Further work on residues from lead/silver smelting at Combe Martin, North Devon

Sarah Paynter, Peter Claughton and Trevor Dunkerley

ABSTRACT: This paper outlines the history of lead-silver mining, smelting and refining at Combe Martin, in north Devon, during the 16th and 17th centuries, and the background to the discovery of large amounts of smelting residues from that period in the centre of the village. The results of the analyses carried out on those residues are presented along with an interpretation of the processes which produced them.

Introduction

Combe Martin, on the north coast of Devon, has a longhistory of mining for silver-bearing lead ores (Claughton 2004). Some aspects of the mines are well documented, from the first record in 1292 through to abandonment in the late 19th century. Although they were worked for short periods in the late medieval period, documentary evidence suggests that the mines were most productive in the 1580/90s, during the tenure of Bevis Bulmer (a mining entrepreneur who came to Devon from Mendip), with intermittent but undefined levels of production through to the end of the 17th century. Deep working in the 19th century revealed extensive, earlier, shallow workings on all the major silver-bearing deposits. However, until recently relatively little was known about the smelting and refining of the ores prior to the 19th century other than that a water-powered smelt mill was erected in the 1520s and new smelting technology appears to have been introduced in the 1580s. There was also a reference to the associated water course and the survival of 'divers monuments, their names yet to this time remaining, as the King's mine, the store house, blowing house and refining house' in the early 17th century (Oliver 1845, 64–65).

In the argentiferous lead mines of Devon, the requirement to treat all the ore mined and maximise the production of silver meant that improved techniques for recovering and processing small fragments of ore had been introduced by the end of the 13th century. The ore was recovered using gravity separation methods and the careful control of the flow of water in the 'buddling' process (Kiernan 1989, 15-16; Gough 1967, 147–149). Where small ore was finely disseminated in the gangue material, it was separated and smelted in the furnace along with lead rich residues recovered from the slags, and not discarded as waste (Claughton 2003, 152–156).

The 16th and 17th centuries saw the introduction of a number of innovations in the lead-smelting industry. Hochstetter may have constructed a charcoal-fuelled blast furnace early in the 16th century. These operated with a reducing atmosphere, so the ore was roasted and oxidized prior to smelting. The slag by-product from this type of furnace would have contained quite a high concentration of lead (and some silver) and so would have been re-smelted (Crossley 1990, 189). However, the documented attempts to use blast furnaces for lead smelting in England in the mid-16th century met with mixed success and did not compare favourably

with alternative technologies introduced at that period, namely the ore hearth (Crossley 1990, 191).

Ore hearths were being used in the Mendips by the mid-16th century and would have been familiar to Bevis Bulmer, who arrived in Combe Martin from the Mendips in the late 1580s. Ore hearths incorporated a 'workstone' and the material being smelted could be pulled onto this and so exposed to an oxidizing atmosphere before being returned to the reducing conditions within the hearth. Ore hearths did not require the ore to be roasted before smelting, could use different types of fuel, such as dried wood, and were able to smelt poorer and smaller ores that were difficult to process using other technologies. The slag by-product of an ore hearth would again be lead-rich and so was processed further to recover as much as possible of the remaining metal. The practice of re-smelting slag was used from at least the late 13th century (Claughton 2003). More metal could be recovered from the slag, minimising wastage, and losses due to lead volatilization were less from the slag than from the ore. In the 16th century, slag hearths were used for this purpose (Gough 1967, 145; Crossley and Kiernan 1992, 6). The slag hearth ran hotter than the ore hearth and was fuelled using charcoal, occasionally peat or, from late in 17th century, mineral fuel (Tylecote 1990, 58; Crossley and Kiernan 1992, 6).

The lead metal produced at Combe Martin would have been further processed by cupellation to extract the silver it contained. Cupellation involves the oxidation of lead to litharge (PbO) in a shallow hearth lined with an absorbent material. The silver is left unaltered whereas the litharge is absorbed by the hearth, lost as fume or skimmed off. The litharge can then be re-smelted to recover the lead (Tylecote 1990, 60).

Aims

Despite the information provided by historical references, the location of the smelting site in Combe Martin was unknown prior to a chance discovery of residues during excavations in the centre of the village during 2000. The material recovered from those, and subsequent, excavations has been investigated to determine the date of operation and the source of the fuel used in the smelting process.

