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Summary

Slag from the smelting of silver-rich lead ore, produced in the 16th / 17th centuries, was recovered by Trevor Dunkerley during excavations in Combe Martin, North Devon. Samples of slag from 19th century smelting in the village were also obtained for comparison. The slag was examined and analysed using scanning electron microscopy and energy dispersive spectroscopy. The 16th / 17th century slag was predominantly a glassy iron silicate, containing small amounts of metal sulphide. This slag is thought to be waste from a slag hearth. The lead content was about 3.5wt% and the silver content was below detectable levels. The 19th century material was a highly crystalline, porous iron alumina silicate slag. The lead and silver contents were below detectable levels. This slag is thought to be waste from the flowing furnace used by the Combemartin and North Devon Smelting Co Ltd.

Keywords

Post Medieval
Lead
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Metal Working-non Fe
Technology

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Introduction

The lead ore mined at Combe Martin in Devon has been particularly sought-after since it was discovered that it contained significant amounts of silver; 0.28kg per tonne have been recorded (Scrivener and Bennett, 1980). There is documentary evidence concerning lead smelting and silver extraction in the Combe Martin area (Claughton, 1989, 1992 and 2003) particularly once the Crown became directly involved in the working of the Devon mines at the end of the 13th century.

The argentiferous lead ores worked at Combe Martin are in the marine Lester Slates and Sandstones formation, concentrated in a unit of mudstone. The ore bodies are irregular reef-like masses of quartz and siderite ($FeCO_3$) with base-metal sulphides that have developed in the cores of overturned folds in the slates. The principal sulphides are galena (PbS) and sphalerite (blende ZnS), with minor chalcopyrite ($CuFeS_2$) and pyrite (FeS_2). Tetrahedrite ($Cu_{12}Sb_4S_{13}$), millerite (NiS) and stibnite (Sb_2S_3) have also been recorded. Traces of galena and sphalerite are also present in the limestones of the overlying Combe Martin slates (Scrivener and Bennett, 1980).

Finding the Combe Martin ores was difficult as they are not cross-cutting hydrothermal veins of the type familiar in Cornwall and South Devon (Scrivener and Bennett, 1980). Problems of access and drainage might then be encountered when attempting to mine the ore and the market price of lead and silver also varied. These factors contributed to the repeated cycles of boom and bust experienced by the Combe Martin lead-silver mining and smelting industry over the centuries. Periods of prosperity generally lasted no more than ten years (Claughton, 1989).

No archaeological evidence of early post-medieval lead smelting was known from the area until Trevor Dunkerley excavated three 2x1m test pits in Combe Martin village in 2001-2002 (Dunkerley, 2002). The first two trenches were positioned in the garden of Christmas Cottage NGR: SS 5868 4631 (trenches CC1 and CC2) and the third in the garden of an adjacent property called Middleton NGR: SS 5870 4630 (trench Mn1). Large quantities of glassy, opaque, grey / green / blue slag, with a low porosity and flowed upper surfaces, were recovered from all three trenches. The slag was identified as probable waste from lead smelting and John Allan of Exeter Museum Services dated the slag-rich deposits to the 16th / 17th centuries by means of the associated pottery and clay pipe fragments.

Lead smelting also took place in Combe Martin in the mid-19th century (Claughton, 1989). Surface finds of a porous, dark grey slag, believed to be waste from the 19th century process, were collected from the village for comparison with the earlier slag.

The slag samples were analysed by Sarah Paynter at the English Heritage Centre for Archaeology. The documentary research was completed by Peter Claughton of the Centre for South-Western Historical Studies at the University of Exeter.

Analytical method

The principal technique used in this study was scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS) analysis. The SEM uses a beam of electrons to obtain an image and can achieve large magnifications. In BSE images, areas of the sample with different compositions are seen as varying greyscale shades. Elements with large atomic numbers, such as lead, scatter back larger numbers of electrons and so lead-rich areas of a sample appear light grey to white. In contrast areas containing large concentrations of elements with low atomic numbers, such as aluminium, appear dark grey to black. The sample microstructure images in this report are back-scattered electron (BSE) images from an SEM. Samples were also analysed using EDS, whilst in the SEM. The microscope electron beam causes the sample to generate X-rays with characteristic energies. The X-rays are detected and used to determine the composition of the sample.

In this study a Leo 440I Stereoscan electron microscope was used with Isis EDS software. The conditions used for analysis were a beam current of between 1.2 and 1.5nA, an accelerating voltage of 25kV and a counting time of 150s. Regular analyses of standard glasses of known composition showed that there was good agreement of the known and measured compositions (appendix table A1). On the basis of these results, an analysis would be anticipated to be within 4% relative of the Na_2O content, 14% of the MgO content, 20% of the Al_2O_3 content, 2% of the SiO_2 content, 5% of the K_2O content, 6% of the CaO content and 13% of the lead content. The detection limits for most elements was about 0.1%, increasing to 0.3% for Sb_2O_5 and SnO_2 and 0.5wt% for Ag_2O.

Assemblage description and quantification

Each trench was excavated in a series of 10cm deep levels, labelled A (0-10cm) to H (70-80cm) in trench CC1, A to I (80-90cm) in trench CC2 and A to V (220-230cm) in trench Mn1. The assemblage from each level comprised various components, including lead smelting slag, iron-working slag, geological material (mainly quartz but including ore fragments and pieces of slate), fuel (predominantly mineral fuel), vitrified clay and calcareous material. These categories are described in more detail below.

The *iron-working slag* was dark, often rusty and vesicular and occasionally contained charcoal inclusions. Most of the fragments were small but those with sufficient diagnostic features were categorised as waste from iron smithing (the process of shaping iron) rather than iron smelting (the process of extracting iron from the ore) (Bayley et al, 2001).

The *geological material* is largely waste from the process of preparing the ore for smelting by removing the majority of the gangue (non-ore material) associated with the ore beforehand. The material in this category was predominantly quartz. In addition to gangue from local ore, calcite ($CaCO_3$), fluorite (fluorspar CaF_2) and carboniferous limestone from imported ore were also identified.

The *vitrified clay* is fired clay that has developed a glassy surface through reacting with materials such as charcoal ashes at high temperatures. Although vitrified clay is often a by-product of metalworking processes, it can also be produced in many other ways and so is not diagnostic of metalworking.

Fuel was found in most levels in all of the trenches and was predominantly mineral fuel, although rare charcoal and turve / peat fragments were recovered.

The *calcareous material* category encompassed all of the lime-rich waste present in the assemblages. This group includes pieces of natural limestone, fragments of melted lime-rich clay or stone and some mortar-type material comprised of lime binder and a coarse aggregate. Samples of this material were analysed and are discussed later in this report.

The different types of waste present in the assemblages from each level of excavations CC1, CC2 and Mn1 were identified and weighed (with the exception of the calcareous material). The results are tabulated in the appendix tables A2, A3 and A4 and plotted in figures 1 to 3. In trench Mn1, below section L (1.2-1.3m), fuel fragments were degraded and difficult to extract as a quantifiable sample.

