Carolingian and Ottonian Brass Production in Westphalia Evidence from the Crucibles and Slag of Dortmund and Soest

Stephen Merkel

Keywords
Archaeometallurgy, Bar Ingots, Calamine, Lead Isotope Analysis, Smithsonite, Viking Age Trade

Abstract

The abundant new crucible and slag finds from the Thier-Brauerei excavation in the center of medieval Dortmund have provided a stimulus to revive the discussion of Westphalian brass cementation technology in the Carolingian and Ottonian periods and to explore unanswered questions concerning the process and its potential outcome. A total of sixteen crucibles and slag samples from stratified deposits in the Dortmund-Thier-Brauerei and Soest-Plettenberg excavations were prepared for optical and scanning electron microscopy to analyze metallic inclusions, slag phases and crucible ceramic. The copper and brass inclusions within the crucibles and their adhering slag from Dortmund show a relationship between lead and zinc contents and indicate that lead-bearing calamine ore was heated with charcoal and copper metal to produce leaded brass. Ternary Cu-Zn-Pb alloys are common for contemporary bar-shaped ingots, which supplied casting industries in early medieval Northern European towns like Hedeby and Kaupang. Concerning the zinc-rich black slag lining the interior of some crucible fragments, they regularly showed increases in lime and iron oxides in relation to the crucible ceramic and thus reflect impurities coming from the zinc ore. The lead-silicate slags often found in association with crucible finds in Dortmund have yet to have a clear interpretation; although the lead isotope analysis of crucibles and lead-silicate slag shows they may have the same source of lead, the production of the lead-silicate slag is definitely unrelated to the metallurgical process occurring inside the cementation crucibles themselves.

Introduction

Pre-modern brass making was a process performed in crucibles. Brass, an alloy of copper and zinc, is known since the Bronze Age (Thornton, 2007), but metallic zinc was first widely available in the post-medieval era. Prior to the invention of zinc distilling technologies, brass was most commonly made through the so-called cementation process, the process where zinc ore such as calamine was heated between 800 and 1100°C in a crucible with copper and charcoal. In this process zinc vapor is absorbed by the copper making an alloy that has an increased volume and mass in addition to an altered color, melting point and technical character. Before zinc metal was known, the process of brass making was the art of making copper yellow or golden, as this is the property regularly mentioned in historical texts, such as from Albertus Magnus of the 13th century (Wyckoff, 1967, pp.224-225), Biringuccio (Smith and Gnudi, 1966, pp.70-72) and Lazarus Ercker in the 16th century (Beierlein, 1960, pp.230) and is optimized in the Latin name for the alloy used by Pliny and Theophilus the Presbyter, *aurichalcum*, which literally means golden copper (Rehren and Martinón-Torres, 2008, pp.169).

There seems to be a gap between the collapse of the Roman brass industry and the beginning of production in the medieval period. Little is known about brass of the Migration and Merovingian periods; however, a well formed brass industry in Christian Continental Europe is clearly attested in the 9th century in the Carolingian Empire during the reign of Charles the Bald. This evidence does not arise from the analysis of copper-alloy objects themselves, which has yet to be carried out in any systematic way, but from the elemental analysis of debased Carolingian silver coinage. Guillaume Sarah (2010, pp.233-236) shows, as others have earlier touched upon (Metcalf and Northover, 1989, p.115), that fresh brass was distributed to mints throughout the Carolingian Empire to be alloyed with silver. The political and economic implications of the brass industry during the reign of Charles the Bald have hardly begun to be investigated; however, the abrupt appearance of brass on such

Figure 1. Examples of three leaded brass ingot fragments found at Hedeby analyzed by ICP-MS (results will be presented in a forthcoming publication). Scale 5 cm. Photo V. Hilberg / S. Merkel.

a colossal scale for the Carolingian coinage points to two conclusions: in the mid-9th century the mining of copper and calamine was actively pursued, and the development and expansion of the brass industry may have been influenced or encouraged by the Carolingian state.

The Vikings had a special preference for brass and ternary Cu-Pb-Zn alloys as attested by the analyses performed on copper-alloy jewelry objects (Eremin, Graham-Campbell and Wilthew, 2002) and bar ingots found in Scandinavia (Drescher, 1983, p.175; Eiwanger, 1996, pp.219-220; Oldeberg, 1942, pp.42-45; Pedersen, 2010, pp.254-255; Sindbæk, 2001) (Figure 1). It is thought that fresh brass was also distributed to the mints of Anglo-Saxon England for use in the silver coinage in the 9th and 10th centuries (Gilmore and Metcalf, 1980; Metcalf and Northover, 1985, pp.161-162), and the apparent dominance of tin bronze and heavily mixed quaternary alloys in Anglo-Saxon brooches and other everyday objects (Eremin, Graham-Campbell and Wilthew, 2002; Mortimer, 1988) suggests that the use and distribution of brass in England may have been controlled or otherwise restricted for certain functions. The importance of brass for the economy of Europe only grew over the course of the medieval period and is now the most widely used copper alloy of the post medieval and modern ages.

Due to the lack of historical records on brass production and trade from the Carolingian and Ottonian periods, it is only possible to explore these issues through what remains in the archaeological record. Finding the production centers for the brass of this period proves to be challenging. Early medieval mining traces of calamine zinc ore are difficult to find with archaeological methods and, due to the massive demand of zinc ore in the later medieval and post medieval periods, most superficial evidence of earlier mining are likely to be destroyed. Ingot moulds may be an indicator of primary brass production; however, the search for ingot moulds is problematic because as Theophilus the Presbyter explains the bars were simply cast into grooves scratched into the earth (Hawthorne and Smith, 1979, p.144) and, therefore, ephemeral. Being able to link the shape of the bar ingot to the form of ingot moulds is highly improbable. The archaeometric analysis of brass objects such as ingots, though particularly important to the discussion of trade, cannot identify the production center alone. Even if we can narrow down the potential sources of calamine to a handful of economically significant deposits accessible to the medieval miner, overlap in the lead isotope ratios of lead-zinc ore over large expanses of the Rhenish Massif geologic formation and elsewhere in Europe complicates the task of distinguishing individual deposits.

Evidence for brass production may be found by the presence of crucibles, as the brass cementation process is thought to have always been performed in crucibles. The crucibles were used as reaction chambers where the process could be closely monitored and controlled. Although it was not known that an alloy was being produced in these crucibles, Biringuccio (Smith and Gnudi, 1966, p.75) mentions that the increase in weight and volume of the copper makes the process economical, covering for the expenses of production. The cementation process for making brass was labor intensive: the 12th century treatise of Theophilus the Presbyter (Hawthorne and Smith, 1979, pp.140-145) describes a process requiring multiple steps and several charges of the crucibles, which could be removed and returned to a furnace during heat treatment. The time consuming nature of brass making may be reflected in the organization of workshops at central locations. Hundreds of medieval crucible fragments have been uncovered in excavations in Westphalia around the cities of Dortmund and Soest and at the site of Kückshausen near Schwerte. In all of these contexts, there are a disproportional numbers of crucibles compared to casting moulds. At Kückshausen a sand-filled box was found with pieces of charcoal and copper-alloy droplets pointing towards sandcasting (Capelle, 1974, pp.298-299), and it has been proposed for Dortmund-Thier-Brauerei site that production may have been centered on the sandcasting of ingots for export (Sicherl, 2011, pp.209-210).

The key metallurgical evidence for the manufacture of brass is likely to be found in the crucibles themselves. The medieval crucibles from Westphalia have aroused attention over the last quarter century, and a number of small-scale archaeometallurgical studies were carried out to confirm that brass was actually produced and to explore steps in the production technology (Krabath, et al., 1999; Rehren, et al., 1993; Zientek and Rehren, 2009). The new finds from Thier-Brauerei excavation indicate that Dortmund may have also been a center for Carolingian / Ottonian brass production (Sicherl, 2011), and, hence, an investigation of the crucibles and metallurgical waste material from Dortmund is essential to substantiate this hypothesis, to clarify the production process and to characterize the metal being produced. If Westphalia was an exporter of brass in the Carolingian and Ottonian periods, the analyses of the crucible material might provide the evidence needed to link the brass produced in centers like Soest and Dortmund to the ingots found abroad, at settlements like Hedeby.

The Crucibles

The early medieval crucibles from Soest and Kückshausen are dated by the ceramic assemblage, i.e. Badorf and Pingsdorf pottery, from the second half of the 9th century to the middle of the 10th century (Capelle, 1974; Lammers, 2009). The crucibles from Dortmund-Adlerturm most likely date to the 11th century based on the ceramic assemblage, and the ceramics as well as radiocarbon dates[1] from Dortmund-Thier-Brauerei point to production beginning in the 9th-10th century (Sicherl, 2011, pp.205-206; Sicherl and Brink-Kloke, 2012, p.10). The crucibles found at these sites show different levels of standardization. At Soest-Plettenberg there are at least two distinct crucibles sizes, a smaller type which could contain approximately 60-95 cm^3 of metal and a larger type which is closer to 500 cm^3 (Lammers, 2009, pp.26-28). The crucibles from Kückshausen are described as more standardized with volumes around 150 cm^3 (Lammers, 2009, p.54). The sites of Dortmund-Adlerturm, and Dortmund-Thier-Brauerei have comparable crucible forms with diameters 6-8 cm and heights 6-11 cm. The volumes range from about 75 cm^3 to around 300 cm^3, and are therefore smaller than the group of large crucibles from Soest. It is difficult to distinguish if there is a chronologically correlated increase in the crucible size with the larger crucibles dating later. At least some fragments of the larger type from Soest could date from the 10th century, some of which being found in contexts in conjunction with Pingsdorf ceramics (Lammers, 2009, p.158).

Macroscopically, the crucibles from Soest-Plettenberg and the Thier-Brauerei, like those from Adlerturm and Kückshausen, are made from a dense ceramic that is gray to buff in color. The sherds are often glazed on the exterior surface with colors ranging from clear to cuprite red, green and dark brown. Some sherds from the Thier-Brauerei have a clay coating on the exterior that was applied by brush as a slip: this slip was applied as an intermediary measure probably to extend the life of the crucible because it coats glazed areas of the crucible and the coating itself shows signs of high temperature sintering. The interiors are typically free from slag, but discoloration in various colors ranging from black to reddish brown is common. When a slag layer adheres to the interior of the crucibles it is always black or dark brown in color (Figure 2). Occasionally, copper corrosion products can be seen on or in the crucible ceramic as well as grains of charcoal and sand.