Residues from excavations in 2001–2002 have been analysed, providing information on the processes used in smelting the ores (Paynter *et al* 2003). The results of these investigations, and of preliminary survey work carried out with a view to identifying the furnace site(s),

are presented in this paper.

The excavations

The original test pit (CC1) was intended to period date Christmas Cottage, which is the property at 6 Church Street, Combe Martin. The excavation revealed undisturbed accumulations of material from the early medieval period to the present day, including dense, heavy, black and grey-green smelting slags, thought to be lead-smelting slag, and large quantities of quartz. Whilst the smelting slag was scattered throughout the top 0.6m of the excavation, it was discovered in quantity in the 0.5–0.6m contexts, and dated to the 16th–17th century by the presence of clay pipe bowls and ceramic sherds. Remains of burnt peat turves were found in 18th-19th century contexts but mineral coal was found in association with the 16th-17th century slag. Pieces of calcite and carboniferous limestone were also found, as well as iron-smithing slag, some mineral fuel and broken Flemish bricks of 17th-century type with slag attached to the surfaces (Dunkerley 2002).

Two further 2x1m excavations (CC2 and CC3) were made in the garden of Christmas Cottage (shaded in Figure 1) in an attempt to determine the extent of the smelting debris scatter; they revealed almost identical stratigraphy and contexts as in CC1. CC3, at the western end of the garden, suggested a north-to-south slope of the subsoil with post-holes running east-west filled with slag of cruder composition containing geological inclusions. A Charles II farthing of 1663 and a pipe bowl of 1680, found in secure locations at 0.4–0.5m in the latter excavation, provided a terminal date for smelting activity of around 1670 to 1690.

To the south of Christmas Cottage lies the village War Memorial (Fig 1). Prior to 1909 this was the village pound for enclosing stray animals and was described in the 1842 tithe assessment as 'waste'. To the east boundary is the Combe Martin to Barnstaple road, cut as a turnpike in 1832. Prior to this, the village pound extended further eastward with the original road running past the curtilage of the property known as Middleton. After the cutting of the turnpike, the eastward side of the pound became part of the front garden of Middleton. The river Umber runs through this garden, largely in a culvert.

In 2002 a 2x1m test pit excavation was placed in the front garden of Middleton to determine the extent of smelting debris eastward across the turnpike road (MN1). This excavation was abandoned at 2.4m, due to

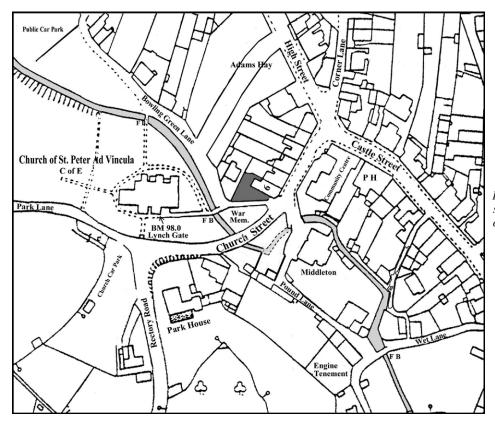


Figure 1: Map of Combe Martin showing the site of the test pit excavations at 6 Church Street.

the difficulty of excavating at this depth, though natural soil/bedrock was not reached. The excavation followed similar stratigraphical patterns to CC1-3, except that the undisturbed accumulations were greater in depth between contexts.

Volume analysis indicated greater proportions of slag in the 16th-17th century period and accumulations of variously-coloured industrial sands and fine grits not discovered in the CC excavations. This excavation cut through three major structural anomalies: at 0.8m depth a lime-ash floor, at 1.5m a cobbled floor and at 2.1m the base of a robbed out wall packed with crude slag like that found in CC3. To the side of this wall was a small sherd of BB1 pottery and at 2.3m a fine hammer-stone.

In 2003 a 2x1m excavation was placed at the southern end of Middleton's front garden to determine the extent of smelting debris in that direction (MN2). This excavation reached a depth of 2.1m before abandonment. The smelting debris, slag and artefacts recovered were similar to those discovered in MN1 except for a large quantity of oval stones (0.25-0.30m in diameter), seemingly large beach stones of Hangman Grit, in the south-west corner. At 1.3m depth lay bands of solidified fine mud of various colours and consistency, the thickest at 2m containing completely preserved vegetable matter and wood. This material had been water-borne and deposited very quickly. This could have been a discharge

from one of the upstream mines.

