On diverse arts: crucible metallurgy and the polymetallic cycle at Scandinavia's earliest Viking town, Ribe (8th–9th c. CE), Denmark

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Abstract

This study presents results from the analytical investigation of the polymetallic, non-ferrous metallurgical cycle at early Viking Age Ribe, Denmark, in the 8th and 9th centuries CE. We combine extensive surface analyses of crucibles and moulds (handheld XRF) with targeted micro-destructive examination (micro XRF, electron microprobe spectroscopy—EPMA) of crucibles, moulds, ingots, blanks, and finished objects from the different stages of the secondary metallurgical production. Results show the working of a range of copper alloys with (leaded) brass as the most common, alongside small-scale working of silver and gold. Analytical evidence suggests a move towards technological standardisation at Ribe workshops from the pre-Viking period to the early Viking Age as reflected in the tighter compositional groupings for the crucible fabrics, the alloy choices for specific artefact types, e.g. keys and brooches, and an overall move towards high Zn brass from the 8th century to the first half of the 9th century CE. Finally, we discuss the limitations and potentials of the surface and micro-destructive analytical methods used and the insights gained from each data set and propose a direction for future research.

Keywords Early Viking Age · Non-ferrous metallurgy · Handheld XRF · Micro XRF · EPMA

Introduction

In this paper, we present a large-scale, multi-material analytical study of the full non-ferrous metallurgical cycle based on 8th–9th century CE workshops from Ribe, Denmark. We analyse and compare crucibles and moulds, metallic traces on technical ceramics and crucible slag, metals and alloys from ingots, blanks, and finished objects. This multi-analytical approach reveals the technological choices and developments at

the non-ferrous, polymetallic metalworking cycle at Ribe. It also presents a key for interpreting the various material remains in relation to the subsequent metalworking stages from raw material provision (metals, ceramic fabrics) to the finished objects and reuse of metals and technical ceramics. Archaeometallurgical studies often focus either on objects, technical ceramics, slag, or raw materials. A single-material approach is often dictated by the nature of the archaeological record. However, these materials form part of a technological production chain. Thus, single-material studies give a partial view of the metallurgical cycle and impede understanding of past technologies by compartmentalising each technological step and type of material. In that, this study complements textual sources on mediaeval metallurgical practices such as Theophilus' renowned manual *De diversis artibus/On diverse arts* (Hawthorne and Smith 1979) which often divert from the archaeological record (Rehren and Martín-Torres 2008). Furthermore, we adopt a contextual approach to the archaeometallurgical study of past technology and expand on more recent relevant multi-material approaches (e.g., Figueiredo et al. 2010; Murillo-Barroso et al. 2010; Merkel 2016; Rademakers et al. 2017; Saage and Wärmländer 2018).

We investigate metallurgical ceramics and metallic remains using large-scale, qualitative, surface analyses (handheld X-ray fluorescence [XRF]) coupled with targeted, quantitative,

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micro-destructive analyses (micro XRF, EPMA). Examination of technical ceramics can provide unique insights into Viking Age metalworking (Merkel 2016, pp. 209–221; Pedersen 2016; Söderberg 2018), which finished objects, representing only part of a complex technological process, cannot on their own (Thornton and Rehren 2009; Martín-Torres and Rehren 2014). We trace chronological developments between the subsequent phases by identifying the shifting characteristics of the metallurgical processes and re-constructing the operational sequences (*chaîne opératoire*) at the Ribe workshops during the pre-Viking period (700–790 CE) and the early Viking Age (790–850 CE) (Fig. 1). While many finds can be ascribed to a more precise chronology, this division is found to be useful in comparing broad trends in workshop development. Finally, we consider how multi-material analyses can improve sampling strategies and comparative interpretation of metallurgical remains.

Background

The early medieval emporium (trading port) of Ribe, on the west coast of Denmark, preserves some of Europe's best evidence for non-ferrous production including thousands of crucible and mould fragments (Brinch Madsen 1984; Frandsen and Jensen 1988; Feveile 2006a, b, 2012; Feveile and Jensen 2006). This rich record is uniquely suited for examining the secondary metalworking cycle in the formative early Viking Age before common metallurgical practices became widespread in Scandinavia. The assemblage's chronology covers major shifts in object style and typology during the 8th and 9th centuries CE providing a window into much wider changes in metalworking traditions (Sindbæk 2011). Ribe's role as a trading hub in the Northern European seaborne network provided local craftspeople with raw materials and widespread markets that fostered on-site production (Sindbæk 2017). Intensified commercialisation and urbanisation enabled and profited from an established metallurgical production, which was part of a prolific operational network (*réseau opératoire*) of craft specialists (Feveile 2006b; Ashby et al. 2015; Orfanou and Birch 2018, p. 193, fig. 3; Croix et al. 2019). Non-ferrous metalworking remains attest to several production stages including the mixing of metals and alloys in crucibles, casting in ceramic moulds, bar ingots, blanks (cast pieces of metal prepared by hammering or rolling and retained for further processing) and

scrap metal used as raw materials, and finished objects. All types of remains testify to the technological process in complementary ways, as elements were transferred, enriched or depleted, and oxidised during the various steps preserving information on the metalworkers' choice(s) of techniques (Dobres 2000; Sillar and Tite 2000). The activity at Ribe's workshops was stable and provided long-term training at workshops with continuity over several generations, as with elsewhere in northern Europe (Capelle 1968; Craddock 1990, p. 170; Ambrosiani 2013; Pedersen 2020). Comparable assemblages are known from other Viking Age towns, namely, Birka (Jakobsson 1996), Hedeby (Drescher 1983), Kaupang (Pedersen 2016), and York (Bayley 1992), as well as from smaller scale, non-urban contexts (Ulriksen 2002; Sahlén 2016; Saage and Wärmländer 2018; Nord et al. 2020).

Materials and methods

Sample description

We selected samples from two separate excavations at Ribe, sites ASR7 (Sct Nicolajgade 8, 1986) and ASR9 (Posthuset 1990–1991), ~70 m apart (Frandsen and Jensen 1988; Feveile and Jensen 2006). The excavations revealed a series of house plots showing intensive workshop activities. Both contexts are well-documented with well-defined stratigraphic layers based on a sequence of phases with a resolution of 10 to 20 years (see Fig. 1) (Feveile and Jensen 2000). Site ASR7, of a total area of 75 m² at the rear part of a plot with mineralised, well-stratified layers to a depth of < 1 m, revealed traces of structures and finds from several crafts including non-ferrous metalworking (Frandsen and Jensen 1988; Frandsen 2006). Site ASR9 covers approximately a total area of 100 m² also with well-stratified, partly mineralised/partly organic stratigraphic layers preserved at a depth of < 2 m (Feveile and Jensen 2006). Site ASR9 revealed traces and waste heaps related to non-ferrous metalworking, particularly from the late 8th century (phase E) onwards (Table 1). The ASR7 assemblage complements the ASR9 chronologically, as most remains cover predominantly the earlier ASR9 phases C–D (Fig. 1). In both workshop areas, a marked change is noted after c. 790 CE (phase F) when the volume of non-ferrous metalworking remains increases, the typological repertoire of cast jewellery

Fig. 1 Dating for contexts at sites ASR7 and ASR9 in Ribe showing the relationships between stratigraphic layers and absolute ages (after Feveile 2006b)

changes, and larger and more elaborate objects appear showing greater control over extensive detailed relief decorations in jewellery castings.

Technical ceramics: crucibles and moulds

We analysed the surfaces of 743 crucible fragments of the 2760 recovered from both ASR7 and ASR9 sites covering all chronological phases (B to H/I) using non-destructive techniques (Table 1). The crucibles were typically small and cylindrical with heights of 3–8 cm, diameters of 3–5 cm, and with a rounded base (Fig. 2). We examined 123 plain mould fragments from ASR7 and 260 fragments with imprints from ASR9 (Fig. 3), to explore the technological attributes of specific artefact types such as bar ingots/blanks, keys, needles, and various types of brooches, namely, equal-armed, square, round, hilt-shaped, horse brooches, types N, P11–P17, and RI9 (P brooch types after Petersen 1928; attribution of mould impressions to artefact types by Feveile 2001) (Feveile 2001). Brinch Madsen (1984, p. 92) reported that mould fragments at Ribe were often finely crushed and re-used as grog in the production of new ones. This practice was also described by Theophilus (Hawthorne and Smith 1979, p. 142) and Agricola (Hoover and Hoover 1950, p. 230) in the twelfth and sixteenth centuries CE, respectively. A subset of 54 crucible and 12 mould fragments were sampled and prepared as metallographic specimens for micro-XRF analysis, of which 12 crucibles containing metallic prills were further analysed by EPMA.