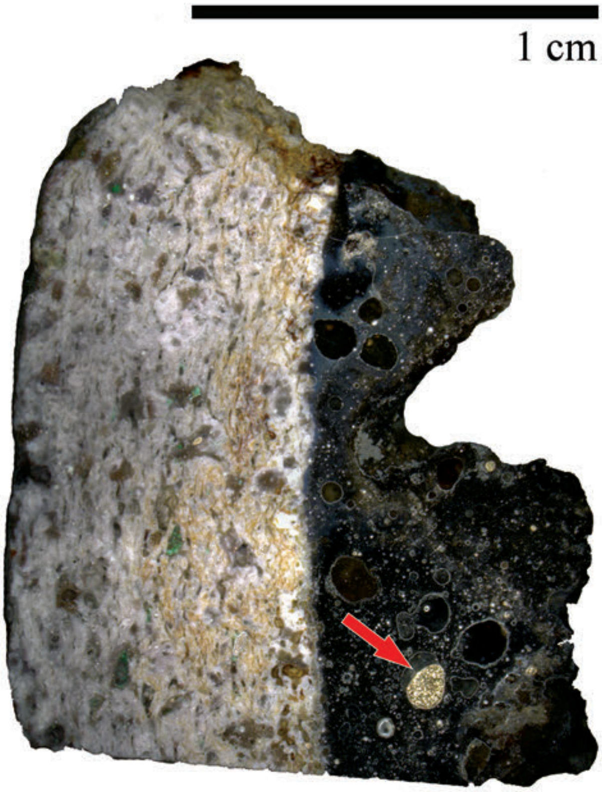


Figure 2. Polished section of crucible with crucible slag (4781-14). There is a sharp boundary between the black zinc-iron-calcium-silicate slag and the crucible ceramic. Marked is a 1 mm sized leaded brass prill trapped in the slag matrix.

The Evidence for Brass Making

One of the difficult tasks is to prove whether brass was being produced from its raw ingredients or if brass was simply remelted for casting. To answer this question we must turn to experimental archaeology and archaeometry. Three characteristics that have been identified in crucibles that point to brass making. A high concentration of zinc oxide in the technical ceramic is the first indication. According to the experimental work of David Bougarit and Nicolas Thomas (2015), the cementation process leaves certain traces in the crucible fabric. Whereas remelting brass leaves superficial traces of zinc that do not penetrate below the surface of the ceramic fabric, the crucible ceramic used for cementation were impregnated with zinc oxide to depths of several millimeters and sometimes through the entire wall thickness. The amount of zinc left within the crucible ceramic is influenced by the temperature and by the number of cementation repetitions.

The composition of metallic prills in the crucibles is the second line of evidence. If brass was produced in the crucible then it only follows that the metal droplets and prills in the crucibles would have concentrations of zinc. The metallic prill compositions confirm if brass is present in the crucible and what kinds of raw materials may have gone into the brass-making process. If prills are consistently tin-free then it may mean that fresh copper was used rather than the haphazard use of scrap metal, and the lead content of the prills helps to show if high quality ingredients were used or for example if lead-bearing 'coarse' brass was produced (see Hawthorne and Smith, 1979, pp.143-145). The crucibles from Dortmund-Adlerturm are clearly connected to brass metallurgy with prill compositions ranging from copper to brass with above 20 percent zinc (Rehren, et al., 1993, pp.309-310).

The third piece of evidence for brass making is the presence of a zinc-rich slag on the interior of the crucible. This must not be present as the experiments of Bouragit and Thomas (2015) have shown, but the formation

Table 1. List of crucibles, crucible slag and lead-silicate slag samples from Soest Plettenberg and Dortmund-Thier-Brauerei. The types of analysis include polarized light microscopy (PLM), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), inductively-coupled-plasma mass spectrometry (ICP-MS) and lead isotope analysis (LIA).

Lab. Nr.	Site	Type	Context	Dating	Analysis
4490-12	Soest	Crucible	F 529, Sch. VIII, P.2	9th C.	PLM/SEM-EDS
4491-12	Soest	Crucible	F 556, Sch. VII-B/IX	c. 900-950 AD	PLM/SEM-EDS
4492-12	Soest	Crucible	F 105	c. 900-950 AD	PLM/SEM-EDS
4493-12	Soest	Crucible	F 139, Sch. III	c. 950-1000 AD	PLM/SEM-EDS
4494-12	Soest	Crucible	F 105j, 9.F.	c. 900-950 AD	PLM/SEM-EDS
4784-14	Dortmund	Crucible	120/594-133	c. 966-1050 AD	PLM/SEM-EDS
4785-14	Dortmund	Crucible	120/594-6	c. 966-1050 AD	PLM/SEM-EDS
4786-14	Dortmund	Crucible	120/595-16	c. 866-933 AD	PLM/SEM-EDS
4787-14	Dortmund	Crucible	120/594-93	c. 966-1050 AD	PLM/SEM-EDS
4788-14	Dortmund	Crucible	120/594-6	c. 966-1050 AD	PLM/SEM-EDS
4789-14	Dortmund	Crucible	120/595-16	c. 866-933 AD	PLM/SEM-EDS
4790-14	Dortmund	Crucible	120/594-133	c. 966-1050 AD	PLM/SEM-EDS
4429-13	Dortmund	Slag	120/594-133	c. 966-1050 AD	LIA
4431-13	Dortmund	Slag	120/594-93	c. 966-1050 AD	LIA
4433-13	Dortmund	Slag	120/594-6	c. 966-1050 AD	LIA
4780-14	Dortmund	Slag	120/594-83	c. 966-1050 AD	PLM/SEM-EDS/LIA/ICP-MS
4781-14	Dortmund	Slag	120/594-6	c. 966-1050 AD	PLM/SEM-EDS/ICP-MS
4782-14	Dortmund,	Slag	120/594-6	c. 966-1050 AD	PLM/SEM-EDS/LIA/ICP-MS
4783-14	Dortmund	Slag	120/594-93	c. 966-1050 AD	PLM/SEM-EDS/LIA/ICP-MS
4380-11	Dortmund	Crucible	120/594-6	c. 966-1050 AD	ICP-MS/LIA
4381a-11	Dortmund,	Crucible	120/595-16	c. 866-933 AD	ICP-MS/LIA
4381b-11	Dortmund	Cr. Slag	120/595-16	c. 866-933 AD	ICP-MS/LIA
4382-11	Dortmund	Crucible	120/830-11/1351	c. 1200 AD	ICP-MS/LIA

of a crucible slag may give an indication of the duration of melting and the types of materials involved. At Dortmund-Adlerturm some crucibles have a zinc-rich slag containing high temperature phases like the zinc-bearing silicate willemite (Zn_2SiO_4), spinells ($ZnAl_2O_4$) and iron oxides similar to wüstite (FeO) (Rehren, et al., 1993, pp.308-309). The slag points to heavily reducing conditions within the crucible, and the slag formation attests to significant amounts of zinc oxides and other impurities that may be associated with the calamine ore. Together, these three lines of evidence support the argument for brass making.

Little analytical work has been performed on the crucibles from Soest-Plettenberg (Zientek and Rehren, 2009) and crucibles and slag from Dortmund-Thier-Brauerei have not previously been studied. These crucibles seem to be slightly older than the crucibles from Dortmund-Adlerturm, and it has yet to be conclusively shown that brass was produced in these crucibles. The elemental compositions of the brass produced are still unclear and its lead isotope signature has yet to be quantified. A question that requires further thought is the role of the lead-silicate slag, which is often associated with crucibles in Dortmund, but also it can be found at Soest-Plettenberg. The explanation proposed by Rehren, et al. (1993, p.313) that the slag is from a purification process to remove lead from copper is not entirely satisfactory: if high-quality lead-free brass was the goal of the process then why are the large prills found in the crucibles from Adlerturm often ternary lead-zinc-copper alloys (see Rehren, et al., 1993, pp.309-310)? To investigate these questions sixteen samples of crucibles from the excavations of Soest-Plettenberg and the Thier-Brauerei were sectioned for microscopy and samples lead-silicate slags and crucibles from the Thier-Brauerei were taken for elemental and lead isotope analysis (Table 1).

Methodology

Three techniques were used to analyze the crucibles and slag samples: optical microscopy, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and mass spectrometry. The samples for microscopy were prepared by sectioning and mounting as either polished thin-sections or as polished samples embedded in epoxy resin at the Deutsches Bergbau-Museum Bochum. Reflected and transmitted light microscopy was performed on a Zeiss Galaxy Axiophot microscope with the capability for 2.5 to 40 times magnification. A Zeiss Gemini SEM with a Thermo UltraDry Silicon Drift X-ray Detector was used for SEM-EDS analysis. Samples were analyzed at a working distance of 10 mm at 20 kV under low vacuum (50 Pascal). The quantification of the elemental spectra was performed using the Nora System Seven software fitted standard calibration and values obtained should be viewed as semi-quantitative.

Quantitative analysis was performed by mass spectrometry. Crucible and slag samples were crushed and milled to powder and dissolved in a solution of hydrofluoric and nitric acids. Elemental analysis was performed by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) with a Thermo Scientific ELEMENT XR ICP-MS at the Deutsches Bergbau-Museum Bochum. The calibration for silica-rich materials was performed using the Brammer standard GBW 07107. A Thermo Scientific Neptune multicollector ICP-MS was used for lead isotope analysis at the Goethe-Universität Frankfurt / Main (see Klein, et al., 2009 for instrumental procedure). The samples were prepared as liquid solutions and were run together with a thallium isotope standard (SRM 997 Tl) to correct for mass bias. To check for mercury contamination ^{202}Hg was measured and interference with ^{204}Pb was corrected. Instrumental drift was corrected using the SRM 981 Pb isotope standard, which was run every 6-14 runs. Using the SRM 981 Pb measurements, lead isotope values were normalized to the values obtained by Todt, et al. (1996).

Results: Microscopy of the Crucibles and Slag

This study relied on the scanning electron microscope for imaging and for semi-quantitative elemental analysis, and four sets of compositions were obtained: the ceramic, crucible slag, metal prill and lead-silicate slag compositions. First the ceramic fabric was characterized morphologically and elementally. The crucibles from both sites contain quartz inclusions typically ranging from 20 to 200 µm and grog made from crushed ceramic. The grog is often between 100 µm and 1 mm in size and contains smaller quartz inclusions. The grog can be distinguished from the crucible ceramic due to thin cracks demarcating the individual grog grains, different orientation of the porosity and a difference in density can usually be seen in the SEM-backscatter imaging that seems to be related to the zinc oxide content, which points to the use of old crucibles for the grog (see Figure 3a).

The analyses presented in Table 2 are bulk analyses of the crucible ceramic. Three or more areas of 1-2 mm in size were averaged together, and metallic inclusions were avoided. For comparison one crucible from Hedeby was also analyzed. This crucible from Hedeby contained the

Table 2. Semi-quantitative analyses of crucible ceramic from Dortmund-Thier-Brauerei, Soest-Plettenberg, and one crucible from Hedeby used to melt leaded brass. Sizable amounts of zinc oxide can be found in the crucible ceramic from Dortmund and Soest, which supports the notion that these crucibles were used in brass production rather than brass casting. Values are in weight percent, normalized to 100 %. Carbon was ignored and oxygen was calculated stoichiometrically. The '<LOD' means under the detection limit, below 0.5 %, and 'n.m.' means not measured.