In 2004 a geophysical survey was carried out in the walled garden south of Middleton using both a gradiometer and resistance. This indicated building foundations and robbed-out trenches on the same alignment as Middleton, an area of possible wall footings and ditches which may represent demolished structures, and ditches on a different alignment to Middleton suggesting an earlier phase of activity on the site.

Quantification of the industrial waste

Similar assemblages of material were recovered from each of the trenches described above. The material from CC1, CC2 and MN1 was separated into different categories, on the basis of appearance, and quantified by context (Fig 2). The types of waste present were identified as lead slag, iron-smithing slag, geological material (predominantly quartz) and mineral fuel. From each trench, more than 60wt% of the material recovered was quartz waste from ore dressing, with small fragments of galena occasionally adhering to some of the quartz pieces. The lead slag comprised between 18 and 35wt% of the waste from each excavation, 2–4wt% of the waste was iron-smithing slag and 4–14wt% was mineral fuel.

Analysis of slag

Methods

Thirteen samples of the early post-medieval lead-smelting slag from a range of levels in trenches CC2 and MN1 were examined using scanning electron microscopy and energy dispersive spectroscopy (EDS) with a beam current of 1.2–1.5nA and an accelerating voltage of 25kV. Samples were chosen by appearance to obtain a representative selection and at least three 1.5mm² areas of each were analysed. Analyses of standard glasses (see Appendix, Table 2) showed that an analytical result would be anticipated to be within 2% of the SiO₂ content, 6% of the K₂O, CaO and FeO content, 10% of the MnO content, 14% of the lead and MgO content and 20% of the Al₂O₃ content. The detection limits for most elements was 0.1%, increasing to 0.3% for Sb₂O₅ and SnO₂ and 0.5wt% for Ag₂O.

Results

The analyses of the early post-medieval smelting slag recovered from Combe Martin confirm that it is waste from lead smelting, generally containing several weight percent of lead. All but two of the slag samples had similar compositions and were mainly iron silicates (Table 1). The compositional data for all of the analysed slag samples is given in Table 3 in the Appendix. Any silver remaining in the slag was present at levels below the detectable limit.

Predominantly two types of slag microstructure were observed. The first consisted of a glassy matrix sur-

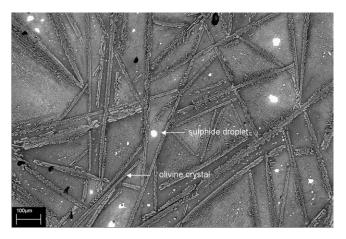


Figure 3: BSE image of slag microstructure showing a glassy matrix surrounding elongated olivine crystals and numerous, small, multi-phase sulphide inclusions (white).

rounding olivine crystals and numerous, small, multiphase sulphide inclusions (Fig 3). The olivine crystals were iron- and magnesium-rich, with ~6wt% MnO plus small amounts of zinc and calcium. The inclusions consisted of a combination of lead, copper, iron and zinc sulphide phases and small amounts of nickel. Antimony-rich inclusions were noted only rarely. The second common microstructure consisted of a very finely dispersed two phase matrix, again with numerous sulphide droplets (Fig 4).

Two of the analysed slag samples were atypical; one (MN1 Ub) was particularly rich in lime and phosphorus and the other (MN1 Ob) contained much higher levels of lead. In the latter sample, lead silicate, calcium pyroxene,

Table 1: The average composition of lead smelting slag from Combe Martin, analysed by SEM-EDS and normalised (wt%)

Na ₂ O	MgO	Al_2O_3	SiO ₂	P_2O_5	SO ₃	K ₂ O	CaO	TiO ₂	MnO	FeO	CuO	ZnO	PbO
0.70	2.49	7.46	41.24	1.39	1.01	1.97	8.83	0.40	2.54	26.33	0.16	1.77	3.53
0.21	0.41	0.53	2.52	0.21	0.27	0.13	2.51	0.03	0.52	2.86	0.10	0.77	1.16

Note: Average of 38 analyses of 13 slag samples; the two atypical fragments have been omitted

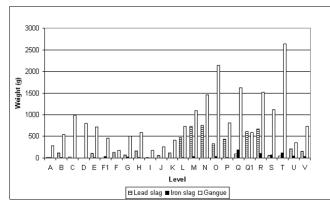


Figure 2: Weight of slags and gangue from each level in test pit MN1. Level A is nearest the surface.