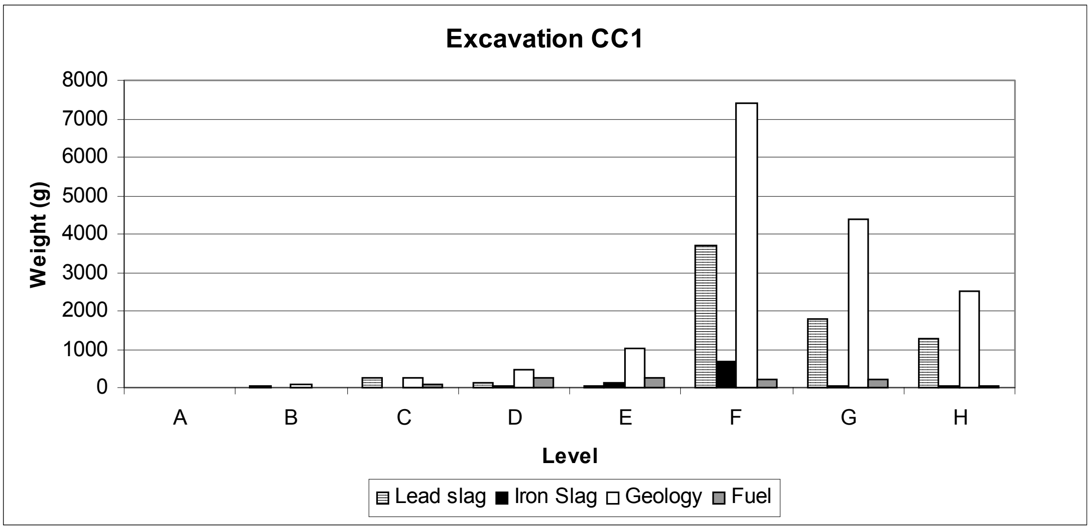

Figure 1: Quantities of lead slag, iron working slag, geological material and fuel (g) recovered by level from trench CC1.

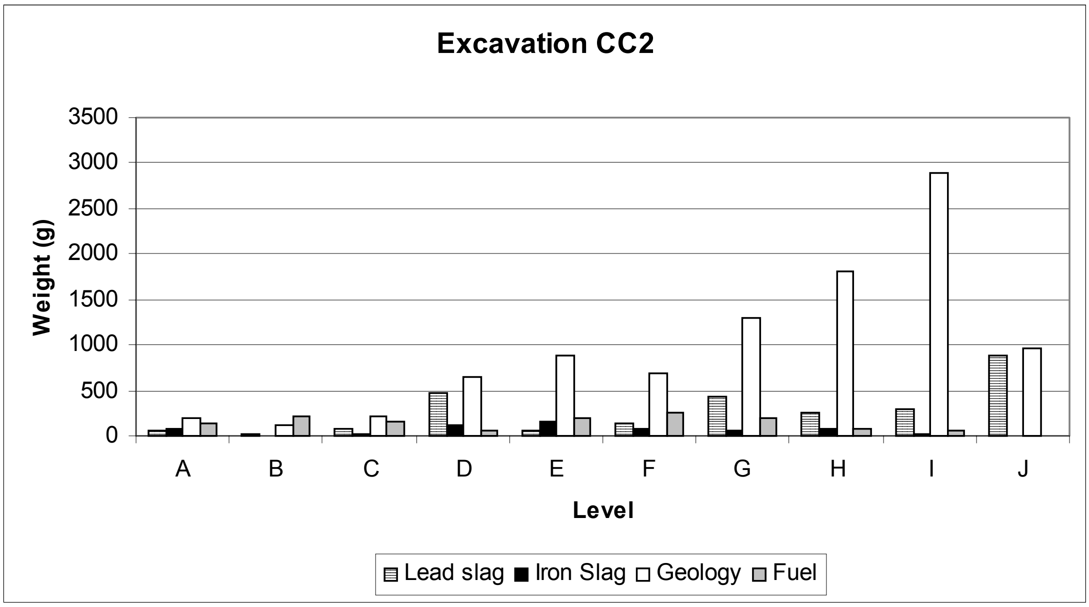

Figure 2: Quantities of lead slag, iron working slag, geological material and fuel (g) recovered by level from trench CC2.

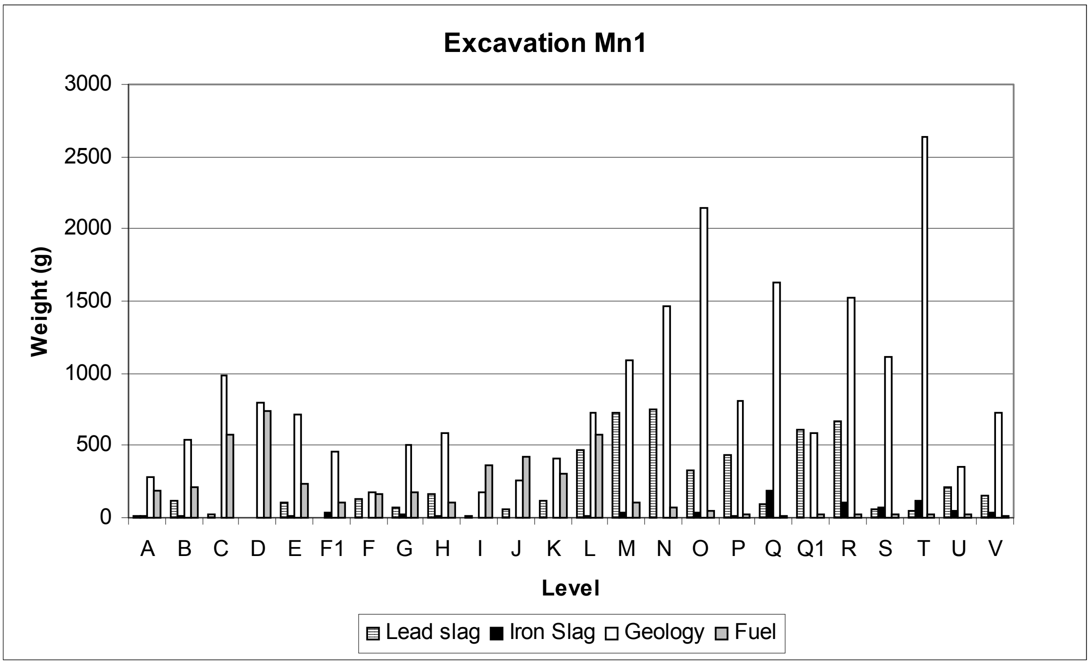

Figure 3: Quantities of lead slag, iron working slag, geological material and fuel (g) recovered by level from trench Mn1.

In trench CC1 (figure 1) over half the slag was found in level F and the rest mainly in levels G and H. The associated pottery and, in level F pipe fragments, suggests mid-16th to mid-17th century dates for these levels. In trench CC2 the most slag was found in level J and to a lesser extent levels D, G, H and I. The absence of pipe fragments in levels H, I and J, and the associated pottery, suggests 16th century dates for these levels. Level G probably dates to the first part of the 17th century. In trench Mn1 the majority of the slag was recovered from levels L to R. Clay pipe fragments, although present, were not in sufficient quantity to offer definitive dating evidence. The dates of the associated pottery suggest that sections L through to Q1 are 17th century and that sections R through U are 16th century in date. Therefore the majority of the lead smelting slag is thought to have been deposited between the mid-16th and mid-17th centuries. Some early medieval, Saxon-Norman and Romano-British pottery fragments were recovered from the lower levels of trenches CC1 (G and H) and Mn1 (T, U and V) along with a Bronze Age hammer stone and Neolithic flint scrapers and cores. These fragments and artefacts are thought to be residual and the slag in these levels was similar in appearance and composition to the slag from other levels (see analytical results) and so was probably produced by the same process during roughly the same period.