Bar ingots/blanks

Eighteen bar ingots or ingot fragments and six pieces that are either ingots or blanks (cast pieces of metal for future use) from ASR7 and 9 were analysed (Table 1). The blanks are included with the ingots since both materials would have been considered a resource for smiths at Ribe. The group of bar ingots (Fig. 4) is typologically variable and, thus, it is not always feasible to assign smaller fragments to this category with certainty as they could be scrap metal or waste (e.g., Kaupang assemblage; Pedersen 2016).

Table 1 Number of metallurgical ceramic fragments (crucibles, moulds with or without casting imprints), bar ingots, and finished objects recovered from sites ASR7 and ASR9 in Ribe

Description	ASR 7	ASR 9
Crucible fragments	158	2602
Mould fragments	141	7237
Mould fragments with imprint of casting	71	1181
Bar ingots (Cu, Cu-based, Ag)	6	18
Finished objects (Cu, Cu-based)	13	22

Finished objects

Twenty-four finished objects, mostly keys and different types of brooches with clear typological links with Ribe, suggesting that they may have been cast at Ribe, recovered from Ribe (Feveile 2002; Feveile and Jensen 2006) and other sites in western Denmark and elsewhere in Scandinavia were examined. These locally made objects have been recovered from various sites in Scandinavia suggesting active exchange activity with Ribe. The keys are typical forms of the 8th century, while the brooches comprise the oval brooch type, namely, a typical female dress accessory (Sindbæk 2011), as well as equal-armed, square and hilt-shaped brooches, all from the late 8th to mid-9th century (Fig. 5). The oval brooch AM6284 (Fig. 5b), though, is not from Ribe as matching mould fragments have been found in Hedeby but is included here for comparison and it relates to the Berdal type of which few brooches are known from Ribe.

Analytical methods

We employed an integrated analytical approach that combined large-scale surface, non-destructive analysis with targeted micro-destructive examination. Metallographic and elemental analyses (handheld and micro X-ray fluorescence) were conducted at the Aarhus Geochemistry and Isotope Research (AGiR) Platform, Department of Geoscience, Aarhus University. Additional chemical data on the crucibles' metal prills were obtained by electron microprobe spectroscopy (EPMA) at the Department of Earth and Planetary Sciences, UC Davis. The large-scale analytical survey of surfaces of 1126 ceramic fragments assisted in the selection of 66 samples with the strongest metallic signals for further micro-destructive investigation.

Surface analyses—handheld X-ray fluorescence

Analyses of 1126 ceramics' interior and exterior surfaces were performed using a Bruker S1 Titan 800 tube-based handheld X-ray fluorescence spectrometer (hhXRF). Each analysis used the Geochem application (General method) and consisted of a two-phase measurement for the heavy and light elements, each of 30 s. Reduced data from the Geochem application are reported here in terms of simple oxide components (e.g., CuO, ZnO, SnO, and PbO) for consistency, although analysed regions of a given sample may represent mixtures of oxides and metals, while Ag and Au are reported as metals. Repeated hhXRF analysis of certified clay and metal reference materials (CRMs) showed a < 25% difference from certified values for elements at or around detection limits and better than 5% for all elements present in higher concentrations (see Online Resources S1 and S2 list results for metals and clay/rock powder CRMs, respectively). The detection limits of 0.2 wt% for

Fig. 2 Photographs of crucible fragments (a) $\times 374$, (b) $\times 057$, (c) $\times 147$, (d) $\times 032$, and (e) $\times 393$ from ASR9. Fragment (a) preserves in its interior copper remnants in the form of carbonates (malachite) and chisel-like tool traces most likely used to remove any residual metal. Fragment (b) shows a thick layer of green vitrification on its exterior, while its interior is macroscopically clean of any metal residues. Fragments (c) and (e) preserve metallic remnants in its interior and a thick vitrified layer forming a reverse conical shape on its exterior. Fragment (d) is clean of metal residues on both faces. Objects are comparable to thimble- to small cup-sized Viking Age crucibles from Kaupang in Norway (Pedersen 2016, pp. 110–114, fig.4.52–4.58) and Hedeby in Germany (Bayley and Rehren 2007, p. 48, fig. 4a) and Celtic crucibles from Lagore Crannog in Ireland (Craddock 1990, p. 172, fig. 4f)

Cu, Sn, and Pb, 0.5 wt% for Zn, and 0.1 wt% for silver were determined based on these standard analyses (Tables S1 and S2). During hhXRF analyses of the metal CRMs (Table S1), Pb was consistently underestimated by a factor of 4 and Sn overestimated by a factor of 1.2. To correct for this, we multiplied all measured lead concentrations by 4 and tin by 0.8

(see columns ‘Pb recalibrated’ and ‘Sn recalibrated’ in Table S1) followed by re-normalisation to 100%. Results on technical ceramics are reported as oxides as this is the bulk state of the material present.

The effect of conservation with Paraloid coating on the ceramics’ surfaces was evaluated using micro XRF on 10

Fig. 3 Photographs of mould fragments with casting imprints from ASR9. Fragments with imprints of oval brooches: (a) type P15 $\times 44.5-8$, (b) type P11 $\times 57.12$, (c) type P12 $\times 208.5$, (d) type P17 $\times 50.2$, (e)

fragment with imprint of equal armed brooch $\times 106.1$ and 2, (f) fragment with imprint of a key handle $\times 105.8$

fragments before and after treatment; see below ‘[Micro-destructive analyses](#)’ for full details of the micro XRF protocol. Three fragments showed traces of ZnO both before and after conservation, while pre- and post-conservation analyses of three fragments with detected zinc $\times 580_1$ show markedly higher ZnO for the latter (c. 5 versus 12 wt% ZnO in fragment $\times 580_1$) as well as elevated CaO, K₂O, TiO₂, and Fe₂O₃ (see Online Resource S3 for detailed comparison).

Micro-destructive analyses

A subset of the metallurgical ceramics (54 crucible and 12 mould fragments), 24 bar ingots, and 24 finished objects

were selected for sampling for more in-depth quantitative analyses. Samples were obtained by cutting small pieces from ceramic fragments, while for metal artefacts (ingots/blanks/objects), samples were obtained via cutting (small pieces or cross-sections) and/or drilling. Ceramic and metal samples were mounted in two-component epoxy resin and prepared as standard metallographic blocks to a 1 μ m polish finish. For 21 objects that could not be directly sampled, an area of $\sim 2 \times 3$ mm of fresh metal was exposed by scraping with a scalpel blade or abrading with Si-C paper, and the entire objects inserted into the micro XRF chamber for analysis.

Fig. 4 Bar ingots from Ribe: (a) two bundled ingots ASR7 $\times 581A$ and bar fragments (b) ASR9 $\times 455$, (c) ASR9 $\times 21$, (d) ASR9 $\times 291$, and (e) complete bar ASR9 $\times 105$. Bar fragments b and e are comparable with bar

from 7th–8th century CE Ireland as seen in Craddock (1990, p. 174, no 150) and Bayley et al. (2014, p. 121, fig. 1)

Fig. 5 Examples of artefacts analysed: (a) oval brooch VHM 8444, (b) oval brooch AM6284 (possibly made in Hedeby), (c) key ASR747 $\times 1$, (d) key AM1037, and (e) key ASR9 $\times 390$

Reflected light microscopy A Nikon Eclipse E600 POL reflected light microscope with an attached Nikon digital shift camera (DS-U1) was used for the microscopic examination of cut and mounted samples, not scraped surfaces.

Micro X-ray fluorescence spectroscopy Elemental maps, area and spot analyses on both cross-sections of ceramics ($n = 68$) and metallic ingots, blanks and objects ($n = 27$), and scraped surfaces of objects ($n = 21$) were made using a Bruker Tornado M4 benchtop micro X-ray fluorescence spectrometer (micro XRF) with a spot size of 20 μm , tube conditions of 50 kV, and 600 μA in dual detector mode (for detailed description of protocol, see Orfanou et al. 2020). The instrument's minimum detection limits and its accuracy, precision, and stability were found satisfactory via the routine analyses of synthetic basalt CRMs GSC, GSD, and GSE from USGS Microanalytical Reference Materials suitable for refractory clays, and Cu-based alloy CRMs $\times 33$ GM21, $\times 32$ LB14, and $\times 21$ SN5 from the CHARM set (Heginbotham et al. 2015) and $\times 32$ ALB2, $\times 31$ 7835.3, and $\times 39$ 17868 from MBH with $< 25\%$ difference at detection limits and $< 5\%$ difference for high abundance elements; see Online Resource S4 for glass CRMs as analysed with micro XRF and Orfanou et al. (2020, supplementary material A) for Cu-based CRMs. During the analysis of copper alloy CRMs, Sn and Pb were consistently underestimated by the micro XRF and measured values were multiplied by factors of 1.1 and 1.2

respectively to account for this. Our analyses aimed at quantifying the metallic remnants and fabrics of ceramics, the bulk compositions of ingot bars and blanks, and finished objects. Results on ceramics and crucible slag layers are reported as oxides, despite some metallic prills visible under RLM, as this is the bulk of material present, except for chlorine and gold which are reported as elements. Mean values are reported along with 1 standard deviation (calculated by IBM SPSS Statistics 26 software). Elemental maps for ceramic fragments are presented as such, even though compounds are reported for bulk compositions, due to one of the limitations of the instrument which only reports elements for these maps. Since elemental maps present information on relative abundances, they are also representative of compound abundances.