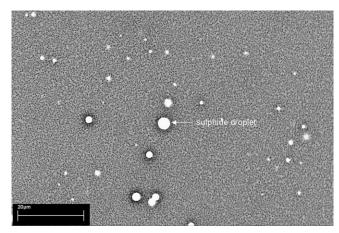


Figure 4: BSE image of slag microstructure with sulphide droplets (white) in a very finely dispersed two-phase matrix.

potassium feldspar, calcium phosphate and magnetite spinel phases were identified, together with numerous metallic lead inclusions. Sulphide phases (copper and lead sulphides predominantly) surrounded the lead inclusions and crystals of copper antimonide (also containing small amounts of nickel) were occasionally present within them.

Discussion

As most of the slag samples analysed, from all levels of the excavations, were compositionally similar, they were probably produced by similar technology. Some literature data on lead smelting slag are available for comparison (Rehren et al 1999; Tylecote 1990, 56; Percy 1870a; Gill 1992). The quantity of lime and iron oxide in smelting slags from different areas varies widely, largely as a result of variations in the type of gangue in the ore smelted in different localities; in some instances materials rich in fluxing compounds may also have been intentionally added. Between 4 and 10 wt% of lead oxide is reported in published analyses of lead-smelting slag ranging from Roman to 19th century in date (Rehren et al 1999; Tyelcote 1990; Percy 1870a) whereas most of the Combe Martin slag contains less than 4wt% lead oxide. Therefore most of the Combe Martin slag is probably a by-product of the final stage, rather than an intermediary stage, of an efficient lead smelting process, such as a slag hearth. In contrast the fragment of leadrich slag, containing particles of metallic lead and some partially reacted ore may be more representative of the slag produced in earlier stages of smelting, ie an ore hearth. Documentary sources suggest that water-powered bellows were used for smelting at Combe Martin and the siting of the smelting operation in the valley, close to the river, supports this. The slag had been heated sufficiently to become very fluid and homogeneous; the pieces examined contained few macroscopic bubbles or inclusions and the upper surfaces had flow marks but were quite flat.

The Combe Martin smelting slag was iron-rich and several weight percent of manganese were also detected. The concentrations of iron and manganese in the slag appear to be roughly correlated, suggesting that these two elements were introduced in the same material. The local orebodies are irregular masses of quartz and siderite (iron carbonate) in the slates (Scrivener and Bennett 1980), and the siderite may be a manganese-rich variety (Deer *et al* 1992) as iron and manganese were consistently present in fragments of gangue associated with ore amongst the waste from the Combe Martin excavations. It is likely, therefore, that the majority of the iron and manganese in the Combe Martin lead-

smelting slag was derived from the gangue in the local ore. Although some iron-smithing slag was also present in the assemblage, and this material is iron-rich, it contained very little manganese and is unlikely to have been the source of the iron in the lead-smelting slag. There is a documentary reference to the practice of adding iron ore as a flux from 1640 in Europe (Tylecote 1990, 58) but the mineralogy of the ore smelted at Combe Martin probably meant that this was unnecessary.

However, the lime content of the Combe Martin slag suggests that some lime-rich materials, not associated with the local ore, were added to the smelt. It is documented that difficulties were encountered smelting the Combe Martin ore and that Bulmer solved these problems. It is also known that ore was brought over from Clomyne, Co. Wexford, during this period and mixing ores may have been part of the solution devised by Bulmer, therefore some of the lime in the Combe Martin slag may derive from the lime-rich gangue of imported ores. Another possibility is that lime-rich compounds were added as a flux; there are references to the use of lime flux at a Yorkshire mill at the beginning of the 18th century and to the addition of limestone or fluorspar in an ore hearth in Derbyshire in 1729 (Tylecote 1990). Various lime-rich materials, including calcite, fluorspar, carboniferous limestone and large quantities of shells were found amongst the waste from Combe Martin.

