voß et al., 1998; Dungworth, 1997; Pollard et al., 2015), elevated lead contents could be linked explicitly to dress accessories associated with the Roman army, namely crossbow brooches (this paper) and also Late Roman military buckles (Van der Meulen, 2021). Contemporary civilian dress accessories and other non-military objects were found to have a considerably lower lead and higher in tin content (Van der Meulen-van der Veen, in prep.; Roxburgh et al., 2017; Roxburgh, 2019).

The main material used for crossbow brooches found in Krefeld-Gellep (and in the comparative datasets on crossbow brooches) is skewed towards high lead levels, resulting in a FLAME label of leaded gunmetal. This applied to all typological groups (Swift 1-6), although some differences between groups were noted. Most notably, the Swift 3/4 group showed the most variation in PCA analyses. Although some of this will be due to the fact that this type made up the majority of the brooches that were analysed, it is noteworthy that this was also the only group in which leaded brasses were identified.

Given the known properties of lead (improved casting, extending limited supplies, adding weight), this provides an interesting insight in Late Roman military supply and use. Although it has been suggested that lead was increasingly used in later periods as a cheap additive to bulk production (Ponting and Segal, 1998, 115; Craddock, 1985), it seems counterintuitive to interpret the high lead contents of crossbow brooches as signalling insufficient army supplies, when local civilian brooch manufacturers could still produce brooches with a much lower lead content. One possibility may be that the Roman state had a lot of lead available through military connections to mining or silver production through cupellation (Hughes and Hall, 1979). Alternatively, the added weight and silvery colour of the cast surface resulting from the high lead content could have been something that was preferred for military dress accessories as a marker of status.

The background to this 'military lead signal' is composed of objects showing indications for extensive mixing and recycling of copper alloys in the Late Roman period. Both leaded gunmetal and leaded bronze crossbow brooches showed incredibly similar tin and lead levels, despite the former alloy also containing zinc. Their similarity may be taken as a sign that they were largely treated as one alloy group by ancient smiths. It appears that in the Late Roman period, a large majority of copper alloys circulating were made of a highly mixed, low-zinc material.

5.2. Copper alloy use in the Late Roman West

The overrepresentation of mixed alloys touches on the issue of recycling, raising the question to what degree craftspeople were able to make informed decisions about which materials to use or whether this was largely determined by availability. Generally, the majority of Late Roman copper alloys appears to have been leaded, although crossbow brooches seem to have been more heavily leaded than other, contemporary dress accessories. This likely shows the deliberate addition of further lead to already leaded alloys by military craftspeople. On average, crossbow brooches appear to have contained about a third more lead than contemporary non-military brooches (Van der Meulen-van der Veen, in prep.; cf. Roxburgh et al., 2017). The state's involvement in silver mining in the Late Roman period (Edmondson, 1989) would likely mean military or state-led production centres had a lot of lead available as a by-product. This could be a further argument for state involvement in the production of crossbow brooches.

Further evidence for the prevalence of recycling was found in comparing the Krefeld brooches to other datasets. These showed that in the Late Roman period, both civilian and military dress accessories contained high amounts of alloying ingredients, likely as a result of a scarcity of copper. The close similarities in composition between leaded bronze and leaded gunmetal alloys is also a good indication of how widespread recycling of scrap metal must have been in the Late Roman West. Despite all this, however, craftspeople producing dress accessories were able to make different technological choices in the way they mixed and recycled materials, as evidenced by the different compositions of military and civilian dress accessories.

5.3. The use of corrosion data in archaeometallurgy

Finally, the presented dataset may be used to showcase the possibly of applications of non-destructive pXRF technology to the study of archaeological metals. Previous studies comparing the chemical data obtained of destructive measurements and non-invasive surface techniques, have noted the selective depletion of copper and zinc and relative enrichment of tin and lead in the surface spectra. These inevitably reflect the differences in composition between the corroded surface and the original bulk material. However, despite the effects of the corrosion, each dataset discussed in this paper showed the same trend of metal use and the expressed preference to produce crossbow brooches in highly leaded alloys that occasionally contained (relatively small quantities) zinc. What this shows is that, using properly designed protocols and provided the datasets are large enough to alleviate the impact of analytical errors, compositional data of the corrosion product will be sufficient to address several archaeological questions. The most important contributing factors to a high-quality dataset are the use of a large assemblage, running multiple analyses and the use of an independent reference set specifically designed for archaeological materials (Fernandes et al., 2013; Roxburgh et al., 2019; Heginbotham et al., 2015).

Specifically, pXRF can play an important role in archaeometallurgical studies, as it can potentially be used to analyse entire assemblages, quickly, cheaply, and non-destructively, allowing chemistry to inform complex, nuanced, debates around material culture aside from 'large modes' like 'provenance' 'recycling' or 'specialisation'.

In the light of corrosion processes negatively affecting the survival and detecting of zinc and copper on the uncleaned surface, it is advisable to execute several analyses per object to give these elements the best chance of detection. This is especially important in objects with low amounts of alloying ingredients where the limit of detection may be the same or higher than the elemental threshold used here (1 %). The repeated analyses of the Krefeld brooches showed remarkable consistency and reproducibility of qualitative and semi-quantitative results, showing that under favourable circumstances, surface pXRF can generate high quality datasets. Furthermore, using standards such as the CHARM reference set is advisable to ensure that as many extraneous factors may be eliminated from interpreting important patterns in the dataset. This will hopefully aid adequately supported archaeological interpretations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All original data in this paper are made available in a appendix A, available for download alongside this paper. Bibliographic references are provided for all comparative data cited.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jasrep.2023.103839.

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