

# Scientific examination of zinc-distillation remains from Warmley, Bristol

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*ABSTRACT: Recent archaeological recording at William Champion's zinc and brass manufactory at Warmley (NGR ST66927283) has allowed the investigation of materials related to the distillation of zinc. William Champion obtained a patent for the production of zinc by a distillation process in 1738 and was producing zinc on an industrial scale from the 1740s. The Champion process enabled the production of zinc-rich yellow brasses which were widely used by the Birmingham 'toy' industry. The materials examined include a fragment of a refractory vessel and a residue from zinc distillation. The results highlight the limitations of many patents of this period but provide some indications of how the distinctive process residues generated by zinc distillation can be recognised.*

## Introduction

Zinc has been used in the manufacture of copper alloys for over two thousand years (Bayley 1998; Craddock 1998; Day 1998), but before the 18th century the metal was rare in Europe. Metallic zinc is difficult to obtain from its ores because of the chemical and physical properties of the metal: it boils at 907°C and is easily oxidised in air or carbon dioxide. The reduction of zinc oxide to metallic zinc can be easily achieved in a variety of furnaces but the zinc is generally lost as a fume. Nevertheless, brasses (alloys of zinc and copper) were manufactured in Europe from at least the late 1st millennium BC by a cementation process (Craddock 1978; 1998). Copper was heated in a sealed vessel with zinc oxide and charcoal; the charcoal reduced the zinc oxide to metallic zinc and this was absorbed by the copper producing brass. Experimental reconstructions of this process (Newbury *et al* 2005; Werner 1970), and analyses of Roman (Dungworth 1997) and medieval (Cameron 1974) brasses, suggests that the cementation process could not be used to produce brasses that contained more than 28wt% zinc. Nevertheless, by the 18th century it was appreciated that brasses with a high zinc content were desirable, not least because they had

a colour more closely approximating to that of gold. In 1723 Nehemiah Champion patented (No 454) a method for making brass in which the copper was first granulated by casting in water. The increased surface area of the copper improved the absorption of zinc resulting in brasses with up to 33wt% zinc (Day 1991, 172). The nature of the cementation process was such that it was not possible to produce brasses with more zinc; high-zinc brasses could only be made by adding metallic zinc to copper. Small amounts of zinc were available but this was expensive. In Europe it was recovered from the flues of some furnaces (Hoover and Hoover 1950, 394) while in India a process had been developed in which zinc was smelted using retorts (Craddock *et al* 1998). It was in this context that William Champion began the manufacture of zinc in the mid 18th century.

## William Champion and his Patent

William Champion (a son of Nehemiah Champion) appears to have followed his father into the brass business in the 1730s and in 1738 he patented a method for the manufacture of zinc. Near contemporaries (*eg* Angerstein and Watson) were in little doubt that Champion had developed a method for producing

metallic zinc but the patent document is quite unhelpful. While the patent (No 564) is entitled *A Method of Invention for the Reducing of Sulphureous British Minerals into a Body of Metallik Sulphur*, there seem to be no grounds for believing that Champion was actually engaged in the manufacture of sulphur. The exact nature of the raw materials used by Champion is even less clear. The patent refers to the use of 'calamy or other sulphureous British mineral or minerals' but calamy (calamine) was used to refer to non-sulphide zinc ores. It is possible that William Champion used the term 'sulphureous' to deliberately obscure the nature of his process. Patents of the 17th and 18th centuries frequently omit key technical details partly due to the limitations of contemporary scientific knowledge (especially chemistry) but more often in order to avoid revealing the crucial details (MacLeod 1989). Patents were still used to effectively establish monopolies in the production of particular materials.

Champion appears to have gone to some lengths to hide details of the process from possible competitors (Berg and Berg 2001, 126; Watson 1786, 38). The earliest account of Champion's zinc distillation is found in Watson's *Chemical Essays*, published in 1786 but which recording a visit 'nearly twenty years ago'; he describes how the distillation took place (Watson 1786, 38–9):

'In a circular kind of oven, like a glass house furnace, there were placed six pots of about four feet each in height, much resembling large oil jars in shape; into the bottom of each pot was inserted an iron tube, which passed through the floor of the furnace into a vessel of water. The pots were filled with a mixture, of calamine and charcoal, and the mouth of each was then close stopped with clay. The fire being properly applied, the metallic vapour of the calamine issued through, the iron tube, there being no other place through which it could escape, and the air being excluded, it did not take fire, but was condensed in small particles in the water.'