Electron probe microanalysis Spot analyses on metal prills in 12 crucibles were performed by EPMA using a Cameca SX-100 microprobe with wavelength and energy dispersive spectrometers and a 1–2 μm spot size. Calibration standards included pure metals and Cu-based certified reference materials (for more details, see Orfanou et al. 2020, supplementary material B). Detection limits for Cu, Zn, and Pb are 0.01 wt%, 0.03 wt% for Fe, 0.02 wt% for S, 0.05 wt% for Sn, Ni, and Sb, and 0.06 wt% for As. EPMA results are reported as elements as the analyses were performed on metallic prills in the crucible slag layers.

Results

Crucibles

Macroscopic observations

Only a few crucibles are complete or near complete. They often bear a small handle on one side, possibly to allow a grip with metal tongs for handling and pouring the liquid metal into the mould. The crucibles' fabric is light grey and ceramic walls are typically 4–7 mm thick, while several crucibles have additional external ceramic layers. The crucibles' exteriors are covered with a reddish and/or grey-greenish vitrified layer, often porous (crucible slag), typically thicker in the bases. The interiors of the crucible fragments are largely clean of metal residues as only few fragments showed macroscopically identifiable metallic corrosion. The exterior surface of base fragment ASR9 ×057 (Fig. 2b) preserves a thick vitrified slag layer, while its interior seems clean of metal traces. Fragments ASR9 ×374, ×147, and ×393 (Fig. 2a, c, e) have visible metallic remnants in their interiors in the form of oxides and carbonates as indicated by the reddish or greenish colours. Base fragment ASR9 ×374 (Fig. 2a) preserves traces of what seems to be chisel-like tool marks. In a few cases, crucible fragments are clean of any metal residues on both surfaces, such as ASR9 ×032 (Fig. 2d). Occasionally, an additional ceramic layer on the exterior of the crucible is found such as in fragments ASR9 ×374, ×057, and ×147.17 (Fig. 2a–c).

Surface qualitative elemental examination

Exterior and interior surfaces of 743 crucible fragments analysed by hhXRF gave a total of 1478 analyses (see Online Resource S5 for full data set of crucible fragments' hhXRF analyses); the curved shape of 8 crucible base fragments did not allow the analyses of their interiors. Traces of CuO, ZnO, SnO, PbO, Ag, and Au were found in 71% of the samples. ZnO is most often detected and is more likely found in interiors ($n = 600$) than in exteriors ($n = 250$) (Fig. 6). CuO is found equally often on exterior and interior surfaces in ~50% of the fragments, while SnO, PbO, and Ag were detected in fewer fragments and mostly in interiors (Fig. 6). The interior surfaces of two 790–850 CE fragments have traces of Au. No arsenic or antimony oxides were detected. Only 5% of the 421 pre-Viking fragments have traces of Ag, compared to 13% of the 1057 early Viking Age fragments (Fig. 6). PbO is more often detected in the 8th century crucible fragments, while CuO, ZnO, and SnO abundances are similar in both chronological periods.

Optical microscopy

Cross-sections of 54 crucible fragments were examined in reflected light. A slag layer of fused metal oxides and compounds from the ceramic in a glassy matrix of < 0.3–3 mm thick is common at the exteriors of 41 fragments and interiors of 11 fragments. The slag layer in the interior of rim fragment ×2488, ~3 mm thick, is one of the thickest found (Fig. 7a). Metallic droplets are visible in the crucible slag on the exterior of 13 fragments and the interior of ×2488 (Fig. 7b), as well as in the ceramic fabric of the interior of ×85.3 (Fig. 8). Metal prills were mostly single-phase metals, except for two large and two smaller prills on fragment ×2488, which consist of a two-phase microstructure (Fig. 7c–d).

Quantitative elemental analyses

Bulk compositions—micro XRF Polygonal areas ($n = 155$) from the 54 crucible cross-sections were analysed with micro XRF targeting interior (53) and exterior (54) surfaces, and ceramic body (48) areas with mean sizes of 8, 6, and 20 mm², respectively (see Online Resource S6 for elemental compositions). Six fragments consisted solely of vitrified ceramic and slag leading to the lower numbers of interior (53) and ceramic body (48) analyses. Elemental maps identified distinct exterior slag and inner surface layers (see Online Resource S7 for elemental maps for Al₂O₃, SiO₂, P₂O₅, SO₃, Cl, K₂O, CaO, TiO₂, MnO, Fe₂O₃, CuO, ZnO, As₂O₃, Ag, PbO, and Au and Online Resource S8 for database with observations based on maps in Online Resource S7).

Crucibles' ceramic bodies consist primarily of SiO₂ (mean 68 ± 7 wt%), Al₂O₃ (mean 18 ± 4 wt%), K₂O (6 ± 3 wt%), Fe₂O₃ (3 ± 2 wt%), Na₂O (mean 2 ± 1.5 wt%), and smaller amounts of CaO (1 ± 1.5 wt%), P₂O₅ (mean 0.8 ± 0.2 wt%), TiO₂ (mean 0.9 ± 0.4 wt%), MgO (0.5 ± 0.3 wt%), and SO₃ (mean 0.2 ± 0.3 wt%) (Table 2). Elemental maps show the enrichment zones of CaO and P₂O₅ to coincide in 41 fragments (Fig. 9), MnO–CaO–P₂O₅ in 21 fragments, Fe₂O₃–P₂O₅ in 12, and PbO–SO₃ in 7 (S8).

CuO concentrations are most often higher in slag (exterior surfaces, $n = 44$) and interior surfaces ($n = 52$) (with means 3 ± 7 and 2 ± 6 wt%, respectively) compared to 1 ± 2 wt% in the ceramic bodies (Fig. 9, Table 2); SD > mean due to a high coefficient of variation. ZnO occurs more frequently in the interior surfaces with variable depths of penetration into the ceramic body ($n = 41$) as well as in slag layers ($n = 37$) with means 6 ± 4 wt% and 2 ± 2 wt%, respectively, while the ceramic bodies show 3 ± 3 wt% ZnO. Despite these overlapping results (due to the high SD values), individual samples exhibit consistent increases in CuO and ZnO in the exterior and interior surfaces (Fig. 10). PbO was found in 13 interiors and 13 exteriors in 23 fragments; SnO in the exterior of ASR9 ×22.7 (0.5 wt%); Ag in the slag of ASR9 ×410.1 and ASR9

Fig. 6 Bar charts showing the proportion of crucible fragments in which CuO, ZnO, SnO, PbO, and Ag were detected per period and surface (interior; exterior)

×2488 (~1.5 wt%), Au in a droplet in ASR9 ×85.3 (55 wt%) (Fig. 8), and MnO in 11 exterior and 2 interior surfaces in 12 fragments (means ~0.5 wt%). P₂O₅, Fe₂O₃, and CaO are enriched more in exteriors compared to the interior surfaces (Fig. 11).

Metal prills–EPMA A further 12 crucible fragments were examined with EPMA to quantify the composition of 42 metal prills in crucible slag, some corroded (Online Resource S9) (Fig. 12). The metallic prills in each crucible fragment show a

distinct elemental signature (Fig. 13), while high tin contents or the presence of iron and sulphur are attributed to the corrosion processes. Analysed prills in fragments ×366.1, ×407, ×88, ×93, ×121, and ×366.10 contain only copper. Copper-silver prills are present in ×2488, ×147, and ×137, and copper-zinc-tin-lead in ×250. The large prill in ASR9 ×85.3 contains gold with some silver (see also Fig. 8). Inclusions rich in titanium and iron with smaller amounts of chromium and magnesium were found in the ceramic fabric of a few fragments (Fig. 14).