		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	Cu_2O	ZnO	PbO
4784-14	Dortmund	n.m.	<LOD	28.5	55.8	2.4	2.5	0.9	1.5	<LOD	5.8	<LOD
4785-14	Dortmund	n.m.	<LOD	25.9	52.5	2.0	3.6	0.8	2.9	<LOD	10.2	<LOD
4786-14	Dortmund	n.m.	<LOD	26.7	55.4	1.9	2.4	0.8	1.6	<LOD	8.4	0.6
4787-14	Dortmund	n.m.	<LOD	26.3	55.4	1.9	2.6	0.9	2.2	0.5	7.9	<LOD
4788-14	Dortmund	n.m.	<LOD	26.4	55.1	2.6	3.0	0.9	2.0	<LOD	7.0	0.6
4789-14	Dortmund	n.m.	<LOD	27.6	55.7	2.3	3.2	1.0	2.3	<LOD	5.1	<LOD
4790-14	Dortmund	n.m.	<LOD	27.0	56.1	1.7	2.0	0.9	1.7	<LOD	7.9	<LOD
4490-12	Soest	1.3	<LOD	20.6	63.0	0.8	0.9	0.8	1.4	<LOD	10.7	<LOD
4491-12	Soest	1.2	<LOD	24.9	53.9	1.5	1.7	0.9	3.1	1.5	11.2	<LOD
4492-12	Soest	2.9	0.7	27.0	58.3	1.8	1.4	1.0	2.7	<LOD	4.0	<LOD
4493-12	Soest	0.9	<LOD	25.2	50.9	1.1	1.4	0.7	5.6	2.1	10.2	1.6
4494-12	Soest	1.0	<LOD	22.3	62.3	0.8	0.9	0.9	1.5	<LOD	9.4	<LOD
4577-11	Hedeby	1.4	0.7	19.5	73.0	2.7	<LOD	1.1	2.5	<LOD	<LOD	<LOD

remnants of the crucible charge, and upon sectioning, the 1.5 x 1 x 0.4 cm globule of metal proved to be leaded brass (80 wt. % Cu, 11 wt. % Zn, 9 wt. % Pb). From the analyses of the crucible ceramic, all of the crucibles from the Thier-Brauerei and Soest contained elevated levels of zinc oxide, and the crucible from Hedeby, which was unmistakably used for melting leaded brass, had no detectable amounts of zinc in the crucible ceramic in depths greater than 1 mm from the interior surface.

One of the most informative facets of the analysis is the prill compositions. Rehren, et al. (1993, pp.309-312) report finding a range of compositions from copper to brass, but lead was also found in various amounts. The metallic inclusions from the Thier-Brauerei and Soest-Plettenberg provide a slightly more nuanced picture. Metallic prills ranging from 20 µm to several millimeters were analyzed by SEM-EDS. Like at Adlerturm, the 44 prills from the crucibles and crucible slag vary from nearly pure copper to brass with more than 18 percent zinc. Lead was usually found in the percentage range, and for the prills from the Thier-Brauerei there is a statistically discernible relationship between the zinc and lead contents. Despite the broadly positive trend, there is substantial heterogeneity in the lead and zinc contents (Figure 4). Most of the larger prills are leaded brasses as seen in Figure 3b-c, and the lead content visible is due to its immiscibility in copper alloys. Upon close examination zinc sulfides were found in the leaded brass prills (Figure 3c). Nearly all of the prills are free of tin. In one crucible from the Thier-Brauerei (4490-14) a large prill of high-tin (bell) bronze was found (16 wt. % Sn) together with prills of a range of intermediate quaternary compositions between bronze and leaded brass and possibly indicates contamination from a piece of scrap metal.

A number of the crucibles contained black slag lining the interior. Multiple millimeter-sized areas of the slag were analyzed by SEM-EDS, and the average compositions are presented in Table 3. Again large metallic prills and heterogeneities were avoided. The alumina to silica ratios are slightly less in the crucible slag compared to the ceramic. Besides the increase in silica in relation to the ceramic, there are notable increases in calcium oxide, iron oxide and zinc oxide. Microscopy revealed that there is a range of textures from vitreous to coarse and crystalline. In some examples the slag is poorly melted and highly porous with grains of quartz held together

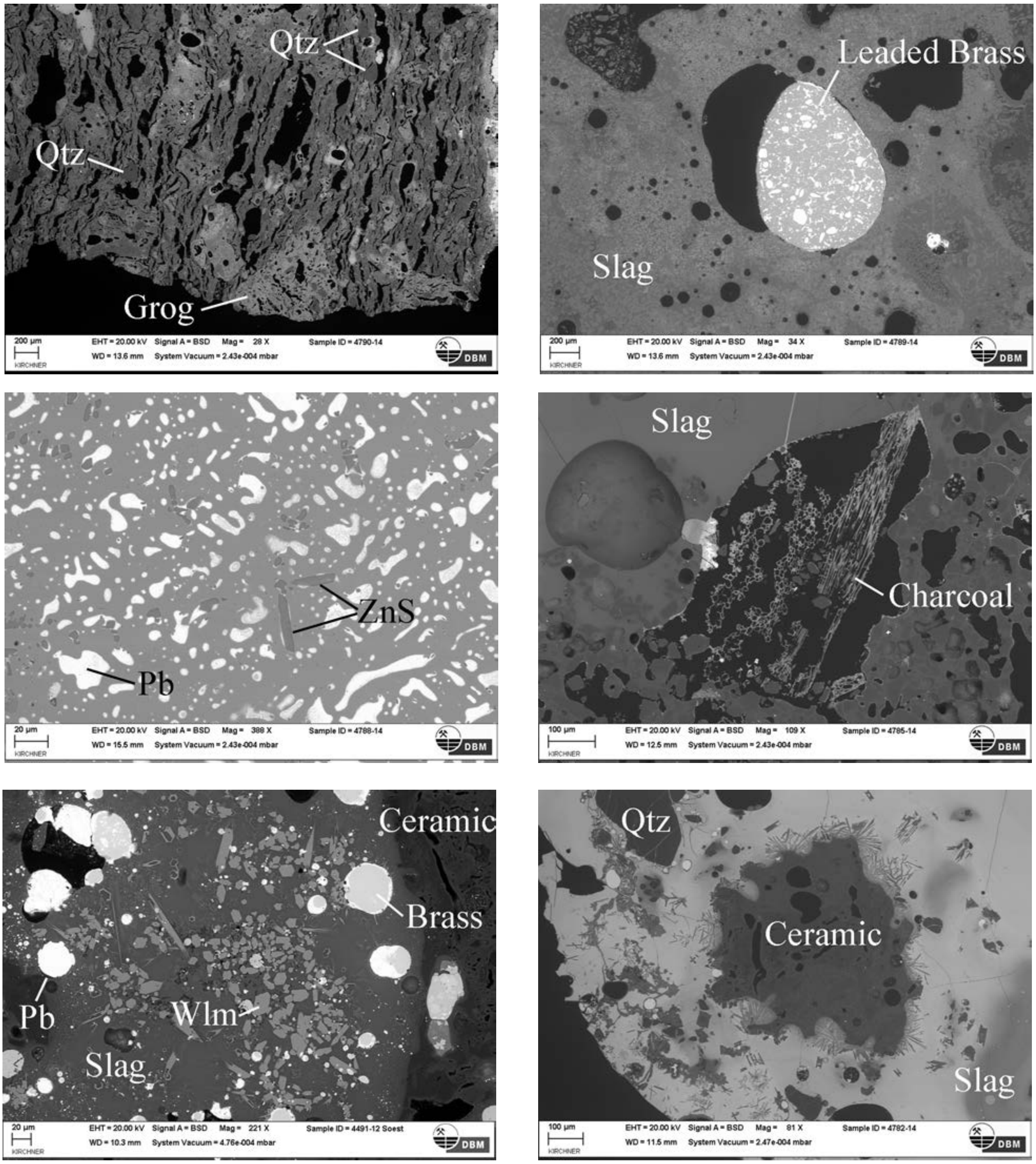
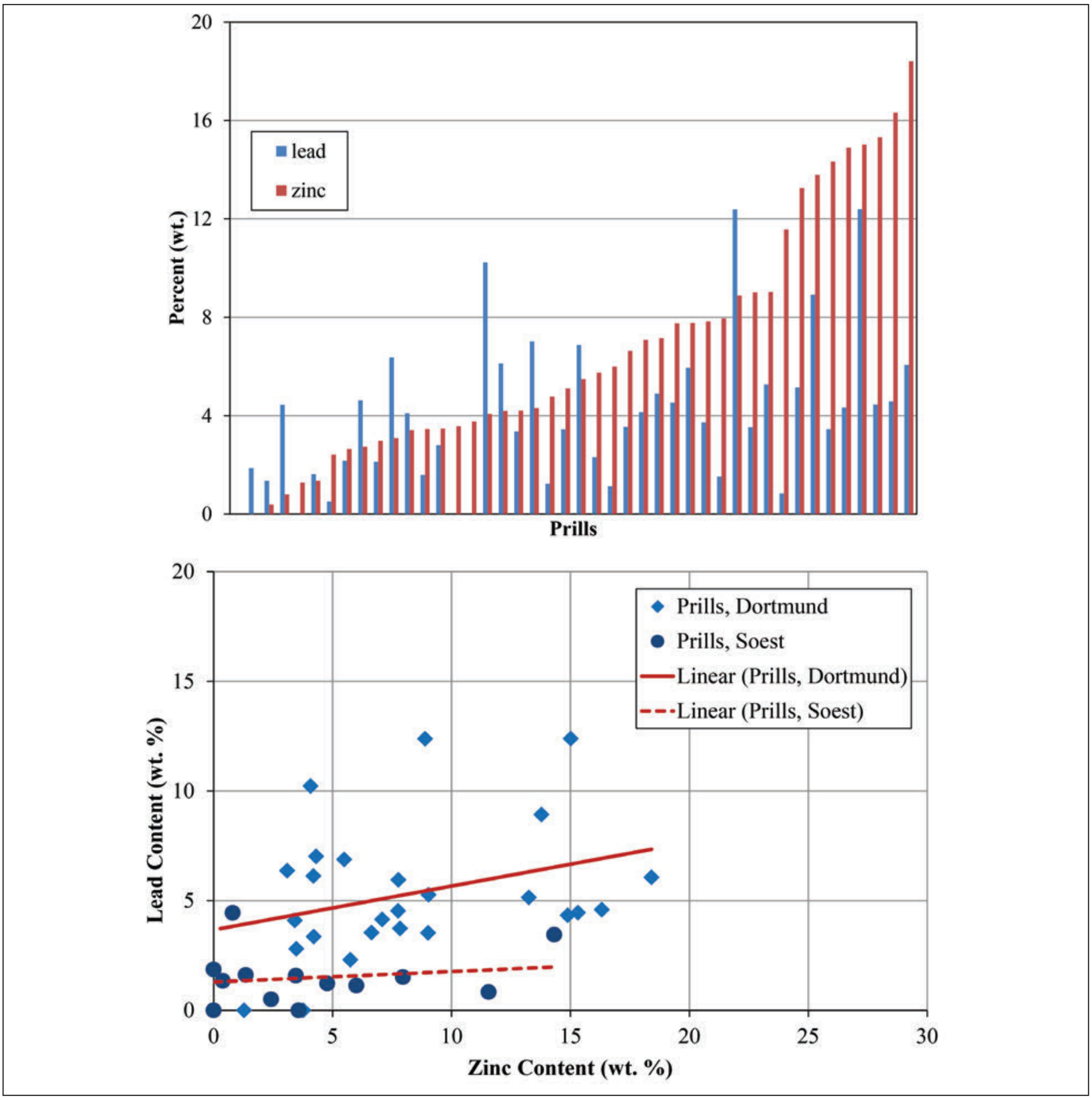


Figure 3. (a) Example of crucible ceramic from Dortmund-Thier-Brauerei showing tempering with both quartz (Qtz) and crushed ceramic (Grog) (SEM-BSE). (b) Prill of leaded brass trapped in crucible slag (SEM-BSE). (c) Detail of leaded brass from crucible from Dortmund-Thier-Brauerei. Lead (Pb) forms a separate phase from the brass, but there are also zinc sulfide phases (ZnS) (SEM-BSE). (d) Charcoal fragment in slag on the interior of crucible from Dortmund (SEM-BSE). (e) Slagged area of crucible from Soest-Plettenberg with zinc-bearing olivines (Wlm) and brass, leaded brass, and lead prills (Pb) (SEM-BSE). (f) Fragment of crucible ceramic and quartz grains (Qtz) inside lead-silicate slag from Dortmund-Thier-Brauerei (4782-14, SEM-BSE).