Angerstein's account of his visit to Warmley in 1754 provides little direct information, however, he did visit nearby works at Crew's Hole where 'there is also a spelter furnace made to the same design invented by Mr Champion and put into operation as long as 15 to 18 years ago' (Berg and Berg 2001, 143). Angerstein's account contains many of the same details as Watson's (in particular the use of calamine, retorts and the iron pipes) but also contains other points which may be relevant. Angerstein describes the crucibles (more properly retorts) as being made from Stourbridge clay.

He writes that the zinc ore was roasted and picked over to remove as much galena as possible before charging. He also refers to the charge containing coal not charcoal. An illustration of one of the Crew's Hole furnaces is provided but this lacks detail (Berg and Berg 2001, fig 149). The zinc-distillation process is also described by Mosselmann (1825) and Percy (1861) who provide additional details and detailed scale drawings of the furnaces and retorts. Percy (1861, 557) records that 20cwt (1 tonne) of calcined zinc ore would give 6 to 8cwt of zinc, suggesting that approximately half the charge would remain in the retort as 'residuum' which would be scraped out at the end of the firing. Various 19th- and 20th-century developments enabled the processing of many retort residues and the extraction of the zinc they still contained (Almond 1998, 208–9). Large quantities of coal were required for the production of zinc by distillation, making the resultant metal expensive. It was mainly used for the manufacture of specialist high-zinc brasses which were popular in the Birmingham 'toy' industries (Watson 1786, 45–6).

### Champion's manufactory at Warmley

To exploit his patent, William Champion established a manufactory at Warmley on the eastern outskirts Bristol in the 1740s. The new site became an early example of an integrated manufactory where copper was smelted, zinc distilled, brass manufactured (both by direct alloying and by cementation) and a variety of finished articles produced, *eg* pins and kettles (Day 1988). Zinc distillation was important, but most of the furnaces were devoted to the smelting of copper and the production of cementation brass; in 1754 only four out of thirty-one furnaces were used for the distillation of zinc (Berg and Berg 2001, 137). Champion continued to expand the business but overexpansion caused financial problems leading to the collapse of the Warmley Company in 1767. It was bought by Champion's rival, the Bristol Brass Company, in 1769 (Day 1973) and limited operations (possibly only zinc smelting) continued at the Warmley site into the early 19th century.

Recent archaeological recording undertaken by English Heritage at Warmley, Bristol (NGR ST 6692 7283) revealed a number of residues thought to derive from the metalworking processes carried out at the site. A full account of the programme of scientific analyses can be found in White (2007) and the copper-smelting slags will be discussed in a future article in this journal. This paper focuses on the residues which may be related to zinc manufacture and comprise a friable zinc-rich

material, and a fragment of refractory material (possibly a retort). Both were identified during field recording as potentially relevant to zinc manufacture due to their distinctive blue or mauve colour (*cf* Freestone 1988). Unfortunately, the zinc-rich deposit was recovered from an undated context while the refractory was an unstratified find.

## Scientific examination and analysis

### Methods

Polished sections of each sample were examined using a scanning electron microscope (SEM) and compositions determined with an energy-dispersive X-ray spectrometer (SEM-EDS, for further details see White 2007). This technique provides no direct information on the valence states of the elements present in the analysed material,

Table 1: Composition of parts of the residue (sample 9)