Analytical results

Early post-medieval (16th / 17th century) slag

Thirteen samples of early post-medieval slag from a range of levels in trenches CC2 and Mn1 were examined. Samples were chosen on the basis of their appearance to obtain a representative selection. At least three 1.5mm^2 areas of each were analysed. The samples generally had similar compositions and were predominantly iron silicates (table 1). Any silver remaining in the slag was present at levels below the detectable limit (0.5wt%). The data is tabulated in full in appendix table A5.

Table 1: The average composition (top row) and standard deviation (bottom row) of 13 slag samples (total of 38 analyses, having omitted the two atypical fragments described below), analysed by EDS and normalised (see appendix)

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	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

A range of microstructures was noted, one of the most common consisting of a glassy matrix containing olivine crystals and numerous small sulphide droplets (figure 4). The olivine crystals $(Mg,Fe)_2[SiO_4]$ contained around 50wt% FeO, 13wt% MgO, 6wt% MnO and small amounts of zinc and calcium. The droplets consisted of a combination of sulphide phases, such as one containing predominantly lead and sulphur, another mainly copper, iron and sulphur and another zinc, iron and sulphur as shown in figure 5. Small amounts of nickel were also detected in the droplets. Antimony-rich inclusions were noted more rarely, for example in a sample from CC2 level F, which contained approximately 80wt% lead, 9wt% antimony, 7wt% copper and small amounts of iron (2wt%), zinc (0.6wt%) and nickel (0.6wt%).

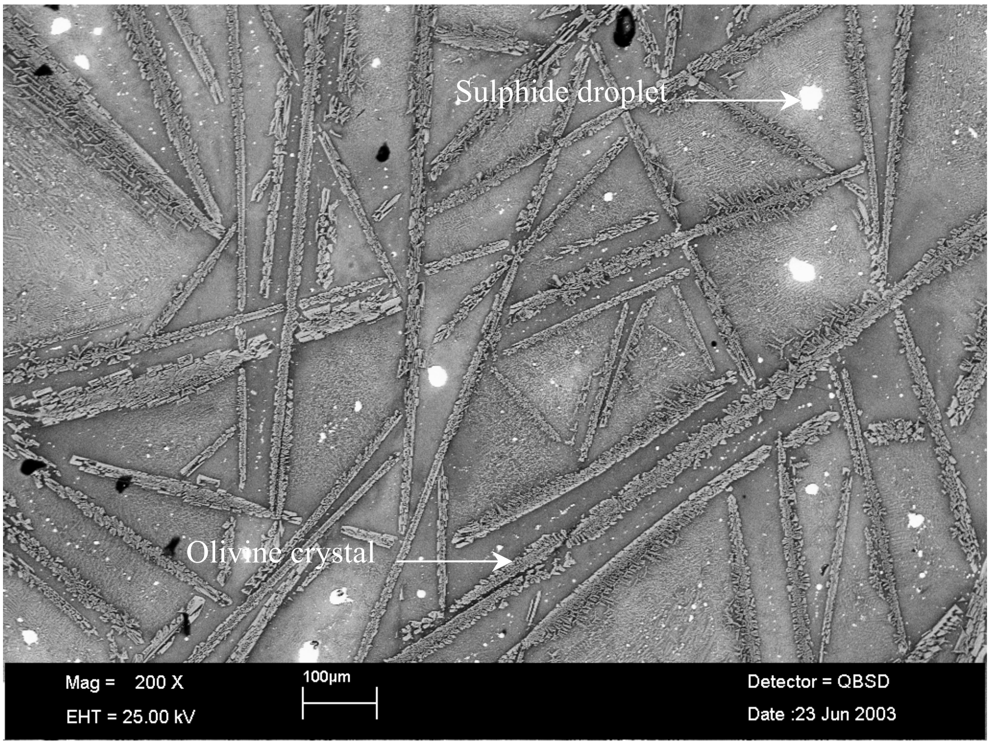

Figure 4: Back-scattered electron image of early post-medieval lead smelting slag, showing olivine crystals and multiphase sulphide droplets in a glassy matrix.

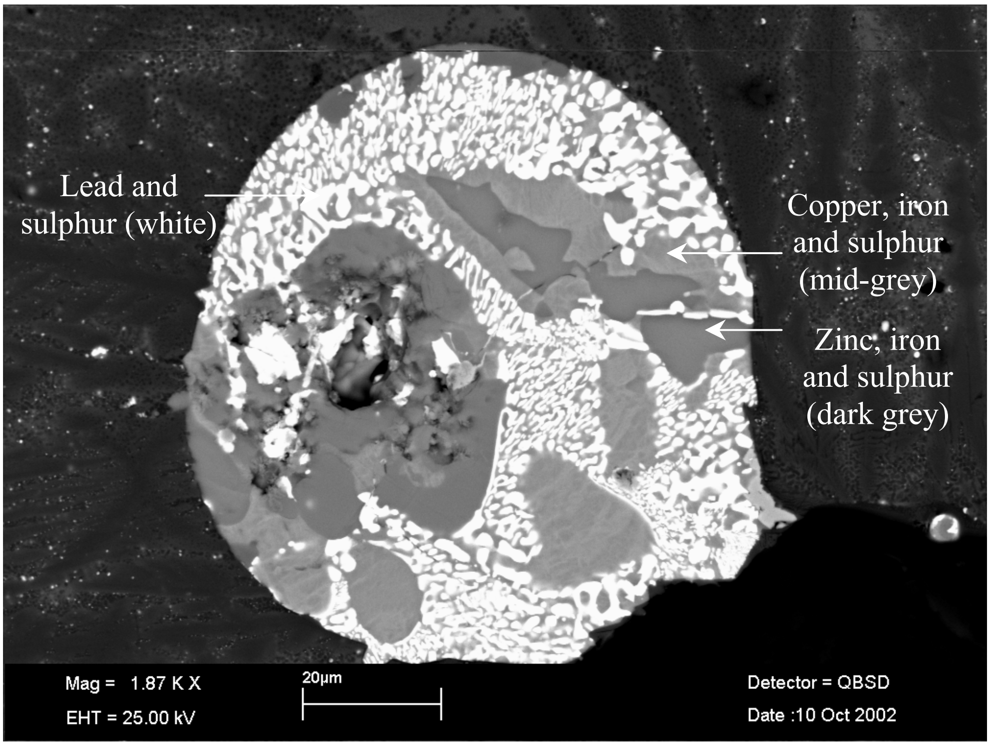

Figure 5: Back-scattered electron image of multiphase sulphide droplet in early post-medieval lead smelting slag.

Another common microstructure consisted of a matrix made up of two very finely dispersed phases, too small to analyse, and again sulphide droplets (figure 6). In many instances, regions of the olivine-type and dispersion-type microstructures described above were observed in the same sample.