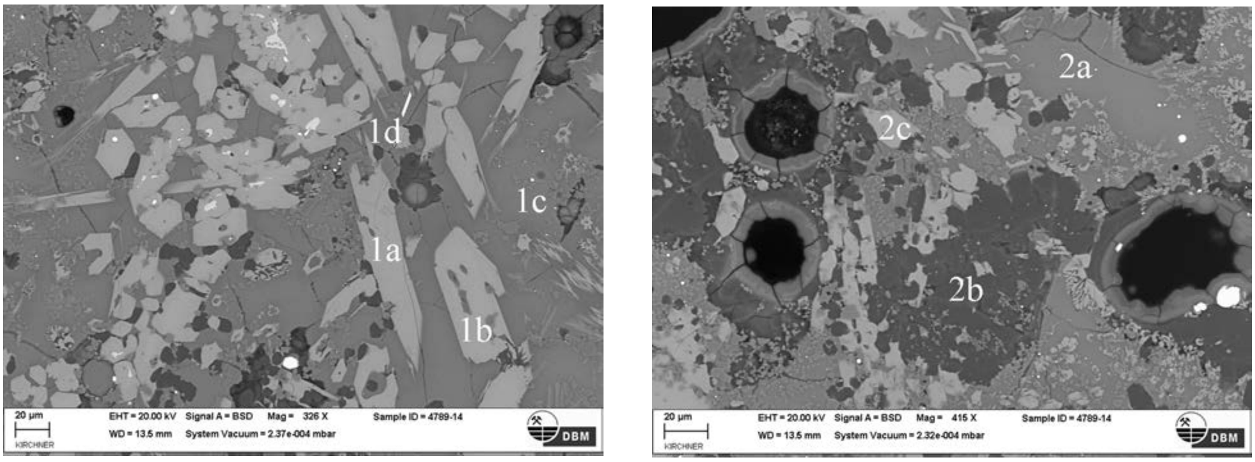
with glass. Sometimes small charcoal fragments up to 1 mm were found in the crucible slag (Figure 3d). These charcoal fragments, though small and difficult to identify specifically, seem to all stem from hardwoods. Some fragments could be identified as oak and common beech (Dr. Nicole Boenke pers. comm. 10.11.14). The slag with high temperature phases are similar to those described by Rehren, et al. (1993). Phases like zinc-bearing olivines and spinels similar to willemite and gahnite were found in abundance (Figures 5a-b, Table 4 and Figure 3e). In addition to prills of copper and brass, localized concentrations of wüstite together with minor amounts of magnetite were found in one of the crucible slags, and metallic iron prills were found in another.

Table 3. Semi-quantitative SEM-EDS analyses of slag adhering to the interior of crucible fragments. Values are in weight percent, normalized to 100 %. Carbon was ignored and oxygen was calculated stoichiometrically. The '<LOD' means under the detection limit, below 0.5 %, and 'n.m.' means not measured.

		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Cu_2O	ZnO	PbO
4789-14	Dortund	n.m.	1.1	11.0	37.1	0.8	2.4	7.1	0.5	1.9	15.5	<LOD	21.9	<LOD
4788-14	Dortund	n.m.	0.9	11.2	41.1	0.8	2.7	7.0	0.5	1.8	18.6	<LOD	14.2	0.8
4787-14	Dortund	n.m.	1.2	15.5	51.6	<LOD	2.6	5.4	0.9	1.4	11.6	<LOD	9.0	<LOD
4786-14	Dortund	n.m.	0.5	13.8	48.8	0.6	1.3	3.3	0.7	0.8	11.4	0.5	16.1	1.8
4785-14	Dortund	n.m.	2.2	13.8	42.1	2.1	4.9	17.8	0.7	1.6	9.4	<LOD	4.9	<LOD
4784-14	Dortund	n.m.	0.7	16.7	37.3	3.8	1.4	6.9	0.7	0.8	9.1	0.6	21.3	<LOD
4491-12	Soest	4.5	0.7	14.5	43.8	<LOD	1.6	5.0	0.6	0.9	15.4	2.7	10.2	<LOD
4490-12	Soest	3.4	4.9	15.5	53.1	<LOD	2.3	4.3	1.0	7.9	3.4	<LOD	3.1	<LOD



Figures 4a-b. The zinc and lead contents of metallic prills in crucibles from Dortmund-Thier-Brauerei and Soest-Plettenberg. Statistically there is a 1:5 relationship of lead to zinc in the Dortmund prills, but there is practically no relationship in the Soest prills. The lead content is heterogeneous and it is difficult to see a relationship with the zinc contents.



Figures 5a-b and Table 4 Semi-quantitative SEM-EDS analyses of phases and glass matrix in the slag from the interior of a crucible from Dortmund-Thier-Brauerei. The presence of zinc-rich phases is an indication that the crucible charge was zinc-bearing. Values are in weight percent, normalized to 100 %. Carbon was ignored and oxygen was calculated stoichiometrically. The '<LOD' means under the detection limit, below 0.5 %.

			MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Cu_2O	ZnO	SnO_2	PbO
4789-14	1a	Willemite	1.5	4.8	34.1	0.4	0.7	2.0	<LOD	1.4	10.6	<LOD	43.7	<LOD	<LOD
4789-14	1b	Willemite	1.3	4.8	34.3	<LOD	0.7	2.2	<LOD	1.6	9.2	<LOD	44.9	<LOD	<LOD
4789-14	1c	Glass	1.3	8.9	41.1	1.1	2.4	11.1	0.8	2.6	15.4	<LOD	15.0	<LOD	<LOD
4789-14	1d	Gahnite	0.5	40.6	15.5	0.4	0.7	2.8	1.1	1.0	8.7	<LOD	28.5	<LOD	<LOD
4789-14	2a	Glass	1.1	8.4	39.0	1.5	2.8	13.5	0.7	2.1	14.7	<LOD	15.7	0.4	<LOD
4789-14	2b	Leucite	0.3	20.0	48.7	<LOD	14.7	2.5	<LOD	0.6	4.4	<LOD	7.5	0.5	<LOD
4789-14	2c	Willemite	1.7	5.5	34.9	0.5	1.3	2.5	<LOD	2.1	11.8	<LOD	38.6	<LOD	0.4

Table 5. Semi-quantitative SEM-EDS analysis of an inclusion of ceramic in lead-silicate slag from Dortmund-Thier-Brauerei. The inclusion could be a fragment of a brass-making crucible, compare to Table 1. Values are in weight percent, normalized to 100 %. Carbon was ignored and oxygen was calculated stoichiometrically.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Cu_2O	ZnO	SnO_2	PbO
4782-14	3.6	0.3	27.6	55.4	0.3	2.2	1.5	0.8	0.1	1.3	0.2	4.0	0.2	2.4

Finally, four lead-silicate slag samples from Dortmund-Thier-Brauerei were analyzed by SEM-EDS. They are all vitreous and nearly free of silicate phases except for the occasional wollastonite crystal, heat-fractured grain of quartz or orthoclase. The glasses are not homogeneous; stripes / bands of denser glass with higher lead oxide contents can be seen. Prills of copper can be found throughout the glass and are usually smaller than 20 µm. The micron-size copper prills are euhedral crystals and could be described as colloidal due to their regular distribution and small size. Red cuprite dendrites were not identified. Colloidal copper may be responsible the bright red in color of two of the slags under cross-polarized light. Prills of metallic lead do rarely occur, and often in conjunction to metallic copper as reported by Rehren, et al. (1993, p.311). No metallic prills containing detectable amounts of zinc were found; however, one inclusion of a piece of ceramic was found enclosed in the slag, and the ceramic is identical morphologically and elementally to the brass-making crucible ceramic, including its elevated zinc content (Figure 3f and Table 5).

Results: Mass Spectrometry and Lead Isotope Analysis

The HR-ICP-MS elemental analysis of crucibles and slag samples from Dortmund-Thier-Brauerei confirms many of the findings from the SEM-EDS but provides a much better resolution for trace elements (Table 6). The

Table 6. Quantitative HR-ICP-MS analyses of crucible ceramic, crucible slag and lead-silicate slag (LSS). Elements Co, Ni, As, Se, Ag, Sn, Sb, Te and Bi are in ppm and the other elements / oxides are in weight percent.

		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	S	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Cu	ZnO
4380-11	Cr. Cer.	0.4	0.4	17.2	57.0	0.4	<0.06	2.1	2.2	1.0	0.2	1.7	0.2	9.4
4381a-11	Cr. Cer.	0.3	0.5	24.7	46.2	0.3	<0.06	2.1	2.9	0.7	0.3	3.8	0.7	8.8
4381b-11	Cr. Slag	0.2	0.7	7.4	21.9	0.5	<0.06	1.8	3.6	0.3	1.1	16.6	0.9	20.1
4382-11	Cr. Cer.	0.7	0.5	21.6	55.9	0.6	<0.06	2.4	1.7	0.9	0.1	2.3	0.8	8.6
4780-14	Red LSS	0.3	0.6	3.8	36.8	0.5	<0.06	1.6	2.4	0.3	0.1	2.4	1.8	0.1
4781-14	Red LSS	0.4	0.5	3.6	34.3	0.4	<0.06	1.7	2.4	0.3	0.1	2.2	2.2	1.0
4782-14	Black LSS	0.3	0.5	4.0	33.0	0.4	<0.06	1.8	2.3	0.3	0.1	3.6	2.2	4.7
4783-14	Black LSS	0.3	0.6	3.6	35.0	0.5	<0.06	1.8	2.6	0.3	0.1	3.5	1.8	2.1

		BaO	PbO	Co	Ni	As	Se	Ag	Sn	Sb	Te	Bi	Total
4380-11	Cr. Cer.	0.02	0.4	8	80	20	<5	20	4	7	0.2	0.2	92.6
4381a-11	Cr. Cer.	0.02	0.6	20	120	65	<5	15	45	10	0.1	0.3	91.8
4381b-11	Cr. Slag	0.1	2.1	95	420	270	<5	25	140	35	0.2	0.9	77.4
4382-11	Cr. Cer.	0.11	0.4	5	30	20	<5	4	200	45	<0.03	4	96.6
4780-14	Red LSS	0.04	51.6	6	10	160	10	2	110	300	2	4	102.4
4781-14	Red LSS	0.04	52.3	9	20	240	15	2	730	230	2	3	101.4
4782-14	Black LSS	0.03	45.6	10	50	100	15	4	1600	160	2	3	98.9
4783-14	Black LSS	0.28	48.9	15	25	310	10	2	30	570	3	4	101.4

Table 7. Results of lead isotope analysis of crucibles and slag samples from Dortmund Thier-Brauerei performed by multicollector ICP-MS at the Goethe-Universität Frankfurt / Main.