	ZS	R01	R02	R03	MX
Na <sub>2</sub> O	<0.5	<0.5	0.9	1.0	<0.5
MgO	<0.3	0.6	<0.3	1.2	0.6
Al <sub>2</sub> O <sub>3</sub>	0.3	20.5	8.2	29.3	12.7
SiO <sub>2</sub>	29.1	71.0	77.8	60.3	43.5
P <sub>2</sub> O <sub>5</sub>	<0.2	<0.2	0.2	<0.2	0.5
SO <sub>3</sub>	<0.2	<0.2	<0.2	<0.2	1.4
K <sub>2</sub> O	<0.1	0.8	0.3	5.3	0.4
CaO	<0.1	0.5	0.3	0.2	2.6
TiO <sub>2</sub>	<0.1	0.9	0.9	1.2	0.7
MnO	<0.1	<0.1	<0.1	<0.1	<0.1
FeO	0.2	1.7	1.7	1.0	3.7
ZnO	70.4	3.5	9.7	0.5	33.1
CdO	<0.3	0.5	<0.3	<0.3	0.3
BaO	<0.3	<0.3	<0.3	<0.3	<0.3
PbO	<0.5	<0.5	<0.5	<0.5	0.5

Note: ZS = zinc silicate, R01–03 = refractory material, MX = matrix

Table 2: Composition of the refractory vessel (sample 5)

	Core	Surface 1	Surface 2
Na <sub>2</sub> O	1.3	1.0	2.5
MgO	0.3	0.7	0.6
Al <sub>2</sub> O <sub>3</sub>	15.4	20.4	19.3
SiO <sub>2</sub>	68.1	64.9	56.6
P <sub>2</sub> O <sub>5</sub>	<0.2	<0.2	0.6
SO <sub>3</sub>	<0.2	0.2	<0.2
K <sub>2</sub> O	0.5	3.3	4.7
CaO	0.2	1.4	1.1
TiO <sub>2</sub>	1.1	1.0	0.9
MnO	<0.1	0.2	<0.1
FeO	1.2	4.4	5.7
ZnO	12.0	2.5	7.9

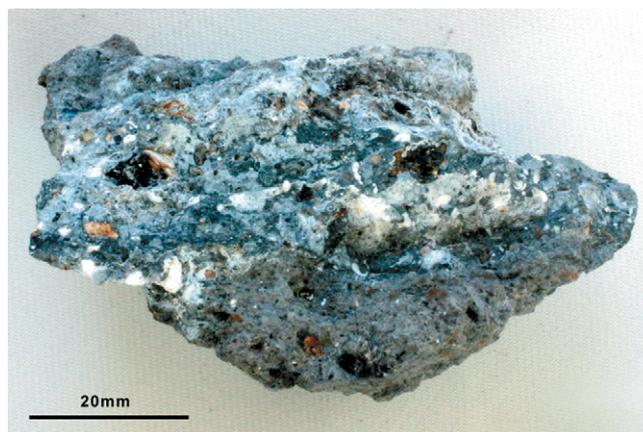


Figure 1: Sample 9; the zinc-rich residue. See also back of cover.



Figure 2: Sample 9; heterogeneous cross-section of the zinc-rich residue (image width 70mm). See also back of cover.

hence appropriate valence states were selected and the oxide weight percent (wt%) of each element was calculated stoichiometrically where necessary. In most cases the porous nature of the materials or phases analysed meant that analytical totals were lower than 100wt%, so all totals have been normalized to 100wt% (Tables 1 and 2).

### Friable zinc-rich residue

The first sample (sample 9) consists of a slightly porous and moderately friable blue zinc-rich material (Figs 1 and 2) and is interpreted as a residue from zinc distillation. SEM examination shows that this material is highly heterogeneous (Fig 3) with metallic zinc (Fig 4), metallic lead (Fig 5), a number of zinc compounds (Figs 4 and 6), fragments of refractory materials (Fig 7), charcoal and coal cemented together in a zinc-rich 'earthy' matrix. The metallic zinc is mainly present as discrete droplets ranging in size from 20µm to 2mm. SEM-EDS analysis only detected zinc; no iron, lead or cadmium were detected in the metal. The SEM images (Fig 4) show the presence of small (<2µm) lead droplets within the zinc droplets. Image analysis suggests that lead makes up 0.34% of the volume of the zinc droplets, which equates to 0.2wt%. The outer