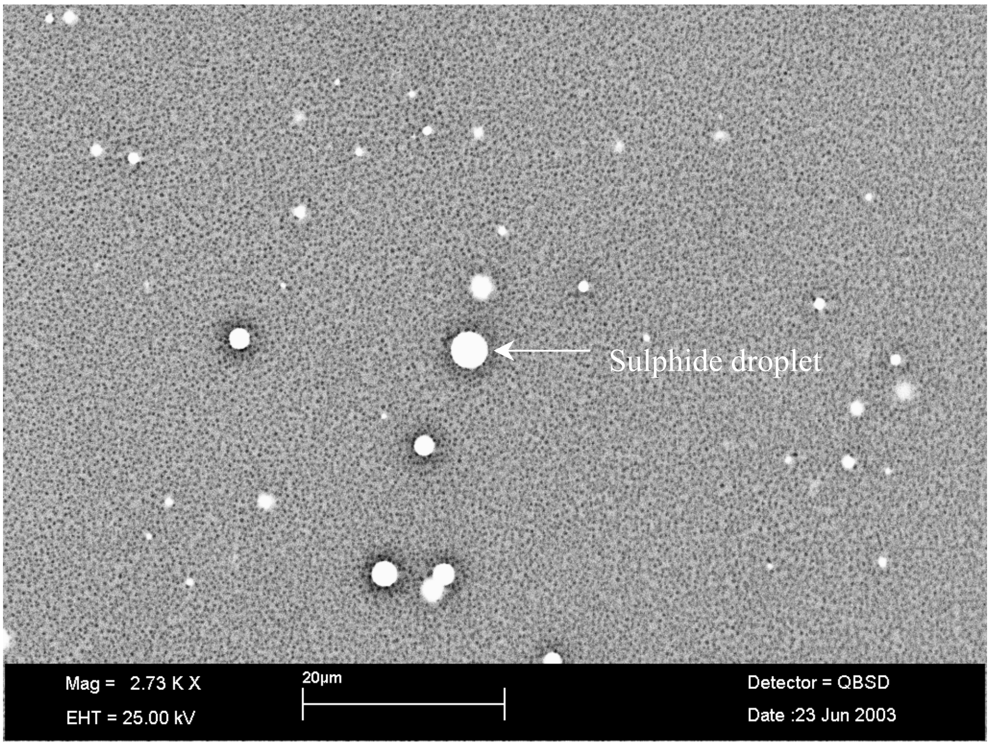

Figure 6: Back-scattered electron image of early post-medieval lead smelting slag, showing multiphase sulphide droplets in a matrix made up of two finely interspersed phases.

Two of the slag samples analysed were atypical. A fragment from trench Mn1, level U, was particularly phosphorus-rich and contained many elongated crystals of calcium phosphate (with some substitution of magnesium and iron for calcium) in a glassy matrix (figure 7).

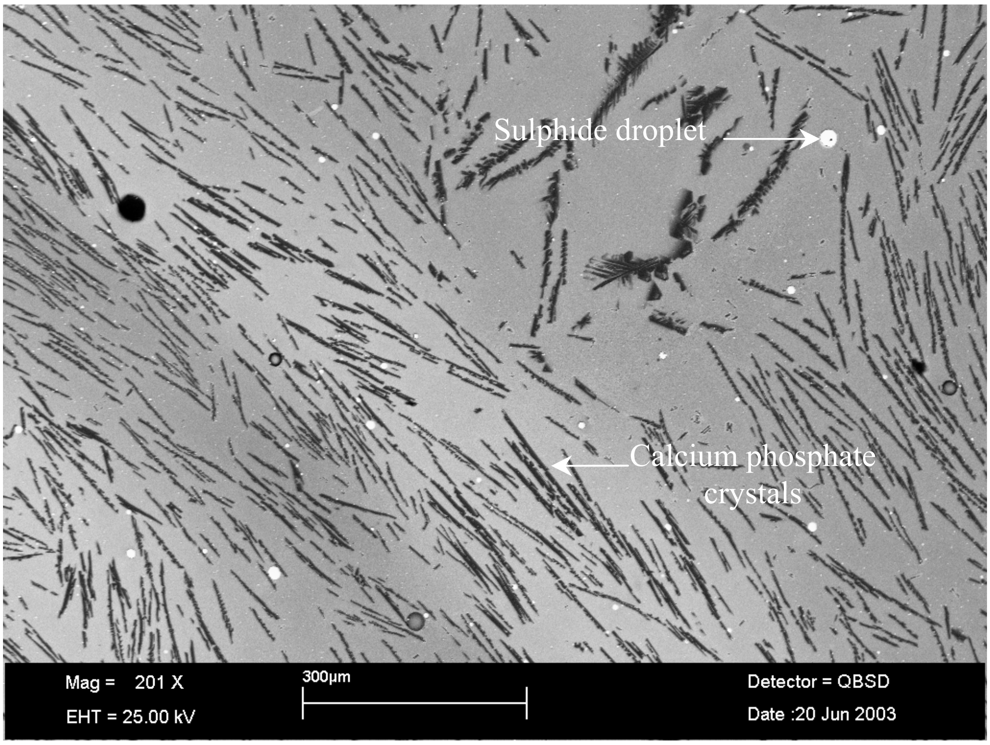

Figure 7: Back-scattered electron image of atypical early post-medieval lead smelting slag sample, showing calcium phosphate crystals and multiphase sulphide droplets in a glassy matrix.

A fragment of slag from trench Mn1, level O, was unusually lead-rich. In this sample needle-like lead silicate crystals, calcium pyroxene crystals (for example $(Ca,Mg,Fe^{2+},Al)_2(Si,Al)_2O_6$), alkali feldspar crystals ($KAlSi_3O_8$), calcium phosphate crystals and magnetite spinel crystals ($Fe^{2+}Fe^{3+}{}_2O_4$) had formed. The slag also contained numerous particles of lead metal, within which small pieces of galena occasionally survived. Sulphide phases (copper and lead sulphides predominantly) were forming around these lead metal particles (figure 8).