Lab. Nr.	Sample	Date	$^{206}Pb/^{204}Pb$	2σ	$^{207}Pb/^{204}Pb$	2σ	$^{208}Pb/^{204}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ	$^{208}Pb/^{206}Pb$	2σ
4380-11	Crucible	A	**18.366**	0.024	**15.622**	0.023	**38.333**	0.059	**0.8506**	0.0003	**2.0870**	0.0007
4381-11-A	Crucible	A	**18.366**	0.019	**15.626**	0.016	**38.339**	0.046	**0.8507**	0.0003	**2.0876**	0.0007
4381-11-B	Crucible Slag	A	**18.358**	0.017	**15.619**	0.014	**38.316**	0.034	**0.8507**	0.0003	**2.0872**	0.0007
4382-11	Crucible Slag	A	**18.286**	0.024	**15.616**	0.022	**38.231**	0.058	**0.8539**	0.0003	**2.0906**	0.0010
4429-13	Lead-Silicate Slag	B	**18.374**	0.018	**15.618**	0.016	**38.331**	0.041	**0.8500**	0.0002	**2.0861**	0.0007
4431-13	Lead-Silicate Slag	B	**18.363**	0.018	**15.619**	0.014	**38.319**	0.038	**0.8505**	0.0002	**2.0867**	0.0008
4433-13	Lead-Silicate Slag	B	**18.373**	0.018	**15.617**	0.016	**38.328**	0.043	**0.8500**	0.0002	**2.0860**	0.0008
4780-14	Lead-Silicate Slag	B	**18.364**	0.017	**15.618**	0.016	**38.317**	0.046	**0.8504**	0.0002	**2.0865**	0.0009
4782-14	Lead-Silicate Slag	B	**18.364**	0.017	**15.618**	0.014	**38.320**	0.039	**0.8504**	0.0002	**2.0866**	0.0008
4783-14	Lead-Silicate Slag	B	**18.365**	0.018	**15.618**	0.016	**38.320**	0.044	**0.8504**	0.0002	**2.0865**	0.0008
Standard	SRM 981 Pb	A	**16.936**	0.015	**15.493**	0.015	**36.702**	0.037	**0.9148**	0.0002	**2.1671**	0.0008
Standard	SRM 981 Pb	B	**16.933**	0.021	**15.487**	0.021	**36.686**	0.056	**0.9146**	0.0004	**2.1665**	0.0012

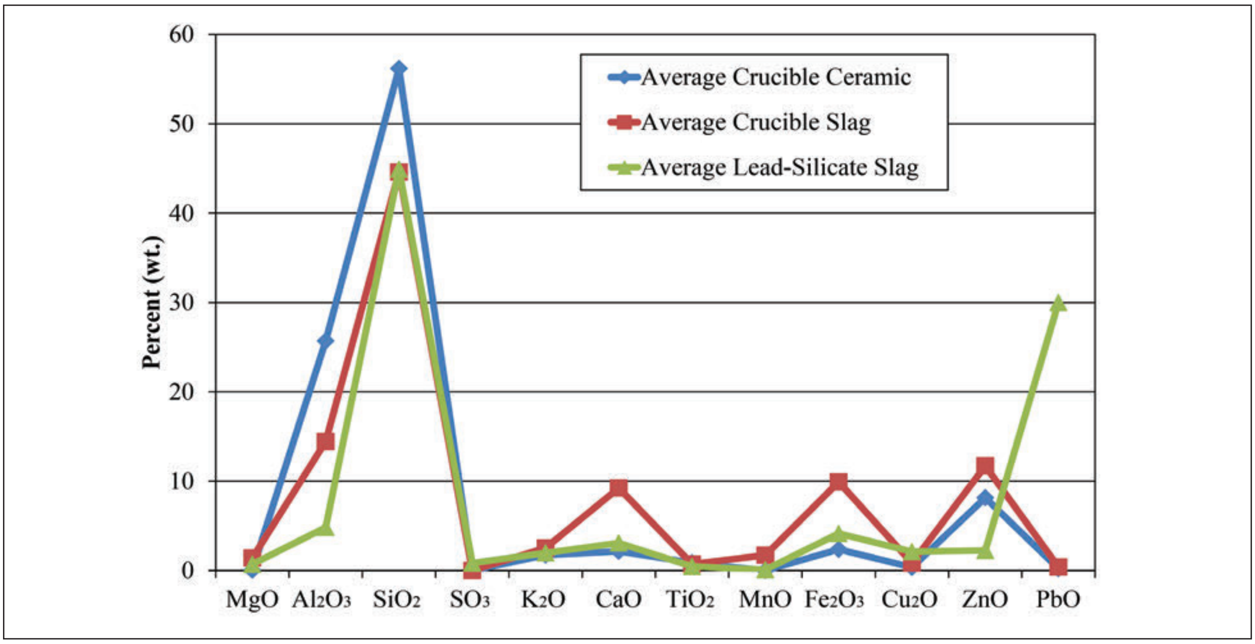


Figure 6. Comparison of average SEM-EDS bulk compositions of the crucible ceramic, crucible slag, and lead-silicate slag. This diagram shows that the crucible slag, due to its high alumina content, is possibly a mixture of melted ceramic fluxed by lime, iron oxide and zinc oxide. The lead-silicate slag, however, is alumina poor and is mostly silica fluxed by lead oxide.

major and minor elements in both data sets are generally compatible with similar alumina to silica ratios, iron oxide, lime and zinc contents in the ceramic. The zinc content by bulk elemental analysis for the three crucible ceramic fabrics was measured to be around 8 to 9 weight percent.

The HR-ICP-MS results of the Thier-Brauerei crucibles and slag closely parallel the analyses of the Dortmund-Adlerturm material (Rehren, et al., 1993). Four lead-silicate slag samples were analyzed, and were determined to be primarily a mixture of silica and lead oxide with minor amounts of alumina, lime, iron oxide, zinc oxide and copper. Sulfur was below the detection limit in all samples (< 0.06 wt. %). The silver content of the slags is measured to be less than 10 ppm and therefore excludes any possible connection to silver metallurgy. As reported by Rehren, et al. (1993), there is a correlation between the color of the lead-silicate slag and the elemental composition. Two black slags have higher zinc oxided contents (2.1 and 4.7 wt. % ZnO) and higher amounts of manganese and iron oxides. The lead-silicate slag with the highest zinc content also has an increased tin content (0.2 wt. %) possibly reflecting the incorporation of some metal scrap into the slag. No relationships among the antimony, arsenic, chromium, bismuth, nickel or cobalt could be determined.

The results of the lead isotope analysis of crucibles, crucible slag, lead-silicate slag and lead isotope standards are presented in Table 7. The lead isotope ratios from the material from Dortmund-Thier-Brauerei form a homogeneous cluster except for one outlier, but this outlier is from a crucible that was found in context that is younger than the other samples (Figure 7). Due to the context in which it was found, it is possible that this crucible could date to as late as the 12th or 13th century.

Discussion: Brass Making and Brass Types

Through the microscopy of the crucible fragments from Soest-Plettenberg and Dortmund-Thier-Brauerei several features have been identified that clearly point to brass making rather than brass working. The impregnation of zinc oxide, the zinc-rich slag and the prill compositions all support this conclusion. This permits the discussion to be taken a further step and to ask what were the characteristics of the brass produced? The brass prill compositions indicate that a brass free of lead was not the aim of production, but a coarse brass. This ties with the historical account of Theophilus the Presbyter, who defines two types of brass each with specialized functions. The coarse brass of Theophilus is a lead-bearing alloy used primarily for casting, whereas fine brass is lead-poor and can be hammered, cast and gilt (Hawthorne and Smith, 1979, pp.143-146).

Theophilus was obviously aware of the detrimental impact of lead on the ability to gild brass. To reduce the lead content of the final brass, first the copper could be