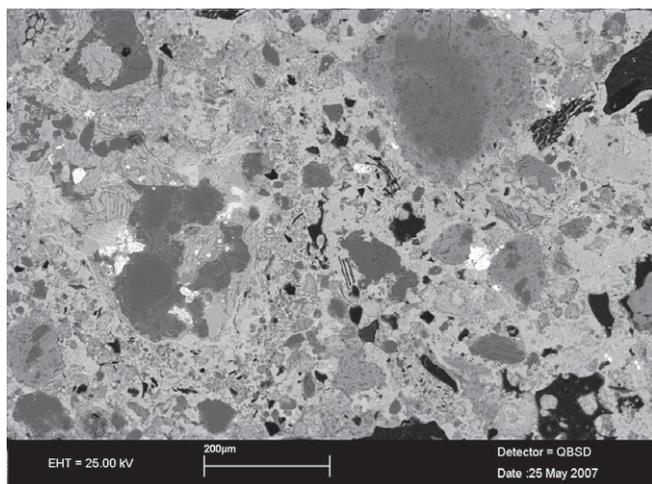


Figure 3: Sample 9; backscattered electron (BSE) image of the zinc-rich residue.

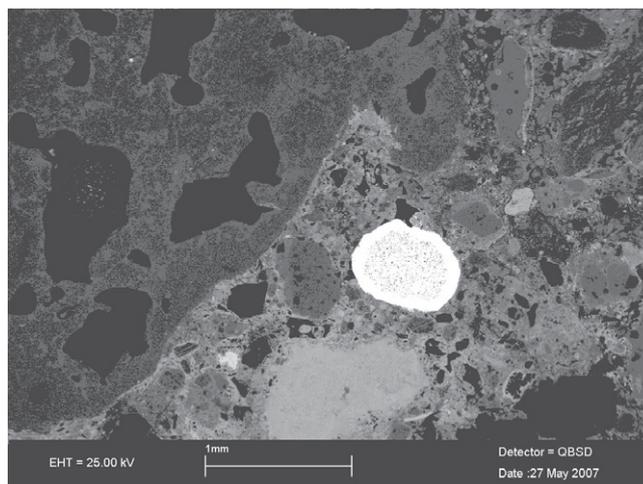


Figure 5: Sample 9; droplet of metallic lead (white) (BSE image).

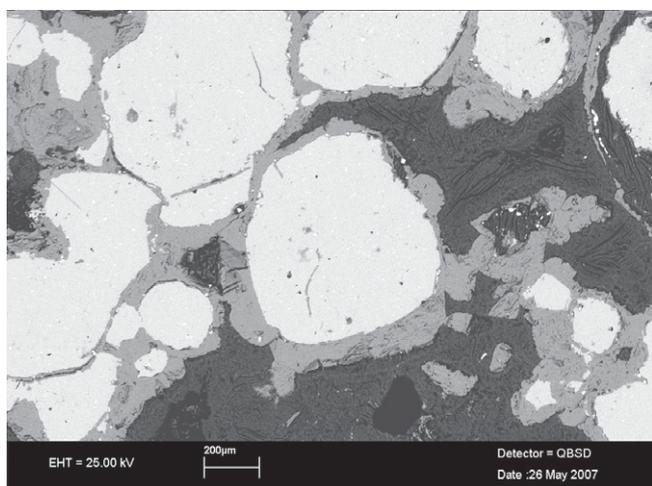


Figure 4: Sample 9; droplets of metallic zinc (pale grey), with zinc oxide (medium grey) and zinc sulphate (dark grey) corrosion (BSE image). The white droplets within the zinc are metallic lead.

regions of the metallic zinc droplets usually have a coating of zinc oxide which has probably formed after the material was discarded. The metallic zinc and zinc oxide are present in a matrix of zinc oxide and zinc sulphate which has also probably formed after deposition. Zinc is present in one region as a zinc silicate (Fig 6; Table 1, ZS) with a composition approximating to hemimorphite ( $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ ). Hemimorphite would be unlikely to survive the zinc-distillation process (typically  $1200^\circ\text{C}$ ) and it has probably formed post-deposition. Droplets of metallic lead up to 1mm across (Fig 5) are occasionally found throughout the sample but no droplets of metallic iron were detected. Fragments of two sorts of refractory material can be seen throughout the sample. In most cases the refractory has a microstructure which resembles most post-medieval refractory ceramic: grains of silica in a vitrified clay matrix. The refractory usually contains