It is known that some of the lead smelted by Bulmer was refined in Combe Martin. Materials used to construct absorbent cupellation hearths include bone ash (calcium phosphate) (Tylecote 1990, 60) and marl (a clay rich in calcium carbonate) (Percy 1870b, 188). Ash from tan turves (bark residue from the tanning process) held in an iron cradle were used to form cupellation hearths in 14th century Devon (Claughton 1992, 14) and ash from bark is rich in lime and phosphate (Tylecote 1990, 223–24). Although some calcareous material was found in the assemblages from the three Combe Martin excavations, analysis showed that it was not associated with the refining process and neither was any litharge recovered. Between 1–2wt% of phosphorus oxide was present in all of the slag samples analysed, and one atypical sample contained almost 10wt%. This sample also contained twice the amount of lime (17wt%) present in the majority of samples. The phosphorus is unlikely to have entered the slag with the ore or gangue. Phosphorus is present in the ashes of plants such as oak, although at varying levels depending on factors such as the species of plant, where it has grown, what part of the plant was ashed and at what temperature. However plant ashes are unlikely to be the predominant source of the phosphorus in the

Combe Martin slag as considerable quantities would be required to produce these concentrations of phosphorus. In addition, the other major constituents of more phosphorus-rich plant ashes include potash and lime and so associated increases in the levels of these oxides would also be expected if plant ashes were the predominant source of the phosphorus. Although the atypical phosphorus-rich sample contains elevated levels of lime, the concentrations of potash are comparable with the rest of the samples. Therefore the increased levels of lime and phosphorus in this atypical sample are more likely to be due to the incorporation of a more phosphorus-rich material like bone ash, Ca₃(PO₄)₂, which would contribute roughly similar amounts (by weight) of lime and phosphorus oxide to the slag. In summary, the quantities of phosphorus detected in the slag suggest that some litharge-impregnated hearth material, likely to be bone ash in this case, was smelted in the ore hearth, together with local ore and an additional source of lime such as an imported ore with lime-rich gangue or a lime-rich flux. (The lime-rich flux or gangue from imported ore and the cupellation hearth lining would all have contributed to the lime content of the slag). Reworking of the cupellation hearth lining would enable the smelters to recover the lead from the litharge, and in particular any silver lost in cracks and fissures in the hearth, and may also help to explain the absence of cupellation hearth material at the site.

The use of coal as fuel

There is a general acceptance amongst historians that one of the factors stimulating the industrial revolution of the late 18th and early 19th century in Britain was the shift to mineral sources of fuel, and the use of that fuel to generate power, releasing human and agricultural resources to industrial purposes (Wrigley 2010, 36–46). The move away from organic fuel for domestic purposes was well underway in Britain by the end of the medieval period, and coal had certain industrial uses throughout, but its presence at Combe Martin suggests that the transition was taking place in non-ferrous metallurgy, perhaps up to one hundred years before the perceived change with the introduction of the reverberatory furnace. (The iron-smithing slag that was also present in all of the industrial waste assemblages from Combe Martin contained preserved fragments of charcoal indicating that mineral fuel had not been used for iron smithing).

Two samples of coal recovered from excavation MN2 were analysed by Dr John M Jones, late of the Fossil Fuels Institute at the University of Newcastle, using vitrinite reflectance determination. Sample 1 (1.4–1.5m

depth) had a maximum oil reflectance of 2.50% (indicating a carbon content of 92.0% and 8% volatile matter) and Sample 2 (0.9–1.0m depth) had a maximum oil reflectance of 2.24% (carbon content 91.9%, volatile matter 10%). Both samples are therefore semi-anthracite, 102 in the old NCB (National Coal Board) ranking. Such coals were mined in south-west Wales, close to the coast of the Burry Inlet west of Llanelli, where there is evidence from the portbooks (PRO E190) of shipments overseas from the late 16th century, and coastwise from the early 17th century.

It is not surprising that Combe Martin should be at the forefront of the transition to coal given its proximity to a coastal coalfield and the ease with which the fuel might be shipped. By the mid 17th century the port supported a small fleet of ships of 15 to 20 tons engaged in a regular trade in coal from Pembrokeshire and Swansea for both lime-burning and domestic use (TNA: PRO E190/953/4 et seq). Unfortunately, no shipments to Combe Martin from the Burry Inlet have yet been identified in the documentary sources.

Conclusions

Although in the middle of Combe Martin village, between the church and the manorial centre, the site now occupied by the property Middleton was probably the location of lead smelting activity in the 16th–17th century with a terminal date of perhaps 1690. The recovery of large quantities of quartz, pieces of slate and fragments of ore from the site suggest that ore dressing was also taking place nearby, making use of the water supply. Large quantities of waste were generated and dumped, some of it in the direction of Christmas Cottage. A geophysical survey failed to reveal any clear evidence for the hearth(s), however permission has been received to investigate the anomalies in the walled garden south of Middleton.