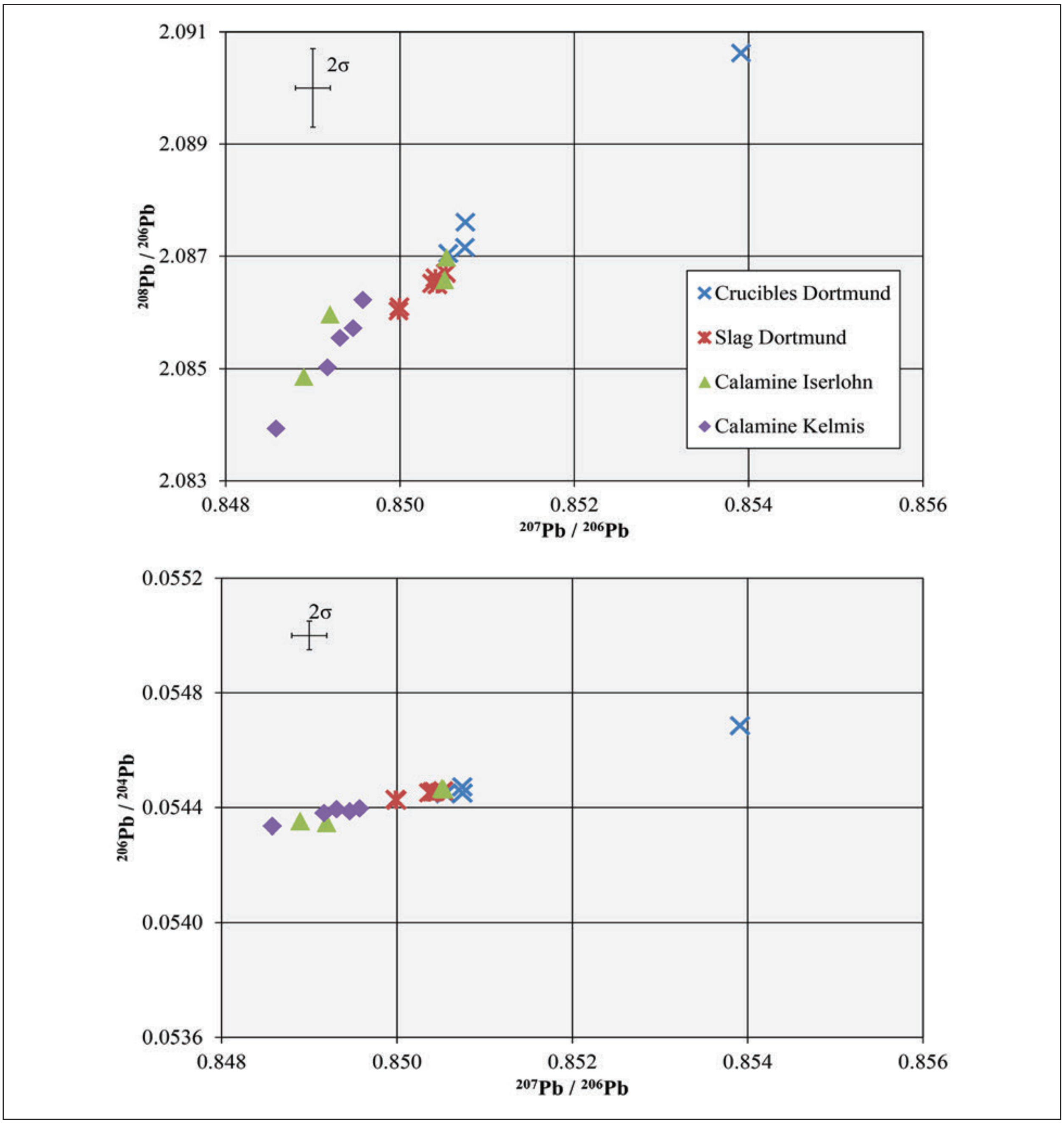


Figure 7. Lead isotope diagram comparing the analyzed crucibles, crucible slags, and lead-silicate slags from Dortmund-Thier-Brauerei and calamine samples from Iserlohn, in Sauerland, and Kelmis-Moresnet near Aachen.

purged from lead. The metallurgical process described by Theophilus would remove the lead from the copper, but there are no mentions of the quality of the calamine used and the lead associated with it. Certainly if lead is present in the calamine, it will be present in the brass. In their experimental work, Bougarit and Thomas (2015, p.58) have recognized that the lead from the ore is concentrated during the cementation process and that the lead to zinc ratio of the ore can be doubled in the brass produced. From the account of Theophilus it is unclear if he was aware of the possibility of lead contamination coming from the calamine, and there is no mention of calamine ore grades with differing lead contents, such as that hinted by Lazarus Ecker in the 16th century (see Beierlein, 1960, p.232).

The lead content of the brass could be controlled with the purity of the copper and calamine used. The prill compositions in the crucibles from Dortmund and Soest indicate that lead-bearing brass was produced. The zinc contents of the brass prills are higher on average than the lead contents, but lead contents between 3 and 10 percent are normal. The correlation in the zinc and lead contents from the prills from the Thier-Brauerei crucibles demonstrates that at least some of the lead came with the calamine zinc ore, but whether the copper was refined beforehand to remove excess lead cannot be determined at the moment. There is almost no correlation between the zinc and lead contents in the prills from the Soest crucibles, but this may be because of the smaller sample size. In both cases, it is possible that the origin of the lead stems from both the copper and the calamine, however, a stronger statistical basis would be helpful in exploring this question further.

Discussion: The Lead-Silicate Slag

The relationship of the lead-silicate slag to the brass-making process is poorly understood. Not only are shards of lead-silicate slag, along with sand and charcoal, found in the fill around the crucibles (Rehren, et al., 1993, p.310), but one slag piece from the Thier-Brauerei had a small fragment of a brass-making crucible inside it (Figure 3f). Although a spatial and chronological relationship exists, the elemental analysis of the slag from crucible fragments and the lead-silicate slag indicates that they undoubtedly belong to two different metallurgical processes. While the slag adhering to the crucibles is highly impure with amounts of alumina and calcium, iron and zinc oxides, the lead-silicate slag is much cleaner and seems to primarily be made from a reaction of common quartz-rich sand with lead oxide (Figure 6).

A solution is proposed by Rehren, et al. (1993, p.313) in that the lead-silicate slag was possibly for the refining of copper to remove lead. As explained, the compositions of the slag are similar to those of the Hobokener process, a process that has parallels to the process described by Theophilus Presbyter for the purification of copper in order to produce gilding-quality brass. However, the fact that there are usually significant amounts of lead associated with the copper and brass prills in the crucibles seems to contradict the interpretation that gilding-quality brass was produced.

Another possible interpretation worth consideration is that enamel for metalwork could have been produced; though this may seem rather impractical due to the amount of slag abandoned at the site. There are precedents where copper-bearing lead-silicate glasses and slags have been used to produce brightly-colored red enamels (Stapleton, Freestone and Bowman, 1999). Contemporary with the crucibles, late Carolingian and Ottonian brooches such as the enameled disk brooches with cruciform motifs (Kreuzemailfibeln) and saint motifs (Heiligenfibeln) relied heavily on the use of red enamel, and particularly the brooches with cruciform motif are highly concentrated in the Hellweg region of Westphalia (Haseloff, 1990, pp.91-107) and casting moulds for this type of enameled brooch were found in excavations at Dortmund (Sicherl and Brink-Kloke, 2012, p.11). The colloidal copper found in the lead-silicate slags produces a range of colors from red to brown and black, but perhaps with proper heat treatment the striking of dendritic cuprite, which makes the brightest red colors, could have been attained. Two reheating experiments on slag samples from Dortmund-Thier-Brauerei were performed: in one experiment slag samples were heated to 550°C producing a dark lustrous crust presumed to be tenorite (CuO) and the second at 750°C at which the glass slumps. The crystallization of what appears to be tenorite on the surface of the glass indicates the presence of metallic copper or copper ions dissolved in the glass, but there was no noticeable formation of cuprite on the surface or within the glass itself, something which may require more experimentation at the temperature range of 900-1100°C to achieve (Greiff, 2012, pp.226-228). The melting temperature of the lead-silicate glass is well below the melting point of most brasses and in this regard would be ideal for use as enamel. Elemental and lead isotope analyses of the red enamels of the disk brooches would help to shed light on any possible connections to the lead-silicate slag.

Discussion: The Contribution of Lead Isotope Analysis

The lead isotope analysis of crucibles and the lead-silicate slag may not only help to clarify the relationship between these two materials, but also helps to build a framework for potential provenance studies of brass distributed in the North Sea region and beyond. Firstly, let us look at the relationship of the crucibles to the lead-silicate slag because this may tell us at what stage the lead enters the system. Theoretically, if the refining of copper did occur then the lead in the lead-silicate slag would stem from the copper and the lead in the crucible would stem from the calamine. The lead isotope ratios of the lead-silicate slag samples are nearly identical to two of the three crucible fragments, the third crucible fragment dating perhaps to a more recent period. It seems that the origin of the lead found in the two Carolingian / Ottonian crucibles and the contemporary lead-silicate slag may be the same. If it stems from the copper then despite the refining process it still outweighs the contribution from the calamine. The process becomes more complex if we approach from the viewpoint that the lead comes mostly from the calamine. In this case, the calamine controls the lead isotope ratios of the brass, but what does this say about the lead-silicate slag? Could the raw calamine have been somehow treated or beneficiated to separate the lead-rich minerals from the zinc minerals, each then used for different processes, i.e. glass making and brass making? It is perhaps premature to speculate further as a larger sample size is required to properly untangle this issue. What can be said from the initial analyses is that the lead used in both process appears similar and may have the same origin.

Without knowing the true nature of the lead from these metallurgical processes, provenancing through lead isotope analysis becomes more complex. It is clear, however, that the lead isotope ratios from the Dortmund-Thier-Brauerei slag and crucibles are consistent with Post-Variscan ore from the Rhenish Massif and align well with the analyses of Westphalian crucibles and slag presented by Krabath, et al. (1999, p.436). Geologically younger deposits like Wiesloch near Heidelberg (Ströbele, et al., 2012) and older Variscan and Pre-Variscan deposits like the Rammelsberg, in the Harz, (Lehmann, 2011) can be excluded. If we assume that Rammelsberg copper was used in the brass-making process, then the majority of the lead present could not have entered the system with the copper. Additionally, the Marsberg copper ore deposit, which may have been of importance for the Hellweg region in the Carolingian period, is typically poor in lead and this option can be disregarded as the origin of the lead in the brass (Krabath, et al., 1999, p.435). The calamine may be what is represented with lead isotope ratios as lead and zinc minerals are often found together. The two most probable regions for the supply of calamine are Sauerland immediately to the south of Dortmund and Soest and the more distant Aachen area. A comparison of published analyses of calamine and lead-zinc ore from Aachen-Stolberg and from Sauerland show extensive overlap and cover the region of the crucibles and lead-silicate slag (compare Bode, 2008; Bielicki and Tischendorf, 1991; Chatziliadou, 2009; Durali-Müller, 2005; Krahn and Baumann, 1996). Calamine ore from Kelmis-Moresnet and Iserlohn (see appendix) are plotted together with the crucibles and slag from Dortmund in Figure 7. Two calamines from Iserlohn are consistent with the Dortmund material and support the possibility that local zinc ore could have been used; however, due to the similar geologic origins of the many ore deposits in the Rhenish Massif they are difficult to distinguish from one another with lead isotope analysis alone. There may be other, more indirect, ways of solving this problem. If a Carolingian / Ottonian brass-making industry would be identified in the Meuse, Aachen, or Cologne regions, perhaps there are enough elemental and / or isotopic differences to distinguish it from the Westphalian.

Conclusions

The archaeometallurgical investigation of crucible fragments from Carolingian / Ottonian Dortmund and Soest has been successful in confirming the production of leaded brass at this early date, but the analyses have further implications. We can conclude from the compositions of copper and brass prills found within the crucibles and adhering slag that the source of the lead is probably a mixture between lead coming from the copper and lead from the calamine ore. The contribution of lead stemming from a lead-bearing calamine may overshadow the lead originating in the copper, or otherwise significantly influence the final lead composition. This has important implications in the provenancing of Carolingian, Ottonian and Viking brass objects and particularly leaded brass bar ingots through lead isotope analysis.

It has been traditionally thought that the source of brass for the Carolingians was near Aachen where large, high-quality calamine deposits are found (Werner, 1977). Though there are historical records from the 10th century that hint at a brass working industry along the Meuse river near Liège (Day, 1998, p.133), currently there is no archaeological evidence of primary brass production in the Meuse, Aachen, or Cologne regions dating to the Carolingian or Ottonian period. Calamine ore deposits are present at Aachen-Stolberg and Aachen-Kelmis-Moresnet and along the Meuse River, but the massive numbers of crucibles required for production have not been found. It is highly probable that there were multiple brass-making centers, and, perhaps, through the elemental and lead isotope analysis of metal finds and production debris from well-dated contexts in Cologne and in Westphalia, the existence separate production centers can be identified.