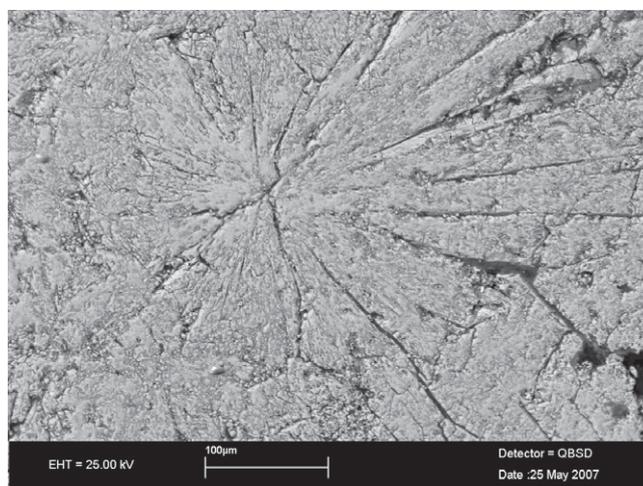


Figure 6: Sample 9; zinc silicate (hemimorphite) (BSE image).

some zinc oxide and cadmium oxide, suggesting a link with zinc working (Table 1, R01). The concentrations of cadmium are in places relatively high compared to those seen in the zinc-distillation retorts from Zawar (Freestone *et al* 1991, table 3). Cadmium has lower melting and boiling points than zinc and it is expected that most cadmium would be removed from retorts during smelting. Some fragments of refractory (Fig 7) have a microstructure resembling the refractory vessel described below, *ie* grains of silica and small crystals of zinc-aluminium spinels (Table 1, R02–03). The various inclusions and phases of sample 9 are present in a zinc-rich ‘earthy’ matrix (Table 1, MX).

The presence of metallic zinc, a possible zinc ore, refractory materials, coal and charcoal suggest that this material derives from the smelting by distillation of zinc. Percy’s description of the Champion zinc-distillation process says that it was carried out for 67 hours until no more zinc could be profitably be extracted (Percy

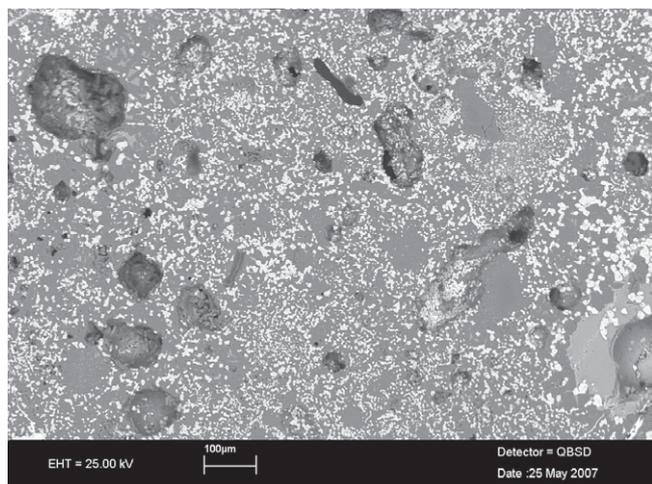


Figure 7: Sample 9; an example of a refractory particle showing grains of silica (dark grey) and small crystals of zinc-aluminium spinel (white) (BSE image).

1861, 557–8). Once the retorts had cooled the exhausted charge ‘residuum’ (*ibid*, 558) or retort residue (Almond 1998, 209) was scraped out. Almond (1977) notes that the large numbers of 19th-century zinc retorts at Tindale Fell, Cumbria have remains of the charge adhering to them. This is described as lumps of coal or coke in a matrix of carbonaceous matter and zinc calcine. Developments in the 19th and 20th centuries enabled the re-processing and smelting of retort residues (Almond 1998), so it is likely to be rather scarce on those sites which were readily accessible to later zinc works. The residue analysed here shows significant differences compared with those from Zawar, India (Freestone *et al* 1985; 1991). The presence of two different sorts of refractory and the relatively high levels of cadmium in some regions may indicate that the material derives from more than one source. One source is likely to be retort residue but other waste materials associated with zinc manufacture may also have been incorporated.