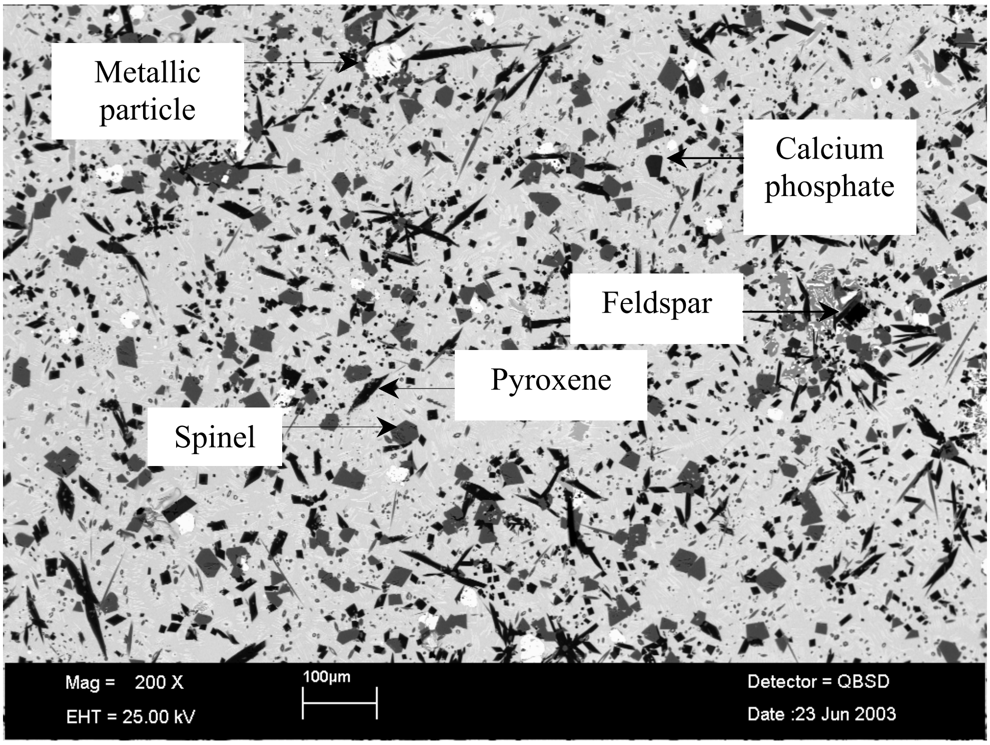

Figure 8: Back-scattered electron image of atypical early post-medieval lead smelting slag sample, showing lead silicate crystals (very fine, needle-like, white crystals dispersed throughout the matrix), alkali feldspar crystals, calcium pyroxene crystals, calcium phosphate crystals, magnetite spinel crystals and metallic particles in a glassy matrix.

Other early post-medieval materials

Samples of the iron-working slag and calcareous material found with the lead smelting slag were also analysed. The iron slag was distinguishable from the lead smelting slag as it contained no lead, zinc or copper. The microstructure was consistent with that expected for iron smithing waste and consisted predominantly of wustite (FeO) and olivine crystals. The calcareous material fell into two categories. Some appeared to be mortar and consisted of a lime-rich binder and coarse particulate inclusions. No lead, zinc, copper or silver was detected in this material and so it is unlikely to be associated with either the lead smelting or silver refining processes. The second category included natural lime-rich stone, sometimes associated with slate. Small amounts of zinc and traces of arsenic were detected in this material but probably occurred naturally (Scrivener and Bennett, 1980). Traces of zinc and arsenic were also occasionally detected in the fragments of melted lime-rich clay or stone in the assemblage. Therefore, although this material had been strongly heated there was no diagnostic evidence to link it to the lead smelting or silver refining processes.

Late post-medieval (19th century) slag

The 19th century smelting slag contained high concentrations of alumina, iron oxide and lime and several weight percent of phosphorus (table 2). The amounts of lead, silver, zinc and copper in the bulk composition were below detectable limits. The data is tabulated in full in appendix table A6.

Table 2: The average composition (top row) and standard deviation (bottom row) of 2 slag samples (total of 7 analyses), analysed by EDS and normalised (see appendix)

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	FeO	CuO	ZnO	BaO	PbO
1.12	2.66	29.87	36.78	2.07	0.15	1.24	8.07	0.65	0.31	16.23	bd	bd	0.78	bd
0.42	0.29	2.90	2.43	0.39	0.14	0.22	2.05	0.22	0.07	2.16	-	-	0.44	-

The highly crystalline microstructure of the 19th century slag (figure 9) differed greatly from the more glassy microstructure of the earlier slag samples. The 19th century slag contained angular crystals and dendrites of a spinel phase (for example hercynite $Fe^{2+}Al_2O_4$, with considerable substitution of Mg for Fe^{2+} and Fe^{3+} for Al, and magnetite $Fe^{2+}Fe^{3+}{}_2O_4$, with some substitution of Mg, Mn, Co and Ni for Fe^{2+}, Al for Fe^{3+} and some titanium also detected), corundum (Al_2O_3 also containing a small amount of iron), anorthite ($CaAl_2Si_2O_8$ with small amounts of iron and barium also present) and olivine crystals ($(Mg,Fe)_2[SiO_4]$). Surviving pieces of iron sulphide were occasionally present, also containing several weight percent of nickel and lead and small amounts of cobalt, copper and zinc. In an area with a very high localised concentration of barium, barium feldspars were identified ($Ba[Al_2Si_2O_8]$). Some plate-like, refractory inclusions were also noted, containing about 40wt% alumina and 50wt% silica, which may be unreacted slate that was introduced with the ore.

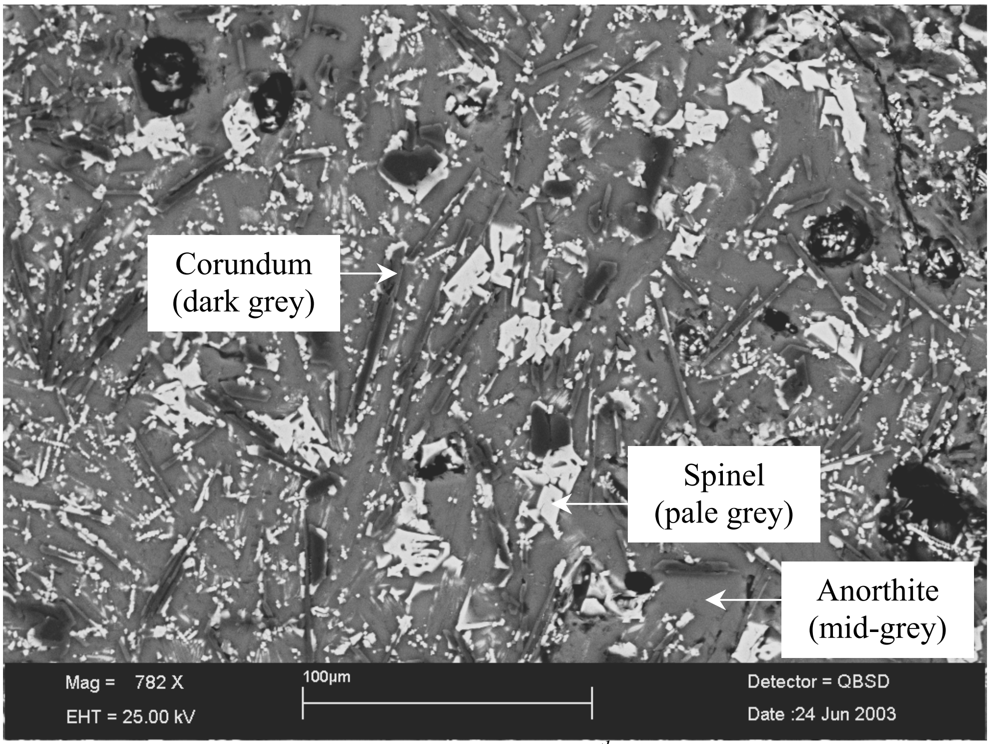

Figure 9: Back-scattered electron image of 19th century lead smelting slag, showing crystals of spinel, corundum and anorthite.

History of metalworking at Combe Martin

As a consequence of the Crown prerogative exercised over the working of silver-bearing ores from the mid-13th century, there are relatively frequent references to the operations at Combe Martin, with the first documentary evidence dating to 1292 (Claughton, 1989). At this date the ore was smelted to extract the lead using small, wind-blown, wood-fired hearths known as boles. In that year 125½ feet of lead (with the foot weighing 70 lbs mercantile, i.e. 30.6kg, this was equivalent to nearly 4 tonnes) were produced from the local ore. The lead, which contained significant amounts of silver, was then sent to Maristow, near Bere Ferrers, on the Tavy estuary in South Devon for refining.