Most of the slag analysed, from all levels of the excavations, was compositionally similar and so produced by similar technology. The slag was probably produced by the mining entrepreneur Bulmer, and later lessees, using an ore hearth and a slag hearth blown by water-powered bellows. The low lead content of the slag indicates that it was a by-product from the final stage of an efficient smelting process, *ie* a slag hearth. The single sample of lead-rich slag identified may be more representative of the slag produced in the earlier stages of the smelting process, *ie* the ore hearth. Whilst the evidence for the introduction of the ore hearth into Combe Martin is largely circumstantial, Bulmer became

involved because he was able to resolve the problems that had been encountered by others smelting the local ores. This would be consistent with the introduction of an ore hearth as these were in use on Mendip where Bulmer was based prior to his arrival at Combe Martin.

The slag was rich in iron, probably derived from the siderite gangue in the local ore. The slag also contained lime, some of which may be from the gangue of imported ores or added lime-rich fluxes, as suggested by historical references and the identification of minerals from outside the immediate locality, such as fluorspar and calcite, amongst the waste. No waste from lead refining, to extract silver, was identified in the excavated assemblages, although both mineralogical and documentary evidence indicates that silver would have been the primary product at Combe Martin. However the quantities of phosphorus detected in the slag suggest that some litharge-impregnated hearth material, probably bone ash, was smelted in the ore hearth, together with local and imported ore. This is further evidence that the refining works were located near to the smelting site. Reworking the cupellation hearth lining would enable any silver-bearing lead remaining in the lining material to be recovered and would have further increased the lime content of the slag.

The presence of coal provides some of the earliest evidence for the transition to mineral fuel in the processing of lead ores. It is possible that the coal was only used in the slag hearth to affect a complete recovery of the lead and silver. However, with no organic debris being found amongst the residues, we should consider the possibility that coal may have been the only fuel used throughout the smelting process.

References

Archive sources

TNA: PRO: The National Archives: Public Record Office, Kew Exchequer: Portbooks (E190)

Published sources

Claughton P 2004, *The Combe Martin mines*, 2nd edn (Combe Martin).

Claughton P 1992, 'Mediaeval silver-lead smelting in Devon', in L Willies and D Cranstone (eds), *Boles and smeltmills* (Matlock Bath), 12–14.

Claughton P 2003, Silver mining in England and Wales, 1066–1500. Unpublished PhD thesis, University of Exeter.

Crossley D 1990, Post-medieval archaeology in Britain (Leicester).

Crossley D and Kiernan D 1992, 'The lead-smelting mills of

Derbyshire', Derbyshire Archaeological Journal 112, 6-47.

Deer W A, Howie R A and Zussman J 1992, *An introduction to the rock forming minerals* (Harlow).

Dunkerley T 2002, Archaeological evidence as to the smelting of silver-lead ores during the 16th and 17th century in Combe Martin, North Devon (unpublished report).

Gill M C 1992, 'Analysis of lead slags', in L Willies and D Cranstone (eds), *Boles and smeltmills* (Matlock Bath), 51–53.

Gough J W 1967, The mines of Mendip (Newton Abbot).

Kiernan D 1989, *The Derbyshire lead industry in the sixteenth century* (Chesterfield).

Oliver G (ed) 1854, A View of Devonshire in MDCXXX with a pedigree of most of its gentry by Thomas Westcote, Gent. (Exeter).

Paynter S, Dunkerley T and Claughton P 2003, *Lead smelting waste from the 2001–2002 excavations at Combe Martin, Devon* (Portsmouth: Centre for Archaeology Report 79/2003).

Percy J 1870a, Metallurgy, Volume III - Part 2, Lead (London).

Percy J 1870b, Metallurgy, Volume III - Part 1, Lead desilverization (London).

Rehren T, Schneider J and Bartels C 1999, 'Medieval lead-silver smelting in the Siegerland, West Germany', *Historical Metallurgy* 33(2), 73–84.

Scrivener R C and Bennett M J 1980, 'Ore genesis and controls of mineralisation in the Upper Palaeozoic rocks of North Devon', *Proceedings of the Ussher Society*, Annual Conference of the Ussher Society, January 1980, 54–58.