#### Fragment of refractory vessel

The refractory material (sample 5) is a small fragment of a vessel approximately 48mm thick with vitrified layers on both surfaces (Fig 8). The fragment is too small to provide any information on the overall size and shape of the vessel from which it came. The core of the refractory shows a microstructure (Fig 9) with small sub-angular quartz grains in a ceramic matrix which contains angular crystals of zinc-aluminium spinel ( $ZnAl_2O_4$ ). Compositional analysis of the matrix shows it contains significant concentrations of silica, alumina and zinc oxide, and minor amounts of iron- and sodium-oxides (Table 2). If the zinc oxide content is discounted, the refractory material has a fireclay composition. This refractory is similar to the blue stoney material analysed



Figure 8: Sample 5; fragment of possible zinc retort (48mm thick). See also back of cover.

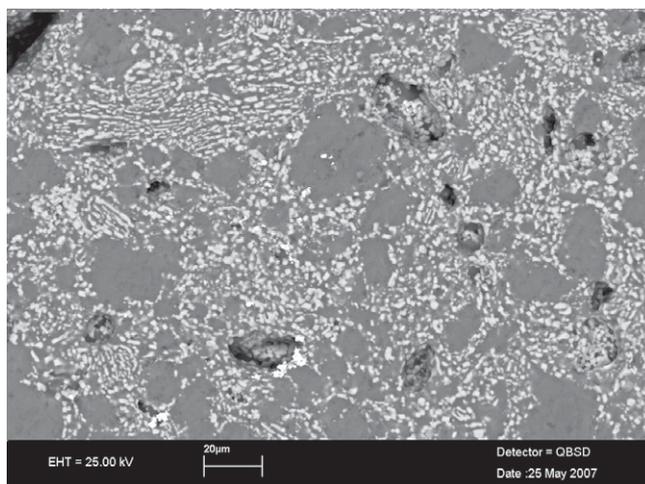


Figure 9: Sample 5; possible zinc retort showing grains of silica (dark grey) and small crystals of zinc-aluminium spinel (white) (BSE image).

by Freestone (1988), and to some of the refractory fragments in sample 9 discussed above (*cf* Figs 7 and 9). The vitrified surfaces of sample 5 contain elevated levels of oxides of potassium, iron and calcium, which suggest they formed through their interaction with coal ash. Surface 1 (believed to be the interior surface) also contains tiny droplets of metallic iron. Freestone *et al* (1985, 238) noted the presence of metallic-iron droplets in the vitrified interior surfaces of zinc-distillation vessels from Zawar, India. The reduction of iron oxides to metallic iron is to be expected given the highly reducing conditions required to smelt zinc oxide (Freestone *et al* 1985, fig 3). The core of the vessel contains higher levels of zinc than either of the surfaces; while the reasons for this are not apparent, the same trend can be seen in

zinc-distillation retorts from Zawar (Freestone *et al* 1985, table 1). The presence of zinc throughout the ceramic matrix and vitrified outer layers, and the absence of copper, indicate that it is a fragment of a zinc-distillation retort rather than a brass-cementation crucible.

## Discussion and conclusions

Historical sources provide only limited information about Champion's zinc-distillation process so the scientific analysis of archaeological residues from Warmley provides an opportunity to reconstruct the processes carried out there. The zinc-rich residue (sample 9) is a complex conglomerate containing numerous particles and phases, suggesting it was a waste material produced during zinc manufacture, including residues from the distillation process. The presence of coal and charcoal suggests that both may have been used as reducing agents. The varied nature of the refractory materials in the residue may reflect formation of the conglomerate from more than one source. Much more research is required to fully understand how such residues formed. The fragment of refractory vessel (sample 5) contains high levels of zinc throughout the ceramic core but no detectable amounts of copper, and is therefore interpreted as a fragment of a zinc-distillation retort. Should opportunities arise in the future to recover larger samples, it may be possible to confirm that this is from a retort, and reconstruct its size and shape.