The Combe Martin mines are mentioned intermittently over the following centuries along with those at Bere Ferrers in South Devon. The latter were the leaders in silver production in the period up to 1500, with development there in smelting techniques reflecting the requirement to treat all the ore mined and maximise silver extraction. By the mid-15th century a smelting complex combining the bole with charcoal-fired, manually-blown furnaces had been replaced by the 'fynyngmyll', where all ores were smelted in water-powered, charcoal-fired furnaces. These furnaces operated with a reducing atmosphere and a preliminary roasting stage was required for the ore; techniques that were comparable with those employed in continental Europe at that period (Claughton, 2003, 170-173).

In the 1520's Joachim Hochstetter arrived in Combe Martin, at the behest of the English Crown, with a group of experienced lead smelters from Germany (Claughton, 1989). Hochstetter proposed using continental, water-powered, furnace smelting technology for the initial smelting of the lead. There is a possible reference to a smelt mill and an associated water course that reads "the house and buildings built by Henry VIII to the necessary use of his workmen upon the mines in Combmertyn upon the garden in tenure of John Bennett together with the commodity of the conduit (? Rivi) and water running through" (Claughton, 1989, 33). The intention was to bring ore from other mines for smelting along with that from Combe Martin but the shipping of ore from Mendip met with opposition and the enterprise was short lived.

Late in the 16th century a mining entrepreneur named Bevis Bulmer became involved with smelting at Combe Martin after he helped to resolve problems that were encountered with the smelting of ore from a new deposit that had been discovered. Some of the lead produced was refined locally, along with metal sent from elsewhere, and another portion was refined at Ashburton. Ore was also brought from Clomyne, Co. Wexford for smelting and refining at Combe Martin at this time (Claughton, 1989, 34).

In the mid-17th century Thomas Bushell, the lessee of productive silver mines in mid Wales, saw the potential for renewed production from the Devon mines, which he described as "deserted and drowned". It was probably during his tenure at Combe Martin that deep adit drainage was initiated, although the documentary evidence as to when this was achieved is inconclusive. However it is clear that substantial amounts of lead / silver ores were extracted from the upper parts of all the major deposits prior to the 19th century. Christmas Cottage is thought to have been constructed in the early 16th century and Middleton was built in 1792 on the site of an earlier farmhouse of that name. From 1700 there was probably a long period of inactivity until the end of the 18th century. Thereafter, with the lead market improving, attempts were made to drain the mines, resulting in substantial production during the mid-19th century as steam-powered pumping allowed access to lead and silver deposits below the early workings (Claughton, 1989).

Discussion

Early post-medieval (16th / 17th century) smelting

The analyses of the early post-medieval slag recovered from Combe Martin confirm that it is lead smelting waste. Although no structures were identified during the excavations, the large amounts of waste recovered indicate that lead smelting took place nearby. The majority of the waste appears to have been deposited from the mid-16th to mid-17th centuries. Most of the slag samples analysed, from all levels of the excavations, were compositionally similar suggesting that it was produced by similar technology. The iron-working slag in the assemblage is waste from iron-smithing, which may also have taken place nearby.

The early post-medieval slag from Combe Martin is a by-product of the final stage, rather than an intermediary stage, of the lead smelting process because it has low lead and silver contents indicating that a very efficient smelting process was used. The lead in the slag was replaced with iron, probably derived from the local ore, which contains minerals such as iron sulphide. It is possible that some supplementary iron-rich material, such as iron-working slag, was added as a flux (Gill, 1986, 73). However there is no documentary reference to this in Europe until 1640 (Tylecote, 1990, 58) and the mineralogy of the ore smelted at Combe Martin probably meant that this was unnecessary. The slag would probably have had a melting temperature of around 1200-1300°C, which could be achieved using bellows. Documentary sources suggest that water-powered bellows were used and the siting of the smelting operation in the valley, close to the river, supports this.

There are several possibilities for the construction of the furnace. 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 to oxidise it before smelting. The slag by-product would contain quite a high concentration of lead (and some silver) and so would be resmelted (Crossley, 1990, 189). The practice of resmelting 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 volatilisating at the high smelting temperatures were less from the slag than from the ore. 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 1580's. Ore hearths incorporated a workstone and the material being smelted could be pulled onto this and so exposed to an oxidising atmosphere before being returned to the reducing conditions within the hearth. Therefore 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. However the slag by-product of an ore hearth would also be lead-rich and so would again be processed further to recover as much as possible of the remaining metal. 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 introduction of the ore hearth into the non-argentiferous lead mining districts, e.g. Mendip and the Peak of Derbyshire, was attended by changes in ore preparation to recover the small ore that was not suitable for smelting in the bole, much of which had been discarded as waste. This entailed improved gravity separation methods, using sieves to 'jig' or shake the mixed ore and waste in water tubs, and the careful control of the flow of water in the 'buddling' process (Kiernan 1989, 15-16; Gough 1967, 147-149). However, in the argentiferous lead mines of Devon, the requirement to treat all the ore mined and maximise the production of silver meant that such techniques had been introduced by the end of the 13th century. Small ore, where finely disseminated in the gangue material, 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).

There is a lack of compositional data in the literature on smelting slag generated by different processes at different dates. The composition of the slag from Combe Martin cannot therefore be used to confirm what type of smelting technology was being used there (table 3). In addition to the data in table 3, Gill (1992, 52) describes two samples of 17th century slag as containing around 10wt% lead oxide, with one of these also containing 40wt% iron oxide. The rest of the samples analysed by Gill contained around 3wt% lead oxide with samples from later smelting sites generally containing less lead than samples from earlier ones. The quantity of lime and iron oxide in the slags varies widely, probably largely as a result of variations in the type of gangue in the ore smelted in different localities. (At later dates different types of flux may have been added, which would also affect the slag composition). However the overall efficiency of the Combe Martin smelting process, in terms of the amount of lead remaining in the slag, is demonstrated by comparison with data from the literature.

Table 3: Literature data for slag compositions from a variety of smelting processes.

Source	Date	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	FeO	CuO	ZnO	PbO	BaO	Reference
West Germany	13th C	0.5	1.8	4.6	35.9	1.2	1.8	0.2	7.6	35.8	0.5	3.1	7.0		Rehren et al, 1999
		0.5	1.8	4.8	33.0	1.3	1.7	0.2	7.3	37.1	0.7	2.6	9.1		
Arla Burn	Med.	4.2	1.2	6.31	42.9	1.30	11.0			24.6		1.8	6.6		Tylecote, 1990, 56
Blast furnaces	19th C			1.1	36.8	0.0	6.2			40.0		8.4	7.4		Percy, 1870a, 314
			0.7	3.2	43.6	0.0	5.5			33.4		7.9	5.7		
			0.6	5.9	28.6	0.0	7.8			37.9		7.7	7.5	3.9	
			0.9	7.0	27.8	0.0	9.1			42.3		8.9	4.0		
Slag hearth	19th C			12.3	37.9	0.0	19.6			11.7		8.3	10.1		Percy, 1870a, 420

The formation of antimony-rich phases in lead-silver smelting slag is unfavourable to silver recovery because large amounts of silver can be lost in this type of phase. However very few antimony-rich phases were found in the early post-medieval slag samples from Combe Martin. This suggests that the treatment of the ore and the atmospheric conditions to which the ore was exposed in the hearth during smelting were expertly managed to inhibit the formation of antimony-rich phases and the accompanying loss of silver (Rehren et al, 1999).