Fig. 7 Photomicrographs of crucible rim fragment ASR9 ×2488 showing (a) an overview of the cross-section (×20) where the refractory ceramic is distinguished by the glassy vitrified layer; (b–c) reflected light images of

metallic prills in crucible slag (×100–×1000); (d) back-scattered electron (BSE) image of two prills showing the two-phase microstructure

Fig. 8 Photomicrographs of crucible fragment ASR9 $\times 85.3$ showing (a) overview of cross-section ($\times 10$) where a thin, uniform vitrified layer covers the exterior surface, (b) in reflected light image of gold-silver prill ($\times 500$) found on the interior surface and not associated with a slag layer

Table 2 Mean values (wt%) and standard deviation (SD) of bulk compositions of crucibles' interior and exterior faces, and the ceramic body and the moulds' interior faces and ceramic body as measured with micro XRF (N for number of fragments). As₂O₃, SnO, Ag, and Au are not included as they were

detected in few crucible fragments and they were not detected in any of the mould fragments. '-' is used for oxides or elements not detected. For the full data set, see Online Resources S6 and S12. In cases that SD is $>$ mean, this is due to a high coefficient of variation

Area		Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	CuO	ZnO	PbO
Crucibles Interior	N	20	26	53	53	13	15	21	53	39	53	2	52	26	39	10
	Mean	3.48	0.58	15.50	63.60	2.08	0.39	1.49	6.20	1.53	0.80	0.62	3.19	2.19	6.10	4.06
	SD	2.77	0.70	4.48	11.27	2.96	0.41	0.99	3.03	1.56	0.38	0.45	2.07	5.68	4.41	9.89
Ceramic	N	15	28	48	48	3	9	10	48	25	48	-	48	15	30	5
	Mean	2.16	0.47	17.73	68.28	0.80	0.24	0.8	5.91	1.19	0.88	-	2.81	1.01	3.32	0.22
	SD	1.45	0.26	3.99	6.51	0.18	0.27	0.27	3.24	1.61	0.38	-	1.82	2.20	3.42	0.11
Exterior (crucible slag)	N	21	48	55	55	21	13	12	55	54	54	9	54	40	26	7
	Mean	3.14	1.01	11.79	63.85	3.28	0.56	1.70	6.26	4.74	0.74	0.67	4.88	3.09	2.41	1.92
	SD	1.28	1.27	5.66	13.08	4.70	0.73	3.33	2.72	4.49	0.44	0.35	5.38	7.05	2.06	4.58
Moulds Interior	N	11	-	12	12	4	3	1	12	8	12	-	12	2	12	6
	Mean	2.43	-	10.07	73.98	1.95	0.38	1.07	3.00	1.26	0.94	-	4.29	0.15	3.24	0.82
	SD	0.97	-	1.86	4.54	0.84	0.17	-	0.26	0.88	0.10	-	2.20	0.07	1.68	0.77
Ceramic	N	10	-	12	12	3	5	1	12	11	12	-	12	-	-	-
	Mean	0.62	-	10.87	78.71	2.01	0.26	0.83	3.22	1.09	1.03	-	3.92	-	-	-
	SD	0.19	-	2.21	2.81	0.31	0.07	-	0.35	0.54	0.13	-	1.74	-	-	-

Fig. 9 Elemental maps for Zn, Cu, Ca, and P of crucible fragments (a) ASR7 $\times 1896$, (b) ASR9 $\times 107.21$, (c) ASR9 $\times 137$, (d) ASR9 $\times 250$, and (e) ASR9 $\times 407$ produced with the micro XRF. The first column shows photographs of the fragments at $\times 10$ magnification. Zn is enriched in the

fragments' interiors (a–e) and occasionally in the exterior slag layer (e). Cu is enriched in the slag (a–c and e), and occasionally on the interiors (c–d). Ca and P are often enriched in both surfaces. Scale bar 4 mm. See Online Resource S7 for all elemental maps

Moulds

Surface qualitative elemental examination

Non-destructive analyses by hhXRF of a total of 383 mould fragments showed traces of zinc, and less frequently of copper, tin, and lead in the moulds' interiors

(see Online Resources S10.1 and S10.2). Zinc was detected on 275 interiors and 2 exteriors surfaces, copper on 4 interiors and one exterior surface, lead on 35 interiors and 2 exteriors surfaces, and tin on 5 interiors and one exterior surface. Arsenic, silver, and gold were not detected. Mould fragments with impressions of horse, hilt, round, RI9, P11, and P12 brooches showed only traces of zinc. Both zinc and lead are found in moulds with impressions of needles, keys, equal-armed, round P13, P14, P15, P17, and N brooches. Tin was detected in 3 out of 7 ingot moulds (S10.2, no. 4) and in one type P17 brooch.

Fig. 10 Ternary diagram for Al_2O_3 -ZnO-CuO for the ceramic body (red cross, $n = 48$), the exterior slag layers (blue circle, $n = 54$), and the inner surfaces (green triangle, $n = 53$) of crucibles as analysed with micro XRF. Enrichments in CuO and ZnO are often observed for the slag and interior layers. Graph based on data presented in S6

Microscopic observation

Cross-sections of 9 out of 12 moulds produced with the micro XRF ($\times 10$) show evidence of layering (see Online Resource S11 for mosaic images of mounted cross-sections and photographs before sampling). Most fragments comprise two or three visible clay layers (Fig. 15), while fewer have only one layer (S11) (for compositions, see below 'Quantitative elemental analyses'). The innermost layer is typically dark grey, whereas the outermost layers usually are lighter brown or orange. Layer boundaries in most fragments are gradual (Fig. 15a, c), but in $\times 186.33$ and $\times 205.17$ layers have rather sharp boundaries (Fig. 15b, d). Fragments ASR9 $\times 363.20$ (orange fabric), $\times 348.1$, and $\times 319.5$ (dark grey fabric) are made from one or possibly two clay layers.

Fig. 11 Ternary diagrams for $\text{PbO}-\text{CaO}-\text{Al}_2\text{O}_3$ (top) and $\text{Fe}_2\text{O}_3-\text{CaO}-\text{Al}_2\text{O}_3$ (bottom) for the ceramic body (red, $n = 48$) and the exterior slag layers (blue, $n = 54$) of crucibles as analysed with micro XRF. Enrichments in Fe_2O_3 , CaO , and PbO are often observed for the slag layers. Graphs based on data presented in [S6](#)

Quantitative elemental analyses

Compositional analyses of 12 mould cross-sections showed bulk ceramic body compositions to be comparable to the crucibles except for relatively low Na_2O , Al_2O_3 , and K_2O and higher SiO_2 compared to the crucibles. Enrichment in metal oxides takes place in the interior surfaces (Fig. 16, Table 2); see Online Resource [S12](#) reporting micro XRF elemental analyses, and [S13](#) for

elemental maps. All fragments' interiors were enriched in ZnO (1–7.5 wt%), 6 in PbO (< 2 wt%), and 2 (ASR9 $\times 348.1$, $\times 319.5$) in CuO (~ 0.1 wt%). Na_2O was enriched in 10 of 12 interiors. We found no noticeable enrichment in Fe_2O_3 , Al_2O_3 , SiO_2 , SO_3 , K_2O , P_2O_5 , CaO , MnO , or TiO_2 ; note that ASR9 $\times 348.1$ (Fig. 16) showing enrichment in SO_3 , Fe_2O_3 , and CaO is an exception. The moulds' exteriors and interior showed comparable compositions despite the multiple coloured layers noted during microscopic observation (Fig. 15). Mould fragments ASR9 $\times 319.5$, $\times 348.1$, and $\times 501$, which consist wholly of a dark grey ceramic fabric, showed consistently ~ 3 wt% Fe_2O_3 . Fragment ASR9 $\times 205.17$ is an exception as the darker layer closer to its interior (layer 1 in Fig. 14b) contains more Fe_2O_3 (5 wt%) than the two light-coloured layers (layers 2 and 3, 3 wt%).

Ingot bars and blanks

Microscopic examination

Dendritic, as-cast structures were found in 8 bars and recrystallised metallic grains in 6 (see Online Resource [S14](#)). The microstructures of 3 fully corroded samples (ASR9 $\times 21$, $\times 350$, and $\times 400$) were identified based on 'ghost' structures, namely, corrosion products imitating the original metallic structures (for 'ghost' structures, see Oddy and Meeks 1982). The bars' cross-sections varied widely in shape including round ($n = 2$), square ($n = 3$), rectangular ($n = 3$), trapezoid ($n = 3$), and polygonal ($n = 3$), and all shapes included bars with cast and recrystallised structures. Re-deposited pure copper as a result of corrosion processes was found in ASR9 $\times 350$ and $\times 364$; copper-rich dendrites surrounded by a zinc-rich phase as expressed in a light bluish colour (and as also confirmed by micro XRF, see below 'Elemental compositions (micro XRF)') in ASR9 $\times 411$, and lead inclusions in 5 bars.