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## References

- Almond J K 1977, 'Zinc production at Tindale Fell, Cumbria', *Historical Metallurgy* 11, 30–38.
- Almond J K 1998, 'Zinc production technology 1801–1950: a review', in P T Craddock (ed), *2000 Years of Zinc and Brass* (London), 159–228.
- Bayley J 1998, 'The production of brass in antiquity with particular reference to Roman Britain', in P T Craddock (ed), *2000 Years of Zinc and Brass* (London), 7–26.
- Berg T and Berg P (eds) 2001, *RR Angerstein's Illustrated Travel Diary, 1753–1755: Industry in England and Wales from a Swedish Perspective*. (London).
- Cameron H K 1974, 'Technical aspects of medieval monumental brasses', *Archaeological Journal* 131, 215–237.
- Craddock P T 1978, 'The composition of the copper alloys used by the Greek, Etruscan and Roman civilisations 3: The origins and early use of brass', *Journal of Archaeological Science* 5, 1–16.

- Craddock P T 1998, 'Zinc in classical antiquity', in P T Craddock (ed) *2000 Years of Zinc and Brass* (London), 1–6.
- Craddock P T, Freestone I C, Gurjar L K, Middleton A P and Willies L 1998, 'Zinc in India' in P T Craddock (ed), *2000 Years of Zinc and Brass* (London), 27–72.
- Day J 1973, *Bristol Brass: A History of the Industry* (Newton Abbot).
- Day J 1988, 'The Bristol brass industry: Furnace structures and their associated remains', *Historical Metallurgy* 22, 24–38.
- Day J 1991, 'Copper, zinc and brass production', in J Day and R F Tylecote (eds), *The Industrial Revolution in Metals* (London), 131–199.
- Day J 1998, 'Brass and zinc in Europe from the Middle Ages until the mid-nineteenth century', in P T Craddock (ed), *2000 Years of Zinc and Brass* (London), 133–158.
- Dungworth D 1997, 'Roman copper alloys', *Journal of Archaeological Science* 24, 901–910.
- Freestone I 1988, 'Appendix 1. Report on the examination of blue material from industrial remains at Warmley', in J Day 1988, 37–38.
- Freestone I C, Craddock P T, Hedge K T M, Hughes M J and Paliwal H V 1985, 'Zinc production at Zawar, Rajasthan', in P T Craddock and M J Hughes (eds), *Furnaces and Smelting Technology in Antiquity* (London), 229–244.
- Freestone I C, Middleton A P, Craddock P T, Gurjar L K and Hook D R 1991, 'Role of materials analysis in the reconstruction of early metal extraction technology: zinc and silver-lead smelting at Zawar, Rajasthan', in P B Vandiver, J Druzik and G S Wheeler (eds), *Materials Issues in Art and Archaeology II* (Pittsburgh, Penn: Materials Research Society Symposium Proceedings 185), 617–627.
- Hoover H C and Hoover L H (eds) 1950, *Georgicus Agricola. De Re Metallica* (New York).
- MacLeod C 1989, *Inventing the Industrial Revolution: the English Patent System, 1660–1800* (Cambridge).
- Mosselmann E 1825, 'Fusion des mineraux de zinc en Angleterre', *Annales des Mines* 10, 486–90.
- Newbury B D, Notis M R and Newbury D E 2005, 'Revisiting the zinc composition limit of cementation brass', *Historical Metallurgy* 39, 75–81.
- Percy J 1861, *Metallurgy. Fuel; Fire-clays; Copper; Zinc; Brass; Etc* (London).
- Watson R 1786, *Chemical Essays Vol 4* (Cambridge).
- White H and Dungworth D 2007 *Warmley Brassworks, Siston, Bristol: Analysis of some 18th-century brass-working debris* (London: EH Research Department Report).
- Werner O 1970, 'Über das vorkommen von zink und messing im altertum und im mittelalter', *Erzmetall* 23, 259–269.

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