Quite large quantities of mineral fuel were recovered in the excavations. The iron working slag contained charcoal fragments, therefore mineral fuel does not appear to have been used for smithing. The lead smelting slag did not contain any surviving fragments of fuel to indicate the type used, so it is possible that, although the mineral fuel was deposited with lead slag, it was actually used for some other industrial process. However the large quantities recovered suggest that mineral fuel may have been used in some stage of the lead smelting, even though this was not thought to have occurred until late in the 17th century (Gill pers. comm., Tylecote, 1990, 58; Crossley and Kiernan, 1992, 6). Charcoal may also have been used but this is fragile and would be less likely to survive removal and dumping.

The lead metal produced 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 resmelted to recover the lead (Tylecote, 1990, 60). 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). It is known that ash of tan turves (bark residue from the tanning process) held in an iron cradle were used to form the cupellation hearth in 14th century Devon (Claughton, 1992, 14); bark ash is also rich in lime and phosphate (Tylecote, 1990, 223-224). However although 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.

Late post-medieval (19th century) smelting

In the 19th century, the Combmartin and North Devon Mining Co. worked the mines at Combe Martin, and the Combmartin and North Devon Smelting Co Ltd was registered to smelt the ore in 1845. However by June 1847, the local mine was supplying only 28% of the ore with the rest being imported by sea and so the venture was short-lived.

Analyses of the 19th century slag showed that the efficiency of the smelting process had increased still further relative to the 16th / 17th century process as virtually all of the metal had now been extracted. However even higher temperatures were probably required, of the order of 1400-1500°C. Despite this the alumina-rich slag was quite viscous when it was removed from the furnace, due to its refractory composition, resulting in a high porosity and uneven surface. The high furnace temperatures would cause lead to volatilise and condensers were incorporated into the long flues of these furnaces so that more lead could be recovered. Percy (1870a, 261) and Crossley (1990) discuss lead smelting and silver refining technologies of the 19th century. Many of the furnaces in use at that time produced a slag rich in lead, which would need to be further processed to produce slag with a low lead content. However Percy (1870a, 261) describes a coal-fired, reverberatory flowing furnace, used in conjunction with a calcining furnace, that resulted in the formation of a "clean" slag (i.e. one containing little lead). In one stage of the smelting process lime was added, and iron and culm (i.e. anthracite coal) were added to reduce the lead compounds present to lead metal, and sometimes barium sulphate or calcium fluoride were also added as fluxes. The slag produced was tapped out and was predominantly an iron and lime silicate, containing less than 1wt % of lead by dry assay (Percy, 1870a, 261). The composition of the 19th century Combe Martin slag is consistent with the use of a flowing furnace and documentary evidence shows that this type of furnace was employed by the Combmartin and North Devon Smelting Co. in the period 1846-52. The barium content of the slag suggests that barium sulphate was deliberately added during the smelting process. However, baryte ($BaSO_4$) is a common gangue mineral occurring in metalliferous hydrothermal veins (Deer et al, 1992) so another possibility is that some of the barium in the slag was introduced with imported ore (Claughton, 1989, 45-46).

Conclusions

The early post-medieval slag at Combe Martin, deposited in the late 16th to early 17th centuries, was probably produced by Bulmer, and later lessees, using an ore hearth and slag hearth blown by water-powered bellows. 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 smelting ore from a recently discovered deposit in the Fayes Mine in 1587. This would be consistent with the introduction of an ore hearth, as these were in use on Mendip prior to Bulmer's arrival at Combe Martin, and reputedly were better able to smelt difficult ore. Whilst the hearths on Mendip, where there was a lack of surface water, used manually operated bellows, the transition to water-power had been effected in Derbyshire in the 1570’s (Kiernan 1989, 134). The low lead content (around 3.5wt%) of the early post-medieval slag analysed in this study indicates that it was a by-product from the final stage of the smelting process, i.e. the slag hearth. The fragment of lead-rich slag identified containing particles of metallic lead and some partially reacted ore may be more representative of the slag produced in earlier stages of smelting, i.e. the ore hearth.

There is a reference to the occurrence of blende (ZnS) in the ore smelted by Bulmer (Claughton, 1989, 34). Percy (1870a, 411) describes the presence of blende as being disadvantageous to smelting because it increases the viscosity of the slag formed and inhibits the separation of metal from the slag. Therefore the problems with smelting the Fayes Mine ore may have been a result of the proportion of blende it contained. Gill (1992, 52) also suggests that the presence of pyrite, as in Combe Martin ore, makes it more refractory. It is not clear how Bulmer solved the smelting problems, but it is known that ore was brought over from Clomyne, Co. Wexford, during this period and so mixing ores may have been part of the solution. Calcite, fluorspar and carboniferous limestone, thought to be gangue from imported ore as they are not associated with the Devonian slates and local ore, have been identified amongst the Combe Martin assemblages. The Combe Martin slag contains several weight percent of zinc but this value is not particularly high when compared to literature data for medieval and post-medieval smelting slag from elsewhere (table 3). However if a mixture of zinc-rich and zinc-poor ores were co-smelted this would dilute the concentration of zinc in the resulting slag.

The recovery of large quantities of quartz, pieces of slate and fragments of ore from the site suggest that ore dressing was taking place nearby, probably making use of the water supply. Dressing the ore involved a variety of processes, including breaking up the ore, sieving it and repeatedly using water to separate the denser mineral-rich material, which would settle to the bottom, from the lighter waste gangue (Gough, 1967, 147-149). Such techniques had been employed in the Devon silver mines over the previous three centuries and would have been familiar to Bulmer from his experience on Mendip.

A documentary source from the early 17th century refers to “divers monuments, their names yet to this time remaining, as the King’s mine, the store house, blowing house and refining house” and it is known that some of the lead smelted by Bulmer was refined in Combe Martin. However no waste from lead refining was identified in the excavated assemblages.

The large quantities of mineral fuel associated with the lead slag suggest that this type of fuel may have been used in some stage of the smelting in the late 16th / early 17th centuries in addition to, or instead of, other types of fuel, such as charcoal. The earliest use of mineral fuel for lead smelting was thought to be late in the 17th century and so it would be an important innovation if used at an earlier date.

The composition of the 19th century Combe Martin slag is consistent with compositional data from the literature for the slag from a coal-fired, reverberatory flowing furnace, used in conjunction with a calcining furnace. A reverberatory flowing furnace was used by the Combmartin and North Devon Smelting Co. during the period 1846-52. Fluxes such as barium sulphate and calcium fluoride may been used and / or the Combe Martin ore may have been mixed with an imported ore containing these minerals as gangue.

Future work

There is potential for further work on the post-medieval industrial waste from Combe Martin. Historical references indicate that ore was imported to Combe Martin for smelting and some non-local geological material was identified amongst the assemblages. Expert advice is being sought on distinguishing local from non-local gangue (Dunkerley pers. comm) and samples of the mineral fuel will be analysed. The potential of lead isotope analysis for determining the sources of the ore smelted at Combe Martin will also be investigated. Excavations at Combe Martin are continuing and these may also provide more evidence as to the type of smelting technology employed and the fuel used.