Tylecote R F 1990, *The prehistory of metallurgy in the British Isles* (London).

Wrigley E A 2010, Energy and the English Industrial Revolution (Cambridge).

The authors

Sarah Paynter is a materials scientist who worked in industrial research before completing a PhD in archaeological sciences in 2001. Since then she has worked for English Heritage investigating a range of materials of all periods including glass, ceramics, metals and waste products from high temperature industrial processes

Address: English Heritage, Fort Cumberland, Eastney, Portsmouth PO4 9LD

e-mail: Sarah.Paynter@english-heritage.org.uk.

Peter Claughton is an Honorary University Fellow in the College of Humanities at the University of Exeter. For further details see previous paper by Peter Claughton and Chris Smart

Address: Department of History, University of Exeter, Amory Building, Rennes Drive, Exeter EX4 4RJ

e-mail: P.F.Claughton@exeter.ac.uk

Trevor Dunkerley

Address: Christmas Cottage, 6 Church Street, Combe Martin, North Devon EX34 0LQ

e-mail: trevordunkerley@waitrose.com

Appendix

Table 2: EDS analyses of standard glasses (normalised wt%), compared to their known compositions given in italics.

	Na ₂ O	MgO	Al_2O_3	SiO ₂	P_2O_5	SO ₃	K ₂ O	CaO	TiO ₂	MnO	FeO	CoO	CuO	ZnO	SnO ₂	$\mathbf{Sb_2O_5}$	BaO	PbO
Corning D	1.31	4.07	5.41	55.00	4.00	0.30	11.41	14.99	0.40	0.47	0.44	0.02	0.40	0.10	0.13	0.96	0.33	0.27
Av (4)	1.28	4.01	5.16	55.61	3.94	0.33	11.27	14.85	0.43	0.56	0.47	bd	0.37	0.15	bd	0.94	0.26	0.18
St.Dev	0.11	0.05	0.06	0.17	0.02	0.05	0.03	0.07	0.03	0.04	0.04		0.03	0.05		0.14	0.09	0.03
Corning A	14.49	2.8	1.01	66.43	0.14	0.16	2.92	5.29	0.8	0.96	0.98	0.15	1.22	0.04	0.28	1.72	0.54	0.08
Av (4)	13.93	2.53	1.04	67.46	0.14	0.20	2.89	5.12	0.81	1.03	0.95	0.20	1.23	bd	bd	1.63	0.50	bd
St.Dev	0.19	0.09	0.06	0.32	0.10	0.07	0.03	0.03	0.04	0.01	0.03	0.10	0.05			0.07	0.07	
Corning C	1.21	2.85	0.88	35.03	0.09	0.16	2.74	5.08	0.82	0.00	0.30	0.17	1.18	0.04	0.22	0.00	12.15	37.08
Av (3)	0.77	2.75	1.07	35.66	bd	bd	2.89	5.09	0.80	bd	0.27	0.15	1.22	bd	bd	bd	11.94	37.13
St.Dev	0.18	0.13	0.01	0.17			0.05	0.05	0.07		0.07	0.01	0.11				0.11	0.12

Note: bd = below detection limit

Table 3: EDS analyses of smelting slag from the Combe Martin excavations.'