Some details of Westphalian brass making could be clarified, but there are still a number of questions concerning the technological process. It is evident that calamine was heated in the crucibles due to the impregnation of zinc oxide throughout the crucible ceramic. The formation of a metallurgical slag inside the crucible is rare, but when present it contains the iron and calcium impurities likely originating with the calamine ore. The elemental composition of the crucible slag has no resemblance to the frequently found lead-silicate slag, which must have formed during a separate metallurgical process. The lead isotope analysis, however, shows a relationship between the lead in the crucibles / crucible slag and the lead-silicate slag, but the reason behind this is not understood. To explore this relationship more fully, a larger sampling of slag and crucibles would be required for lead isotope analysis, and, additionally, to investigate the possible connection of the lead-silicate slag with the manufacture of red enamel, a series of re-heating experiments could be performed in conjunction with the elemental and lead isotope analysis of contemporary enameled disk brooches with cruciform motifs.

Acknowledgements

I would like to thank Henriette Brink-Kloke (Stadtarchäologie Dortmund) and Walter Melzer and Frederik Heinze (Stadtarchäologie Soest) for supplying crucible and slag fragments from the Dortmund-Thier-Brauerei and Soest-Plettenberg excavations and for their stratigraphic and archaeological interpretation. The analytical work of Sabine Klein at the Goethe-Universität Frankfurt / Main and Michael Bode of the Deutsches Bergbau-Museum Bochum are gratefully acknowledged. Samples were prepared in Bochum by Andreas Ludwig, Sandra Morszeck and Regina Kutz and I would like to thank them for their excellent work. The study was funded by the VolkswagenStiftung as part of the project "Between the Vikings and the Hanse", a project based at the Landesmuseum Schleswig-Holstein exploring the trading connections and craft production over the transition between the Viking age and the High Middle Ages. Last, but not least, I would like to thank the anonymous reviewer whose comments improved the quality of this paper.

Reference

Beierlein, P. R., 1960. *Lazarus Ercker Beschreibung der allervornehmsten mineralischen Erze und Bergwerksarten vom Jahre 1580*. Berlin: Akademie-Verlag.

Bielicki, K. H., and Tischendorf, G., 1991. Lead Isotope and Pb-Pb Model Age Determinations of Ores from Central Europe and their Metallogenetic Interpretation. *Contributions to Mineralogy and Petrology*, 106, pp.440-461.

Bode, M., 2008. *Archäometallurgische Untersuchungen zur Blei-/Silbergewinnung im Germanien der frühen Römischen Kaiserzeit*. Ph.D. Westfälische Wilhelms-Universität Münster. [online] Available at: <http://d-nb.info/992682231/34> [Accessed 21 January 2016].

Bougarit, D., and Thomas, N., 2015. Ancient brasses: misconceptions and new insights. In: A. Hauptmann and D. Modarressi-Tehrani, eds., 2015. *Archaeometallurgy in Europe III*, *Der Anschnitt, Beiheft*, 26. Bochum: Deutsches Bergbau-Museum. pp.255-262.

Capelle, T., 1974. Die karolingisch-ottonische Bronzegießersiedlung bei Kückshausen. *Frühmittelalterliche Studien*, 8, pp.294-302.

Chatziliadou, M., 2009. *Rb-Sr Alter und Sr-Pb Isotopencharakteristik von Gangmineralisationen in paläozoischen Gesteinen am Nordrand des linksrheinischen Schiefergebirges (Raum Stolberg-Aachen-Kelmis) und Vergleich mit den rezenten Thermalwässern von Aachen-Burtscheid*. Ph.D. Rheinisch-Westfälische Technische Hochschule Aachen. [online] Available at < http://d-nb.info/996026843/34> [Accessed 21 January 2016].

Day, J., 1998. Brass and Zinc in Europe from the Middle Ages until the Mid-Nineteenth Century. In: P. T. Craddock, ed. 1998. *2000 Years of Zinc and Brass. British Museum Occasional Paper*, 50, 2nd Edition. London: British Museum. pp.132-156.

Drescher, H., 1983. Metallhandwerk des 8.-11. Jahrhunderts in Haithabu auf Grund der Werkstattabfälle. In: H. Jankuhn, W. Janssen, R. Schmidt-Wiegand and H. Tiefenbach, eds. 1983. *Das Handwerk in vor- und frühgeschichtlicher Zeit. Teil II, Archäologische und philologische Beiträge. Bericht über die Kolloquien der Kommission für die Altertumskunde Mittel- und Nordeuropas in den Jahren 1977-1980*. Göttingen: Vandenhoeck & Ruprecht. pp.174-192.

Durali-Müller, S., 2005. *Roman Lead and Copper Mining in Germany. Their Origin and Development through Time, Deduced from Lead and Copper Isotope Provenance Studies*. Ph.D. Goethe-Universität, Frankfurt am Main. [online] Available at < http://publikationen.ub.uni-frankfurt.de/frontdoor/index/index/docId/2824> [Accessed 21 January 2016].

Eiwanger, J., 1996. Barrenmessing – ein mittelalterliches Handelsgut zwischen Europa und Afrika? *Beiträge zur allgemeinen und vergleichenden Archäologie*, 16, pp.215-226.

Eremin, K., Graham-Campbell, J., and Wilthew, P., 2002. Analysis of Copper-Alloy Artefacts from Pagan Norse Graves in Scotland. In: E. Jeren and K. Biró, eds. 2002. *Proceedings of the 31st International Symposium on Archaeometry*. Oxford: Archaeopress. pp.343-349.

Gilmore, G. R., and Metcalf, D. M., 1980. The Alloy of the Northumbrian Coinage in the Mid-Ninth Century. In: D. M. Metcalf and W. A. Oddy, eds. 1980. *Metallurgy in Numismatics,* Vol. I. London: Royal Numismatic Society. pp.83-98.

Greiff, S., 2012. On the relationship between enameled glass and other opaque glass technologies: The colour red. In: D. Ignatiadou and A. Antonaras, ed. 2012. *Annales du 18e Congrés de l'Association Internationale pour l'Histoire du Verre, Thessaloniki 2009*. Thessaloniki: ZITI. pp.224-230.

Haseloff, G., 1990. *Email im frühen Mittelalter*. Marburg, Hitzeroth.

Hawthorne, J. G., and Smith, C. S., 1979. *Theophilus on the Diverse Arts: The Foremost Medieval Treatise on Painting, Glassmaking and Metalwork*. Toronto: Dover.

Klein, S., Domergue, C., Lahaye, Y., Brey, G. P., and von Kaenel, H. M., 2009. The Lead and Copper Isotopic Composition of Copper Ores from the Sierra Morena (Spain). *Journal of Iberian Geology*, 35(1), pp.59-68.

Krabath, S., Lammers, D., Rehren, T., and Schneider, J., 1999. Die Herstellung und Verarbeitung von Buntmetall im karolingerzeitlichen Westfalen. In: C. Stiegemann and M. Wemhoff, eds. 1999. *Kunst und Kultur der Karolingerzeit. Karl der Große und Papst Leo III. in Paderborn.*

Beiträge zum Katalog der Ausstellung Paderborn 1999. Mainz: Phillipp von Zabern. pp.430-437.

Krahn, L., and Baumann, A., 1996. Lead isotope systematics of epigenetic lead-zinc mineralization in the western part of the Rheinisches Schiefergebirge, Germany. *Mineralium Deposita*, 31, pp.225-237.

Lammers, D., 2009. *Das karolingisch-ottonische Buntmetallhandwerker-Quartier auf dem Plettenberg in Soest. Soester Beiträge zur Archäologie*,10. Soest: Mocker & Jahn.

Lehmann, R., 2011. *Archäometallurgie von mittelalterlichen deutschen Silberbarren und Münzen*. Ph.D. Leibniz Universität Hannover. [online] Available at <http://edok01.tib.uni-hannover.de/edoks/e01dh11/646461346.pdf> [Accessed 21 January 2016].

Metcalf, D. M., and Northover, P., 1985. Debasement of the Coinage in Southern England in the Age of King Alfred. *Numismatic Chronicle*, 145, pp.150-176.

Metcalf, D. M., and Northover, P., 1989. Coinage Alloys from the Time of Offa and Charlemagne to c. 864. *Numismatic Chronicle*, 149, pp.101-120.

Mortimer, C., 1988. Anglo-Saxon Copper Alloys from Lechlade, Gloucesterschire. *Oxford Journal of Archaeology*, 7(2), pp.227-233.

Oldeberg, A., 1942. *Metallteknik under Förhistorisk Tid*. Leipzig/Lund: Otto Harrassowitz.

Pedersen, U., 2010. *I Smeltedigelen, Finsmedene i Vikingtidsbyen Kaupang*. Ph.D., Universitetet I Oslo.

Rehren, T., Lietz, E., Hauptmann, A., and Deutmann, K. H., 1993. Schlacken und Tiegel aus dem Adlerturm in Dortmund: Zeugen einer mittelalterlichen Messingproduktion. In: H. Steuer and U. Zimmermann, eds. 1993. *Montanarchäologie in Europa: Bericht zum internationalen Kolloquium "Frühe Erzgewinnung und Verhüttung in Europa" in Freiburg im Breisgau vom 4. bis 7. Oktober 1990*. Sigmaringen: Jan Thorbecke. pp.303-314.

Rehren, Th., and Martinón-Torres, M., 2008. Naturam ars imitata: European Brassmaking between Craft and Science. In: M. Martinón-Torres and T. Rehren, eds. 2008. *Archaeology, History and Science: Integrating Approaches to Ancient Materials*. Walnut Creek CA: Left Coast. pp.167-188.

Sarah, G., 2010. Charlemagne, Charles the Bald and the Karolus Monogram Coinage. A Multi-Disciplinary Study. *Numismatic Chronicle*, 170, pp.227-286.

Sicherl, B., 2011. Dortmund – ein Zentrum herrschaftlicher Buntmetallproduktion. In: G. K. Stasch and F. Verse, eds. 2011. *911 Königswahl zwischen Karolingern und Ottonen , König Konrad I – Herrschaft und Alltag, Museum Fulda 9. November 2011 bis 6. Februar 2012*. Fulda: Imhof. pp.199-210.

Sicherl, B., and Brink-Kloke, H., 2012. *Zwischen Urt(h)ier und Thier-Galerie. Bausteine und Fundstücke Dortmunder Denkmalheft*, 02. Dortmund: Stadt Dortmund Denkmalbehörde.

Sindbæk, S. M., 2001. An Object of Exchange: Brass Bars and the Routinization of Viking Age Long-Distance Exchange in the Baltic Area. *Offa*, 58, pp.49-60.

Smith, C. S., and Gnudi, M. T., 1966. *The Pirotechnia of Vannoccio Biringuccio*. Cambridge MA: MIT.

Stapleton, C. P., Freestone, I. C., and Bowman, S. G. E., 1999. Composition and Origin of Early Medieval Opaque Red Enamel from Britain and Ireland. *Journal of Archaeological Science*, 26, pp.913-921.

Ströbele, F., Staude, S., Pfaff, K., Premo, W. R., Hildebrandt, L. H., Baumann, A., Pernicka, E., and Markl, G., 2012. Pb isotope constraints on fluid flow and mineralization processes in SW Germany. *Neues Jahrbuch für Mineralogie – Abhandlungen*, 189(3), pp.287-309.