Elemental compositions (micro XRF)

Twenty-one ingot bars with preserved sound metal (3 were fully corroded) are of brass ($n = 13$, 12–32 wt% Zn, < 1.5 wt% Sn, < 2.5 wt% Pb), leaded brass ($n = 3$, 3–7 wt% Pb, 3–13 wt% Zn, < 0.5 wt% Sn, with lead equal to or half the zinc content ($\text{Pb} = 0.5\text{Zn}$ to 1Zn), leaded brass with tin ($n = 3$, 2–6 wt% Sn), and one leaded brass with 6 wt% Ag (Fig. 17) (see Online Resource [S14](#) details of bars' elemental analyses). Iron was found in 19 bars with < 0.6 wt% and mean of 0.2 wt% Fe, arsenic in 14 with < 1.2 wt% As and mean of 0.3 wt% As, and nickel 0.4 wt% Ni in bar ASR9 $\times 391$. Metal traces in corrosion products in 3 bars suggest original compositions of leaded brass for 2 samples, and of bronze in one.

Fig. 12 **a** Photomicrograph ($\times 200$) and **(b)** back-scattered electron (BSE) image of fragment ASR9 $\times 147.17$; copper oxide crystals form in the surrounding of the metal prills. **c** Photomicrograph ($\times 500$) and **(d)** BSE image of ASR9 $\times 366.10$; the vitrification layer is scattered with minute ($< 0.1 \mu\text{m}$) metal prills with some larger prills included. **e** Photomicrograph under cross polarised light (XPL, $\times 200$) and **(f)** BSE image of ASR9 $\times 2488$ showing metal prills surrounded with copper oxide crystals in the slag matrix

Finished objects—elemental compositions

In our alloy classification, we prioritised the elemental compositions of the analysed assemblage and avoided applying classifications based on absolute values or ratios between specific alloying elements. This approach of considering the particularities of each assemblage as opposed to applying prescribed alloy categorisations moves closer to grouping of alloy types having in mind the specific object biographies and life histories (Pollard et al. 2015, p. 699), and further away from rigid classifications based on set element concentrations and ratios (Bayley and Butcher 2004, p. 14). Similarly, for the copper-zinc-tin alloy type, we opt for the ‘tin brass’ term, as opposed to ‘gunmetal’ as we find that the latter is too strongly related to an alloy with a specific use, namely, that of making cannons, which is not suited to our discussion here. Nevertheless, our alloy grouping follows certain commonly agreed conventions that brass contains $> 9 \text{ wt\% Zn}$ and tin

brass $> 5 \text{ wt\% Zn}$, while bronze and tin brass contain $> 3 \text{ wt\% Sn}$, and, finally, leaded alloys $> 4 \text{ wt\% Pb}$.

Of the 24 artefacts analysed with micro XRF, 11 are of brass (9–24 wt% Zn, $< 1 \text{ wt\% Sn}$, $< 2 \text{ wt\% Pb}$), 5 are tin brass (5–9 wt% Zn, 3–8 wt% Sn, $< 3 \text{ wt\% Pb}$), one is a Sn (16 wt%) bronze, 6 are of leaded bronze (5–8 wt% Sn, 4–11 wt% Pb, 1–3 wt% Zn), and one of copper (Fig. 17); see Online Resource S15 for elemental analyses. Iron ($< 0.7 \text{ wt\%}$, mean $0.2 \text{ wt\% Fe}$) and arsenic ($< 0.8 \text{ wt\%}$, mean $0.3 \text{ wt\% As}$) are detected in 22 objects, though not the same ones, and nickel in 4 ($< 0.2 \text{ wt\% Ni}$). The brooches consist of brass ($n = 11$) and tin brass ($n = 3$) and keys of leaded bronze ($n = 6$) and tin brass ($n = 1$). Five objects dating to 700–790 CE comprise 3 leaded bronze keys, a brass bow brooch, and a bronze object. For the 790–850 CE period, 9 brooches are of brass including the oval brooch AM6284 possibly made in Hedeby, while 2 oval brooches, a key, and an object of undefined typology of tin brass, and 2 keys are made of leaded bronze.

Fig. 13 Bar chart showing the metals present in the prills in the 12 fragments analysed with EPMA. Results are not normalised; missing percentages correspond to elements related to the ceramic and glassy matrices that are not illustrated in the chart. Graph based on data in [S6](#)

Discussion

Metallurgical ceramics

We examined the surfaces of 1126 crucible and mould fragments to better understand aspects of workshop organisation that may otherwise be concealed in the finished objects (Braun

1983; Söderberg 2004; Merkel 2016, p. 209; Rademakers et al. 2017) by moving beyond screening of smaller assemblages (e.g., Erb-Satullo et al. 2015; Ioannidis et al. 2016; Farci et al. 2017). Non-destructive analyses were used to select samples (total $n = 66$) for sampling and further examination for quantitative data on the metallic traces.

Fig. 14 BSE images (a) Ti-Mg-Fe-Zn inclusion in crucible ASR9 ×93, (b) rutile (TiO_2) inclusion in crucible ASR9 ×93, (c) rutile (TiO_2) inclusion in crucible ASR9 ×121, and (d) Ti-Fe-Mg inclusion in crucible ASR9 ×147 found in the fragments' ceramic body

Fig. 15 Overview of cross-sections of moulds (a) ASR9 $\times 311.19$, (b) ASR9 $\times 205.17$, (c) ASR9 $\times 378.17$, and (d) ASR9 $\times 186.33$ under $\times 10$ magnification produced by collating photomicrographs produced with the micro XRF. Dark grey and lighter coloured ceramic layers are visible. Numbers in the cross-sections correspond to distinct ceramic layers as identified by colour. Cross-sections (a), (b), and (d) show three layers (possibly 2 layers in a), whereas two layers are visible in cross-section (c). Darkening of clays is probably due to the burning out of organic temper in the clay

Bulk compositions and heat resistance of ceramic fabrics

Macroscopic examination of crucibles suggests that they were heated from below, as was routinely done from the Roman period onwards, by placing the round bases in a hearth or similar structure (Bayley and Rehren 2007, p. 47). Exposures to temperatures of $\sim 1100^\circ\text{C}$ would cause partial melting of the crucibles forming a vitrified outermost layer in part caused by interaction with spillover of

the metals worked and fuel from the workshop area (Freestone and Tite 1986; Thornton and Rehren 2009, p. 2701). Crucible rim fragment ASR9 $\times 2488$ (Fig. 7) with crucible slag in its interior is an exception and the slag must have resulted from remnant molten metal after pouring the alloy.

The crucible and mould fragments fall into two compositional groups (A and B) based on the Al_2O_3 and TiO_2 concentrations as seen in Fig. 18. Group A ($n = 41$) consists of lower

Fig. 16 Elemental maps for Zn, Pb, S, Fe, Ca, and P of mould fragment ASR9 $\times 348.1$ produced with micro XRF. The fragment consists of a single ceramic layer of dark grey colour. Enrichment of the elements on

the mould's inner face (top part in the maps) is visible. For elemental maps of all 12 mould fragments analysed, see Online Resource S13

Fig. 17 Ternary diagrams for Zn, Pb, and Sn showing the ratios between the alloying elements for ingots and blanks (top) and objects (bottom), according to period (red: 700–790 CE, blue/green: 790–850 CE) and alloy type (for ingots: circle/brass, diamond/leaded brass, green diamond is with 6 wt% Ag, triangle/leaded brass with tin; for objects: circle/brass, diamond/leaded bronze, triangle/tin brass, cross/bronze). For both the ingot bars and the objects, a tighter distribution of alloying elements is noted in the later period. Graphs based on data sets in Online Resources S14 and S15

Al_2O_3 on average (15 ± 4.5 wt%) but with a wide range between 8 and 27 wt%, and higher TiO_2 (1 ± 0.2 wt%) and includes all but 3 of the early period crucibles and 9 later ones, and the moulds. Al_2O_3 within group A is higher in most of the crucibles (17 ± 4 wt%) compared to the moulds (11 ± 2 wt%). Group B ($n = 14$) with high Al_2O_3 on average (21 ± 1.5 wt%) and a smaller range than group A (17–22 wt%), and low TiO_2

Fig. 18 Co-variation of alumina (Al_2O_3) and titanium (TiO_2) in wt% as determined by micro XRF in the ceramic body of crucibles ($n = 48$) and moulds ($n = 12$). All the mould fragments fall in the low Al_2O_3 /high TiO_2 group (group A) as with most of the early and a handful of late crucible fragments; group B with high Al_2O_3 /low TiO_2 consists mostly of later period crucible fragments and two early ones. Graph based on data in Online Resources S6 and S12

(0.4 ± 0.1 wt%) is dominated by 790–850 CE crucibles (11 fragments) and 3 earlier ones, one them falling between both groups.