Sample		Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO	FeO	CuO	ZnO	Sb ₂ O ₅	PbO
CC2 Fa (3)	Av	1.02	2.65	8.00	46.56	1.35	1.05	2.22	8.40	0.42	2.44	20.79	0.29	2.54	bd	2.17
	StDev	0.11	0.09	0.07	0.39	0.04	0.30	0.02	0.23	0.01	0.10	0.42	0.21	0.19	-	0.21
CC2 Ga (3)	Av	0.56	2.27	7.90	36.73	1.21	1.40	1.85	6.27	0.41	3.09	31.23	0.13	1.01	bd	5.80
	StDev	0.18	0.12	0.06	0.12	0.03	0.03	0.02	0.07	0.02	0.03	0.23	0.06	0.09	-	0.10
CC2 Gb (1)	-	0.80	2.15	7.89	40.66	1.18	0.55	1.91	6.79	0.38	2.27	27.56	0.19	1.38	bd	6.12
CC2 I (4)	Av	1.00	2.86	7.32	41.81	1.30	1.16	1.96	7.89	0.38	2.59	25.89	0.15	2.90	bd	2.61
	StDev	0.08	0.44	0.06	1.34	0.12	0.17	0.04	1.77	0.03	0.46	1.54	0.07	0.64	-	0.06
MN1 Oa (3)	Av	0.80	2.12	7.58	39.23	1.43	0.82	1.86	7.93	0.42	2.44	27.51	0.28	2.51	bd	4.89
	StDev	0.07	0.21	0.14	0.40	0.02	0.24	0.07	0.59	0.03	0.15	1.04	0.11	0.03	-	0.38
MN1 Ob (3)	Av	0.01	1.55	4.09	22.19	1.85	0.00	1.18	6.60	0.20	0.90	10.13	0.32	0.34	1.65	48.78
	StDev	0.01	0.11	0.47	0.82	0.11	0.00	0.45	0.58	0.02	0.04	0.52	0.15	0.05	0.16	1.91
MN1 Oc (3)	Av	0.54	1.56	6.27	40.42	1.50	1.16	1.90	16.19	0.39	1.25	22.66	bd	1.99	bd	3.98
	StDev	0.05	0.09	0.09	0.30	0.11	0.07	0.02	0.38	0.04	0.01	0.23	=	0.05	=	0.40
MN1 Ta (3)	Av	0.68	2.73	7.65	38.97	1.58	1.14	1.91	7.95	0.40	3.25	29.12	0.17	1.37	bd	2.86
	StDev	0.14	0.18	0.17	0.42	0.08	0.07	0.07	0.06	0.03	0.06	0.50	0.06	0.03	=	0.31
MN1 Tc (3)	Av	0.62	2.18	6.60	40.36	1.09	1.26	1.85	11.04	0.38	2.07	27.35	0.17	2.20	bd	2.62
	StDev	0.05	0.20	0.02	0.58	0.03	0.12	0.04	1.12	0.03	0.23	1.12	0.05	0.12	-	0.29
MN1 Ua (3)	Av	0.45	2.91	7.64	42.68	1.36	0.69	2.01	7.81	0.44	2.88	26.61	0.19	0.82	bd	3.45
	StDev	0.18	0.07	0.22	0.25	0.05	0.03	0.05	0.09	0.03	0.08	0.34	0.04	0.07	-	0.16
MN1 Ub (3)	Av	0.86	2.07	6.22	34.59	9.54	0.45	2.11	17.06	0.37	1.59	17.86	bd	1.66	bd	5.33
	StDev	0.15	0.09	0.20	1.26	0.89	0.05	0.06	0.41	0.03	0.10	0.24	=	0.18	-	0.66
MN1 Uc (3)	Av	0.57	2.61	7.26	41.51	1.59	0.77	2.02	9.16	0.37	2.43	26.89	0.13	1.52	bd	3.03
	StDev	0.07	0.03	0.08	0.14	0.02	0.09	0.02	0.18	0.03	0.06	0.08	0.01	0.04	=	0.13
MN1 Va (3)	Av	0.74	2.67	8.10	43.06	1.09	1.08	2.08	8.36	0.37	2.77	24.85	bd	1.20	bd	3.08
	StDev	0.13	0.23	0.34	0.21	0.08	0.05	0.04	0.07	0.01	0.12	0.26	-	0.05	=	0.11
MN1 Vb (3)	Ave	0.47	2.63	7.61	39.58	1.78	0.59	1.82	7.50	0.39	2.90	29.09	0.21	0.65	bd	4.65
	StDev	0.04	0.22	0.34	0.57	0.10	0.19	0.18	0.22	0.04	0.13	0.98	0.09	0.09	-	0.27
MN1 Vc (3)	Av	0.82	2.68	7.45	43.99	1.50	1.11	2.13	8.43	0.43	2.38	23.73	0.09	2.34	bd	2.71
	StDev	0.13	0.08	0.14	0.13	0.03	0.06	0.03	0.04	0.03	0.02	0.15	0.02	0.20	-	0.07

Notes: Sample details given in the first column include the excavation (CC2 or MN1), the level within the excavation (labelled alphabetically and indicated by the capital letter) and the sample label (indicated by the lower case letter, as multiple samples from the same level were analysed). The number of analyses are indicated in brackets and the normalised average (in wt%) and standard deviation are given. bd = below detection limit.