Thornton, C., 2007. Of brass and bronze in prehistoric Southwest Asia. In: S. LaNiece, D. Hook, and P. Craddock, eds. 2007. *Metals and Mining: Studies in Archaeometallurgy*. London: Archetype. pp.123-135.

Todt, W., Cliff, R. A., Hanser, A., and Hofmann, A. W., 1996. Evaluation of a ^{202}Pb–^{205}Pb Double Spike for High-Precision Lead Isotope Analysis. In: S. R. Hart and A. Basu, eds. 1996. *Earth Processes: Reading the Isotope Code, Geophysical Monograph*, 95. Washington, DC: American Geophysical Union. pp. 429-437.

Werner, O., 1977. Analysen mittelalterlicher Bronzen und Messinge I. *Archäologie und Naturwissenschaft*, 1, pp.144-220.

Wyckoff, D., 1967. *Albertus Magnus Book of Minerals*. Oxford: Clarendon.

Zientek, C., and Rehren. T., 2009. B. Analyse ausgewählter Schmelztiegel und Schlacken. In: D. Lammers, ed. 2009. *Das karolingisch-ottonische Buntmetallhandwerker-Quartier auf dem Plettenberg in Soest. Soester Beiträge zur Archäologie*, 10. Soest: Mocker & Jahn. pp.179-181.

Note

1 120/365-25: GrA 48471: 1180 ± 35 BP or cal. 838 ± 48 AD.
120/595-6: GrA 48890: 1130 ± 35 BP or cal. 913 ± 43 AD.
120/614: GrA 48889: 1195 ± 35 BP or cal. 825 ± 45 AD.

Appendix: The Analysis of Calamine from Iserlohn and Kelmis-Moresnet

Four calamine samples from Iserlohn (Figure 8) and six samples from the Kelmis / Moresnet area were taken from the mineralogical collection of the Deutsches Bergbau-Museum and were analyzed by X-ray Diffraction (XRD) (Table 8), HR-ICP-MS (Table 9) and lead isotope analysis with MC-ICP-MS (Table 10) to compare to the crucibles and slag. Additionally, six fragments were calcined to document the elemental and crystallographic changes that occur. The calamine samples were first checked by XRD to confirm the presence and form of zinc-rich minerals. Pulverized samples were analyzed using a PAN-alytical X'Pert instrument (PRO MPD) with X'Celerator detector and High Score Plus-software for analytical interpretation. The analysis requires about 100 mg of powdered sample (< 0.063 mm 110 fraction size), and the samples were analyzed with ADS (automatic divergence slit) Cu-Kα-radiation of 1.54178 Å at 45 kV (40 mA) with angle array set to 5-70° 2-theta at a rate of 0.017° / 10 sec.

All samples contained zinc-rich minerals like smithsonite, hemimorphite, and willemite, but in various proportions. The samples from Iserlohn primarily consist of smithsonite and goethite with minor amounts of calcite and clay minerals; no zinc silicates were detected. The samples from Kelmis are more heterogeneous. One sample fits the pattern seen in the calamine from Iserlohn, but the other five have detectable amounts of zinc silicates like hemimorphite and willemite. The elemental results mirror the XRD and show that the samples from Iserlohn are silica poor and primarily consist of zinc and iron, which based on the XRD results can be interpretated as smithsonite and goethite. The samples from Kelmis have variable silica contents. One sample (4871-14) is nearly identical to the calamine from Iserlohn only with less magnesium and lead. Three samples (4872-14, 4874-14, 4876-14) seem to consist mainly of hemimorphite due to the silica to zinc ratios, and these samples have considerably less iron and substantially more phosphourus. The lead contents of the calamine samples from Kelmis have half to ten times less lead than the samples from Iserlohn.

Figure 8. Massive calamine from Iserlohn. The sample is approximately 25 cm.

Table 8. Studied samples of calamine from the mineralogy collection at the Deutsches Bergbau-Museum Bochum. The mineral composition was determined by XRD.

Lab. Nr.	Source	Minerals
4867-14	Iserlohn	Smithsonite, Goethite
4868-14	Iserlohn	Smithsonite, Goethite
4869-14	Iserlohn	Smithsonite, Goethite, Muscovite, Calcite
4870-14	Iserlohn	Smithsonite, Goethite, Muscovite, Calcite
4871-14	Kelmis-Eschbruch	Smithsonite, Goethite, Muscovite, Calcite, Quartz
4872-14	Kelmis-Moresnet	Hemimorphite, Smithsonite, Willemite
4873-14	Kelmis-Moresnet	Smithsonite, Hemimorphite
4874-14	Inderevier	Hemimorphite, Smithsonite
4875-14	Kelmis	Smithsonite, Hemimorphite, Willemite, Calcite, Siderite
4876-14	Kelmis	Hemimorphite

A calcination experiment was carried out on four samples from Iserlohn, all smithsonite, and two from Kelmis of which one was mostly smithsonite and one nearly pure hemimorphite. All samples were heated in open porcelain crucibles in air and five were heated to 650°C for four hours and one sample from Iserlohn was heated to 800°C for four hours. All smithsonite samples lost about 30 percent of their weight due to expulsion of carbon and hydroxides. The hemimorphite-rich sample lost 7.5 percent of its weight. The calcined smithsonite-rich samples gained 35 to 50 percent zinc, 20-25 percent iron, 30-50 percent lead, and arsenic contents doubled. XRD of the calcined smithsonite samples confirmed that all detectable carbonates were converted to their respective oxides. The hemimorphite-rich sample from Kelmis showed no increases except for a doubling of the arsenic content though this change was from 10 ppm to 20 ppm. After calcination, hemimorphite was not detected in the XRD nor was zinc oxide; instead a zinc silicates were formed. The smithsonite sample from Iserlohn heated to 800°C had a slightly lower zinc content than the samples calcined at 650°C and may be an

Table 9. Results of HR-ICP-MS of calamine samples from Iserlohn and Kelmis-Moresnet. All values are in weight percent except for P, Co, Ni, As, and Sb which are in ppm. The low totals are due mostly to the carbon content from carbonate minerals.

	4867-14	4868-14	4869-14	4870-14	4871-14	4872-14	4873-14	4874-14	4875-14	4876-14
	Iserlohn	Iserlohn	Iserlohn	Iserlohn	Kelmis	Moresnet	Moresnet	Inde	Kelmis	Kelmis
Na_2O	0.02	0.02	0.02	0.03	0.03	0.01	0.01	0.01	0.02	0.02
MgO	0.26	0.25	0.21	0.20	0.06	0.06	0.23	0.01	0.61	0.02
Al_2O_3	0.23	0.46	1.05	0.88	0.53	0.42	0.04	0.14	0.37	0.21
SiO_2	0.99	1.14	2.16	1.96	1.92	23.1	3.04	23.8	10.3	25.5
S	0.43	0.33	0.28	0.29	0.02	0.04	0.02	<0.01	<0.01	<0.01
K_2O	0.03	0.05	0.29	0.16	0.06	0.03	0.01	0.03	0.04	0.04
CaO	0.63	0.66	0.53	0.47	0.50	0.06	0.07	0.02	3.01	0.13
MnO	0.54	0.21	0.29	0.44	0.46	0.03	0.68	0.01	0.29	0.07
Fe_2O_3	11.4	10.1	10.9	13.2	7.79	3.79	4.46	1.70	8.93	0.21
ZnO	53.0	52.2	51.0	47.8	54.8	62.2	58.2	63.7	51.8	67.5
PbO	0.76	0.68	0.57	0.63	0.35	0.27	0.05	0.09	0.09	0.19
P	150	220	75	110	290	920	540	810	680	2000
Co	25	10	15	20	30	2	10	0.7	20	2
Ni	95	70	40	65	140	160	260	35	350	120
As	120	160	270	250	180	170	20	85	55	10
Sb	45	65	15	10	5	360	45	9	6	3
Total	68.3	66.1	67.3	66.1	66.6	90.1	66.9	89.6	75.6	94.4

Table 10. Results of lead isotope analysis of calamine samples performed by multicollector ICP-MS at the Goethe-Universität Frankfurt / Main.

Lab. Nr.	Sample	Date	^{206}Pb/^{204}Pb	2σ	^{207}Pb/^{204}Pb	2σ	^{208}Pb/^{204}Pb	2σ	^{207}Pb/^{206}Pb	2σ	^{208}Pb/^{206}Pb	2σ
4867-14	Calamine	D	**18.399**	0.020	**15.620**	0.017	**38.36**	0.04	**0.8489**	0.0002	**2.0849**	0.0008
4868-14	Calamine	C	**18.401**	0.016	**15.626**	0.014	**38.38**	0.04	**0.8492**	0.0002	**2.0860**	0.0007
4869-14	Calamine	C	**18.360**	0.018	**15.616**	0.017	**38.31**	0.05	**0.8505**	0.0003	**2.0866**	0.0009
4870-14	Calamine	D	**18.361**	0.018	**15.617**	0.016	**38.32**	0.04	**0.8505**	0.0002	**2.0870**	0.0006
4871-14	Calamine	D	**18.387**	0.011	**15.620**	0.011	**38.35**	0.03	**0.8495**	0.0002	**2.0857**	0.0008
4872-14	Calamine	D	**18.383**	0.013	**15.619**	0.012	**38.35**	0.04	**0.8496**	0.0002	**2.0862**	0.0007
4874-14	Calamine	C	**18.389**	0.014	**15.616**	0.015	**38.34**	0.04	**0.8492**	0.0002	**2.0850**	0.0009
4875-14	Calamine	D	**18.404**	0.015	**15.618**	0.015	**38.36**	0.04	**0.8486**	0.0003	**2.0839**	0.0009
4876-14	Calamine	D	**18.384**	0.015	**15.614**	0.015	**38.34**	0.04	**0.8493**	0.0003	**2.0855**	0.0008
Standard	SRM 981 Pb	C	**16.955**	0.016	**15.516**	0.016	**36.78**	0.04	**0.9152**	0.0002	**2.1692**	0.0008
Standard	SRM 981 Pb	D	**16.934**	0.008	**15.488**	0.009	**36.69**	0.02	**0.9146**	0.0002	**2.1665**	0.0007

indication that at 800°C small amounts of zinc could have been lost in its gaseous state.

To return to the brass-making process, calcination is benificial in concentrating the zinc by converting the zinc carbonate to zinc oxide, but it should be highlighted that zinc in hemimorphite is bound by silica, a state that does not change during calcination. Zinc silicate minerals, therefore, are not a viable source of zinc during brass making and would preferentially form a zinc-silicate slag if suitable temperatures are reached. It would have been advantageous for cementation to use calcined calamine that consisted exclusively of smithsonite.

Autor

Stephen Merkel
Deutsches Bergbau-Museum Bochum,
Research Laboratory for Archaeology and
Materials Science,
Hernerstr. 45,
44787 Bochum, Germany,
stephenwilliam.merkel@bergbaumuseum.de