Crucibles with an average Al_2O_3 of 18 ± 4 wt% (groups A and B) are on the lower side of the refractory scale (cf. Martínón-Torres and Rehren 2014, fig. 6.15, where some crucibles contain up to 40 wt% Al_2O_3). Such Al_2O_3 levels are comparable to other early mediaeval crucibles (Freestone and Tite 1986; Freestone 1989). Higher alumina contents in group B crucibles, similar to high alumina crucibles types 2 and 3 from Hedeby (Merkel 2016, p. 213), would enhance their heat resistance properties. Nevertheless, given that the Ribe crucibles are not highly refractory, additional layering to reduce the effects of brittleness (Rehren 2003; Bayley and Rehren 2007; Gardner et al. 2020), might not have been needed, as exterior layering was found in just one crucible (base fragment ASR9 $\times 147.17$, S7, no. 3). The increase in group B crucibles from the early to the later period suggests that more refractory fabrics were used after 790 CE, possibly based on the craftspeople's practical experience (Braun 1983; Freestone and Tite 1986; Gardner et al. 2020). Alumina-rich crucibles were imported to Hedeby and Kaupang in the 9th c. (Pedersen 2010, p. 191, 2016; Merkel 2016, p. 211) and later (eleventh c. CE) in Viborg, Denmark (Jouttijärvi and Andersen 2005, p. 356). Even though petrographic analysis of Ribe crucibles does not exclude the use of local clays (Brinch Madsen 1984, p. 31), similarly, we cannot exclude the import of high-alumina clays after 790 CE as also found at Hedeby and Kaupang. Moulds made of clay rich in fine-grained sand mixed with organic components (Brinch Madsen 1984) with 12 wt% Al_2O_3 are less refractory. This is justified by the shorter period and lower temperatures they would be exposed

to, along with heating to $\sim 475^\circ\text{C}$ prior to casting as shown by experimental reconstructions (Smith 2005).

The crucibles comprise a single ceramic fabric, except for the sample showing evidence of repair (ASR9 $\times 147.17$), while layering with different ceramic pastes and colour changes from the exterior to the interior surfaces are observed in some mould fragments (Fig. 15). Of the mould fragments, 5 show a gradient colour change from light orange (exterior) to dark grey (interior) with no noticeable chemical change, whereas 4 fragments exhibit no colour nor any chemical changes.

Variations in colour from orange to dark grey within moulds have been shown to reflect local redox conditions from the exterior to the interior surfaces which came in contact with the molten metal (Dungworth and Mclean 2002, p. 2; Katona et al. 2007, p. 162). The dark grey core of the Ribe moulds is best attributed to a clay paste rich in fine organic matter which would have burnt upon firing, for example, the addition of dung has been suggested for mediaeval bell-casting moulds (Dungworth and Mclean 2002, p. 4), and to the contact with the molten metal. Even though colour change alone does not necessarily reflect layering of different ceramic pastes (Dungworth and Mclean 2002, p. 4), sharp boundaries between colour zones as seen in mould fragments ASR9 $\times 205.17$ and ASR9 $\times 186.33$ (Fig. 15b and d) could suggest that ceramic layers with variable concentrations in organic inclusions were occasionally used.

The high SiO_2 contents (crucibles: 68 ± 6 wt%, moulds: 79 ± 3 wt%) and large quartz crystals often present in the crucible and mould ceramic bodies are consistent with the use of clay naturally rich in quartz or, alternatively, heavy mixing of clays with sand that both would improve the ceramics' thermal shock resistance (Martín-Torres and Rehren 2014) (see S7 and S13 for the quartz inclusions in elemental maps).

Highly elevated and variable CaO (5 ± 4 versus 1.2 ± 1.6 wt%) and P_2O_5 (3 ± 5 versus 0.8 ± 0.2 wt%) concentrations within crucible slag (exterior surface) versus ceramics bodies such as seen in elemental maps (Fig. 9) and bulk compositions (Fig. 11) could represent contamination by fuel ash from charcoal as a result of interaction with the ceramic during heating of the crucibles (Tylecote 1980, 1982, 1987; Misra et al. 1993; Crew 2000; Rovira et al. 2007; Wood et al. 2009; Müller 2017; Gardner et al. 2020). However, there is a lack of increasing K_2O concentrations ($\sim 6 \pm 3$ wt%) in the ceramic body and crucible slag as would be typically expected for fuel ash contamination. Instead, K_2O contents in the crucible ceramic bodies are positively correlated with the K_2O in the interior and exterior surfaces, suggesting the increase in the ceramic body is also attributed to the fuel source. The particularly high K_2O contents of group B crucibles at 9–12 wt% can further, but only speculatively at this stage, be attributed to clay rich in potassium feldspars, illite, and muscovite minerals, as detailed petrographic examination of crucible and mould fragments was beyond the scope of this study.

Metallic traces in metallurgical ceramics

Metallic traces in interior and exterior (crucible slag) surfaces

Both crucible and mould fragments exhibit traces of contact with molten non-ferrous alloys given the various concentrations of zinc, lead, and tin, while gold and silver traces were found in only a handful of crucibles. Similarly, evidence from Hedeby shows that crucibles related to copper-based alloys are abundant, while crucibles with visible traces of gold and silver are rare (Merkel 2016, p. 210). The nature of the metallic traces on metallurgical ceramics depends on volatility of the individual metals upon heating, the slagging capacity of the ceramic fabrics depending on the silica content, and the temperature gradient involved. Additionally, traces of specific alloys would also depend on the intended use of the finished objects, namely, remnants of leaded alloys for utilitarian objects and high-zinc brass for brooches as examples of display items. The moulds record traces of single metal batches as they had to be broken to release the casting (see above 'Bar ingots/blanks') (cf. Smith 2005, for a suggestion of mould reuse based on experimental reconstruction). Metallic traces on the moulds are confined to the innermost layers (Fig. 16) as the molten metal cooled quickly and exhibit traces of copper, zinc, and often lead, while moulds with key impressions have traces of a quaternary copper-zinc-lead-tin alloy. Leaded alloys were consistently used for keys, for which improved castability of the alloy is a key aspect, while the bright golden brass was preferred for decorative items such as brooches, especially after 790 CE.

On the contrary, the crucibles preserve a complex record of metallurgical information as they could be reused, and they show enrichment in metallic remains in both the exteriors and interiors, and the ceramic body (Fig. 9). In addition, crucible slag records not just metallic spillage from the charge but also traces from the fuel charge and partially melting clay vitrification during use. The crucible slag layers' variable thicknesses and levels of reaction with the ceramic are due to different temperature gradients during use (Hein et al. 2013, p. 94). Macroscopic examination of crucibles' interior showed an almost complete absence of metallic remnants. The above, along with evidence of mechanical cleaning of crucibles' interiors with a chisel-like tool (Fig. 2a), suggests that care was taken to remove any valuable metallic remnants before discarding the crucibles.

Zinc, most often found in the moulds' and crucibles' interiors, is a volatile metal and reaches a gas phase at 907°C . Depending on the length of exposure to high temperatures, zinc reacted with the ceramic fabric in ways that non-volatile metals would not. Thus, absolute concentrations of metallic elements in metallurgical ceramics' interiors are not proportionately representative of the original alloy's composition as zinc traces tend to dominate in the ceramic (Dungworth 2000; Kearns et al. 2010). The mould analysis is, thus, useful in

detecting the type of alloy, but not sufficient for establishing the original ratios of the alloying elements. The zinc enrichment zone is much deeper in the crucibles due to higher temperatures and longer operation times of the crucibles compared to the moulds (compare Figs. 9 and 16).

Enrichment of crucible vitrification layers in iron resulted unintentionally from the use of iron-bearing copper (Rademakers et al. 2018, p. 513) and/or from the iron-rich clay. As slag inclusions or any evidence for the working of cassiterite (SnO_2) are absent in the sample, these should be excluded as possible sources for the iron in crucible slag at Ribe (Murillo-Barroso et al. 2010).

Metallic traces as prills in crucible slag Analyses of metallic prills in crucible slag with EPMA often detected metals not found by XRF analyses (handheld or micro) such as tin in ASR9 $\times 22.5$ and silver in $\times 147.17$ (Table 3) reflecting the limitations of the latter analytical techniques for quantifying low-abundance trace metals. Several pure copper prills found in slag layers in crucible fragments are the remnants of repeated crucible use as with every heating any zinc would escape in the vapour and other metallic traces would be lost through oxidation (Tylecote et al. 1977; Merkel 1983, 1990; Pernicka 1999, p. 165; Bray and Pollard 2012). As alloying components separate from copper, the layers of crucible slag are often enriched in Zn and Pb (see also maps in Online Resource S7). All evidence from the metallurgical ceramics and objects point to the production of Cu-based alloys as opposed to unalloyed copper, and these copper prills should not be taken as representative of the final product, namely, an alloy, rather as metallurgical by-products of an intermediate production stage.

Crucibles were possibly used for batches of alloys as metallic prills in crucible slag with distinct alloy signatures per

fragment all contain the same metals (Fig. 13). Since, for example, copper-silver-zinc prills are absent, it seems possible that the crucibles were not used across these alloy types, though repeated use is assumed. However, in the interior surfaces of fragments ASR9 $\times 137$ and ASR9 $\times 410.1$, silver (and gold for $\times 410.1$) was detected alongside copper and zinc during micro XRF analysis (see Online Resource S8). In addition, 3D scanning of mould fragments showed that the stratified ASR7 deposits could have related to episodes of ‘waste deposition and accumulation in connection with episode(s) of production’ (Croix et al. 2019, p. 11). Analysis of the slag from individual crucibles with specific alloy signatures such as seen in Fig. 13 matches the evidence from the 3D scanning of moulds by Croix et al. (2019) pointing to the performance of small-scale operations. The assumed repeated use of the crucibles leads to the possibility for the iterative nature of these small-scale metallurgical episodes contributing towards the serial production of objects with specific typologies such as the oval brooches and the keys.

Metal artefacts: bar ingots and finished objects

Bar ingots of the pre- and Viking periods found in Scandinavia and the British Isles (Oldeberg 1942; Drescher 1983; Eiwanger 1996; Sindbæk 2001a; Bayley et al. 2014; Pedersen 2016; Merkel 2018) are not typologically homogeneous, while variation is often found within single sites (Sindbæk 2001a; Pedersen 2016; both note variation in bars’ cross-sections). Nonetheless, some typological groups emerge such as the long bar ingots of various lengths and with rounded edges (Sindbæk 2001a, b) (Fig. 4). Even though these bar ingots formed an integral part of exchange activities, we cannot assign their production to specific workshops or sites making the manufacturing provenance of the bar ingots examined here a matter of ongoing discussion. Nevertheless, a possible Balkan or Andalusian origin has been found for the brass used for the ingots found at Hedeby (9th c. CE), as the metal was not consistent with the ore deposits of the Rhine area (Merkel 2018). The bar ingots studied here could have been brought to Ribe via a long-distance network such as suggested by Merkel (2018), while blanks might have well been produced at Ribe for either own use or storage of metal. Nonetheless, the bar ingots mark an intermediary step between metal refining and/or alloying and the production of finished objects. Finally, mould impressions found at Ribe and the discovery of the matching finished objects elsewhere in Scandinavia testify to the spread of locally cast products (Brinch Madsen 1984; Feveile 2002, p. 21).

Cu-based alloys

Most of the ingots ($n = 13$) and finished objects ($n = 11$) analysed consist of brass with a zinc content range between

Table 3 Table showing the metallic traces apart from copper and zinc as detected during surface hhXRF, micro XRF on polished cross-sections, and EPMA analyses also the metallic prills trapped crucible slag layers; ‘-’ used for elements not detected by the respective analytical technique. The high resolution, low detection, spot EPMA analyses of metal prills is the most reliable protocol for tracing the full set of metallic remnants in crucible slag. Table compiled with data from Online Resources S5, S6, and S9

Find ID	Metals detected		
	hhXRF	Micro XRF	EPMA
ASR9 $\times 22.5$	-	-	Sn
ASR9 $\times 85.3$	Ag	-	Ag, Au
ASR9 $\times 137$	-	Ag	Ag
ASR9 $\times 147.17$	-	-	Ag
ASR9 $\times 250.2$	Sn, Pb	Pb	Sn, Pb
ASR7 $\times 2488$	Ag	Ag	Ag

10 and 31%, most between 15 and 25%. The brass compositions of bar ingots are comparable with bar ingots (9th c. CE) from Hedeby with c. 20–25 wt% Zn (Merkel 2018, p. 296). The rest of the ingots comprise leaded brass ($n = 8$), 4 with tin and one with silver additions, while finished objects more often contain tin and fall in the alloy types of leaded bronze with minor concentrations of zinc and tin brass with variable concentrations of lead (Fig. 19). The presence of tin, lead, and zinc with amounts > 1 wt% in both the leaded bronze and tin brass underlines the affinity between these alloy types (Pollard et al. 2015, p. 699). These ratios for alloying elements are consistent with the routine mixing of various copper-based alloys.

Of the 8 ingots with evidence of cold working, 6 are leaded brass (one is corroded), while 2 are brass. Leaded brass ingots were possibly cast as blanks at Ribe and kept for later use, after mixing with lead-containing alloys had taken place. The variable shapes of the bars' cross-sections (round, rectangular, round, ovoid, trapezoid, polygonal) leave more room for some of these bars to have been blanks produced at the respective workshops rather than standardised forms of ingots for more established metals' trade. Pedersen (2016, p. 146) also notes variable cross-section shapes in ingots from Kaupang and speculates that not all fragments were indeed ingots.

Leaded alloys at Ribe were used for utilitarian objects, such as for the keys, while high-zinc brass and tin brass for ornaments, such as the brooches including the oval brooch AM6284 with possible links to Hedeby (Fig. 5b), most possibly owing to its aesthetically pleasing colour. Five keys are of

leaded bronze (with small amounts of zinc), one of brass and one of tin brass, and the brooches are either brass or tin brass. Analyses of brooches from Birka showed that equal-armed brooches also comprised brass, but gilded oval brooches were reportedly made of unalloyed copper (Nord et al. 2020), while brass oval brooches of Scandinavian origin have been analysed from Norse graves in Scotland (Eremin et al. 2002). The finished objects' relative tin abundance, compared to the ingots, points to mixing of (leaded) bronze with the (leaded) brass ingots or scrap zinc- and lead-containing alloys to form three- and four-part alloys. Tin could have come from scrap bronze, as suggested by the presence of imported object fragments (ASR7), including one of from a Roman statue and two vessel pieces (Frandsen and Jensen 2006, p. 32). The continuity of Roman metal at least until the seventh c. CE in the Early Saxon period has also been noted in the British Isles (Pollard et al. 2015, p. 706). Three brass and 5 tin brass objects from 790–850 CE with ~ 10 wt% Zn could be the result of higher-zinc brass remelting as zinc would be lost during recycling (Caley 1964; Ponting 2002). All the above place metal mixing and reuse at the centre point of the metalworking cycle at Ribe alongside the continuing use of fresh brass with a rather standardised 20 wt% zinc content.

Silver and gold

Silver in Viking Age Scandinavia is common in coins and ornaments from the 9th century, though more widely from the tenth century as also seen in Hedeby (Sawyer 1990; Malmer 2002; Wiechmann 2007; Merkel 2016). Silver and gold objects have occasionally been found in relation to the Viking-age workshops in Ribe, including 6 ornaments and more than 60 coins of silver, and 4 fragments of gold objects from ASR9 (Feveile and Jensen 2006, pp. 145–146). Our study shows that silver and gold were integral elements of the polymetallic metalworking cycle at Ribe. Metallic traces on crucibles (Figs. 6 and 13) and the bar ingot ASR7 $\times 2375$ with 6 wt% Ag (Fig. 17, green diamond) confirm the working of silver at Ribe from the 8th century. The mixing of silver with copper and gold suggests that silver was acquired either as hacksilver and mixed at Ribe or, and as further supported by the 8th century silver-rich ingot, already in an alloyed state. Gold working must have occurred similarly to that of silver, as gold was found on the surface of two crucible fragments and as a large gold-silver prill in ASR9 $\times 85.3$ (Fig. 8), all dating to the 790–850 CE period. Minor silver contents found in contemporary copper-based objects from both Scandinavia and the British Isles in Norse period Scotland are also considered as evidence for limited, random recycling using mixtures of copper and silver alloys (Eremin et al. 2002). At the same time, workshops with a polymetallic character have also been found at Hedeby (Capelle 1968; Drescher 1983; Merkel 2016, pp. 209–210, note 1).

Fig. 19 Ternary diagrams for Zn, Pb, and Sn for ingots and objects (circle: ingot, diamond: brooch, triangle: key, cross: other object) analysed with micro XRF according to alloy type (blue: brass, green: leaded brass including traces of tin and silver, orange: bronze, red: leaded bronze, purple: tin brass). Graph based on data sets in Online Resources S14 and S15

Recycling, mixing, and reusing of metals and alloys

The amounts of zinc, lead, tin, and silver in the copper-based alloys reveal the recycling tradition of the metal workshops at Ribe. One of the main characteristics of non-ferrous metallurgy at Ribe was in part the inflow of fresh binary brass, along with silver and lead (Feveile and Jensen 2006, pp. 145–146) in the form of ingots (silver and lead ingots were not analysed as part of this study). However, these were often mixed and reused in combination with other alloys (scrap metal). Similarly, the presence of small amounts of tin and silver in the leaded brass ingots and blanks suggests that these alloys were also imported at Ribe in addition to binary brass.

Above, we defined the distinct alloy types with various zinc-lead-tin ratios ('Finished objects—elemental compositions' section) to better describe and understand the analysed assemblage in relation to artefact types and phases of activity. The leaded brass (700–790 CE), tin brass (790–850 CE), and leaded tin brass (both periods) with variable concentrations of zinc, lead, and tin are testimonies of the routine mixing of metal. The frequency of these ternary and quaternary alloys further illustrates how prevalent the practice of mixing of metals and alloys was at Ribe. In regard to technological organisation, the boundaries of what constituted the raw materials at the workshops of Ribe are blurred as imported ingots of brass or single metals (silver, lead), blanks of leaded brass with or without tin, and scrap metal or alloys could have all been mixed at the same workshops. Nevertheless, the presence of brooches and keys with distinct and standardised compositions shows that, when needed, attention was given to the production of alloys with specific ratios (see above).

The integrated nature of the alloy making process including the mixing of fresh brass ingots, blanks, and scrap alloys at Ribe is illustrated in Fig. 20. This underlying process of alloy making based heavily on mixing alongside the use of fresh binary brass feeds into iterations of artefact casting, finishing, circulation, and use (artefact treatment). Alloy making is central to any subsequent stage of the objects' life history at Ribe, because even when mixing does not take place, this also be a conscious choice. Here, we acknowledge previous cyclical representations of the metallurgical cycle such as Ottaway's (1994, fig. 1, 2001, p. 88) model that has proven useful in reconstructing metallurgical choices. However, the evidence present here from Ribe suggests that reusing, mixing, and recycling are not distinct steps, but rather integrated activities with the technological organisation (Sainsbury et al. 2021, p. 2).

Continuity and change in non-ferrous technology from the 8th to the 9th century CE

The presence of brass at the workshops of Ribe from the 8th c. falls within the beginning of the third phase of brass making in

Fig. 20 Schematic representation of the non-ferrous metalworking cycle at Ribe. The inner shaded circle (alloy making) illustrates the embedded nature of mixing and recycling of non-ferrous alloys in which imported brass ingots (fresh metal), blanks, and scrap metal were all potentially treated as raw materials that were mixed and recycled to make alloys with variable ratios of Cu, Zn, Pb, and Sn for casting, finishing, circulating, and using objects (artefact treatment)

Europe when fresh brass emerged in Viking contexts after the mid-first mil. CE (Eremin et al. 2002; Rehren and Martín-Torres 2008, p. 173) and from the Mid Saxon period (7th–9th c. CE) in the British Isles (Pollard et al. 2015, p. 711). Developments in the archaeological record at Ribe are noted before and after 790 CE in relation to the alloys used, the raw materials of ceramics, and object typology, alongside elements of continuity throughout the site's use (700–850 CE). Zinc, lead, tin, and silver are worked at Ribe from the 8th and into the 9th centuries. All the same, our study indicates that changes are visible in the treatment and use of alloys. Extensive use of zinc-containing alloys took place in both periods, but from 790 to 850 CE, high-zinc brass became more widespread with a smaller range of zinc contents (cf. 10–32 wt% for the early period to 15–22 wt% for the later one). Furthermore, more heavily leaded alloys in ingots and blanks (leaded brass, often with tin or silver) and objects (leaded bronze) are present in the early period, compared to brass for the ingots and objects and tin brass for the objects. Preference in alloy types for specific object types is found throughout the entire period, as typically leaded bronze was used for keys and brass for brooches. Even though silver was found in the sample from the 8th century, surface analyses of ceramics and silver-copper prills in crucible slag after 790 CE suggest a more generalised use in the 9th century. Finally, gold-silver was found in crucible slag and a gold prill in fragments from 790 to 850 CE. Greater standardisation of alloys noted from 790 CE points to increased access to the inflow of freshly produced brass and a smaller reliance on mixing and recycling of non-ferrous alloys at Ribe. This streamlining of

production in the later phase further coincides with an entirely new set of ornament types with bolder modelling, and possibly, new types of models appear too (Feveile and Jensen 2006; Sindbæk 2012).

As metallurgical ceramics performed the most challenging role of all ceramics (Gardner et al. 2020), their manufacturing choices directly impacted the efficiency of metalworking. Crucibles were made of higher alumina clays and had increased refractory properties from 790 CE onwards suggesting that craftspeople at Ribe reflected upon the ceramics' production and achieved better performance after of almost a century of on-site metalworking. The high-alumina clay was possibly known already from the 8th century, as shown by a couple of early crucibles, but it was from 790 CE that it is more often used.

A multi-material, multi-analytical approach to the study of non-ferrous metalworking

The multi-material approach using a range of analytical techniques has proven well-suited for the examination of the significant and diverse metallurgical record at Ribe. The various analytical methods and scales of investigation allowed for a comprehensive bird's eye view of the whole assemblage such as the thousands of technical ceramics fragments, as well as in-depth insights from miniscule traces such as the metallic prills in crucible slag. This approach surpasses any single-material study of the Ribe assemblage as important aspects of the polymetallic, non-ferrous metalworking cycle would have been unwillingly overlooked. For example, the large large-scale surface analysis of crucible and mould fragments provides a comprehensive overview of the main characteristics of metallurgical production over the various chronological phases. However, a reliance on the above would overestimate the use of brass, whereas leaded and tin were often worked into the Ribe alloys as proven by the micro XRF analyses of sampled crucibles. Furthermore, a focus on the micro-scale, namely, the metallic prills in crucible slag, would tend to overemphasise the use of unalloyed copper over Cu-based alloys, while small concentrations of Sn, Ag, and Au would be missed by hhXRF or micro XRF as seen in Table 3. Meanwhile, examination of metallic prills provided a level of resolution unobtainable by surface hhXRF or cross-sections' micro XRF analyses, which showed the mixing of silver with copper and silver with gold, but not gold mixed with copper. Finally, the comparison between ingots and blanks, and finished objects unveiled a degree of specialisation in the use of alloy types that would have been missed otherwise.

Conclusions

We adopted a multi-material, multi-analytical approach to examine the metalworking cycle across crafts related to metallurgical ceramics, metallic ingots and blanks, and finished objects. Data from qualitative and quantitative analyses, microscopic investigation, and elemental maps informed on the various metalworking steps during the formative period of the Scandinavian Viking Age. Our results shed light into the technological choices of several craftspeople involved in the production of crucibles and moulds, the acquisition and sourcing of ingots, scrap metal, and blanks as raw materials, as well as in matching alloy types with artefacts' intended use.

Polymetallic, non-ferrous metalworking was an integral aspect of the urban community at Ribe, rooted in the working of brass, lead, silver, and scrap bronze, with evidence for a more prolific and standardised production from the late 8th and into the 9th century CE. Brass, together with tin and lead as alloying components to copper, and silver are present early on from the 8th century. However, a wider range of alloys in the early period along with preference for high-zinc brass in the later period point to greater standardisation of alloy types from 790 CE. Specific alloy choices for specific artefact types, namely, leaded bronze for keys and (tin) brass for brooches, attest further to standardisation of techniques. As the non-ferrous production of the Ribe workshop(s) continued for several generations from 700 to 850 CE, we follow the adoption of several new technological choices, such as in clay sourcing for crucibles and alloy type use, which may reflect either learning from centres elsewhere or the arrival of new craftspeople, both consistent with Ribe's role as an emporium, while the integrated observations of local craftsmen could have also contributed towards higher efficiency in the 9th century CE.

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Author contribution VO prepared the original draft, the data visualisation, and presentation, formulated the analytical methodology, and processed the results. All authors contributed to the draft thereafter. VO, TB,

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Declarations

Conflict of interest The authors declare no competing interests.

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