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Table A1: EDS analyses of standard glasses (wt%), normalised, compared to their known compositions (bd = below detection limit).

		Na_2O	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**FeO**	**CoO**	**CuO**	**ZnO**	**SnO_2**	**Sb_2O_5**	**BaO**	**PbO**
Corning D	Measured	1.22	4.07	5.22	55.55	3.91	0.38	11.30	14.94	0.43	0.52	0.42	bd	0.34	0.11	bd	0.99	0.37	0.20
		1.42	3.99	5.17	55.60	3.94	0.26	11.22	14.77	0.45	0.56	0.47	bd	0.37	0.17	bd	0.93	0.16	0.14
		1.18	4.04	5.08	55.84	3.94	0.35	11.28	14.81	0.38	0.62	0.47	bd	0.40	0.13	bd	0.76	0.29	0.19
		1.31	3.94	5.18	55.45	3.96	0.35	11.26	14.87	0.44	0.53	0.51	bd	0.39	0.21	bd	1.10	0.24	0.18
	Average	1.28	4.01	5.16	55.61	3.94	0.33	11.27	14.85	0.43	0.56	0.47	-	0.37	0.15	-	0.94	0.26	0.18
	StDev	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
	Known	1.31	4.07	5.41	55.00	4.00	0.30	11.41	14.99	0.4	0.47	0.44	0.02	0.4	0.1	0.13	0.96	0.33	0.27
Corning A	Measured	13.94	2.45	1.00	67.26	0.21	0.27	2.91	5.14	0.86	1.03	0.92	0.34	1.16	bd	bd	1.66	0.47	bd
		13.69	2.54	1.04	67.92	0.09	0.23	2.91	5.11	0.78	1.01	0.93	0.17	1.29	0.16	bd	1.57	0.43	bd
		13.92	2.47	1.12	67.43	0.23	0.11	2.86	5.09	0.77	1.04	0.98	0.12	1.25	bd	bd	1.71	0.50	bd
		14.16	2.65	1.00	67.22	0.02	0.19	2.88	5.15	0.81	1.03	0.97	0.19	1.22	bd	bd	1.58	0.59	bd
	Average	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	-	-	1.63	0.50	-
	StDev	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	-
	Known	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
Corning C	Measured	0.58	2.61	1.07	35.86	bd	bd	2.94	5.07	0.72	bd	0.29	0.17	1.27	bd	bd	bd	12.00	37.25
		0.92	2.77	1.07	35.55	bd	bd	2.84	5.15	0.86	bd	0.20	0.15	1.28	bd	bd	bd	11.82	37.02
		0.81	2.87	1.08	35.58	bd	bd	2.90	5.04	0.82	bd	0.34	0.14	1.10	bd	bd	bd	12.00	37.12
	Average	0.77	2.75	1.07	35.66	-	-	2.89	5.09	0.80	-	0.27	0.15	1.22	-	-	-	11.94	37.13
	StDev	0.18	0.13	0.01	0.17	-	-	0.05	0.05	0.07	-	0.07	0.01	0.11	-	-	-	0.11	0.12
	Known	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
DLH1	Measured	0.81	0.32	4.34	25.97	bd	bd	0.94	1.03	bd	bd	0.96	bd	bd	bd	bd	bd	bd	65.61
		0.76	0.41	4.39	25.75	bd	bd	0.94	0.96	bd	bd	0.90	bd	bd	bd	bd	bd	bd	65.84
		0.87	0.33	4.34	25.76	bd	bd	0.95	0.96	bd	bd	0.98	bd	bd	bd	bd	bd	bd	65.78
	Average	0.81	0.35	4.36	25.83	-	-	0.94	0.98	-	-	0.95	-	-	-	-	-	-	65.74
	StDev	0.05	0.05	0.03	0.13	-	-	0.01	0.04	-	-	0.05	-	-	-	-	-	-	0.12
	Known	1.01	0.33	3.97	24.89	0.00	0.00	0.96	1.04	0.00	0.00	0.98	0.00	0.00	0.00	0.00	0.00	0.00	66.84
DLH2	Measured	7.62	0.95	4.15	40.94	bd	bd	2.79	2.82	bd	bd	0.86	0.42	bd	bd	3.83	bd	bd	35.59
		7.65	1.01	4.41	40.79	bd	bd	2.72	2.82	bd	bd	0.86	0.43	bd	bd	3.83	bd	bd	35.50
		7.83	1.03	4.31	41.64	bd	bd	0.29	2.90	bd	bd	0.93	0.41	bd	bd	4.09	bd	bd	36.46
	Average	7.70	1.00	4.29	41.12	-	-	1.93	2.85	-	-	0.88	0.42	-	-	3.92	-	-	35.85
	StDev	0.11	0.04	0.13	0.45	-	-	1.43	0.05	-	-	0.04	0.01	-	-	0.15	-	-	0.53
	Known	7.35	0.89	4.16	40.12	0.00	0.00	2.80	2.89	0.00	0.00	0.91	0.39	0.00	0.00	4.07	0.00	0.00	36.43

Table A2: Proportions of various components in the assemblage from trench CC1, (g).

Level	Lead slag	Geological material	Iron-working slag	Fuel	Vitrified clay
A	0	0	0	0	0
B	54	86	0	20	0
C	244	255	0	105	0
D	144	456	32	245	0
E	25	1040	108	245	0
F	3696	7402	691	198	15
G	1768	4397	46	225	0
H	1258	2526	35	27	0
Total	**7189**	**16162**	**912**	**1065**	**15**

Table A3: Proportions of various components in the assemblage from trench CC2, (g).

Level	Lead slag	Geological material	Iron-working slag	Fuel	Vitrified clay
A	51	191	75	146	0
B	29	126	0	226	0
C	88	220	13	160	13
D	464	646	124	63	38
E	60	890	153	200	58
F	136	683	82	247	12
G	436	1299	50	192	12
H	265	1816	82	87	0
I	286	2895	15	56	0
J	882	960	0	9	0
Total	**2697**	**9726**	**594**	**1386**	**133**

Table A4: Proportions of various components in the assemblage from trench Mn1, (g).

Level	Lead slag	Geological material	Iron-working slag	Fuel	Vitrified clay
A	7	277	13	185	14
B	122	541	12	210	0
C	28	980	0	575	22
D	0	800	0	735	0
E	111	715	7	235	0
F	131	460	0	110	224
F1	0	170	32	165	0
G	73	500	26	170	0
H	163	590	14	110	1
I	10	175	0	360	0
J	57	255	0	425	5
K	112	415	0	310	0
L	474	727	16	575	2
M	730	1089	31	100*	5
N	754	1459	0	65*	0
O	327	2140	35	50*	0
P	438	805	13	23*	3
Q	89	1632	192	10*	0
Q1	607	582	0	25*	0
R	666	1523	109	25*	0
S	57	1111	71	27*	6
T	47	2637	119	23*	0
U	215	346	44	25*	18
V	147	725	34	10*	8
Total	**5365**	**20654**	**768**	**4548**	**308**

*Fuel samples below section L were badly degraded and difficult to extract. The values given are the weight of surviving material retained in a 7mm sieve.

Table A5: Average and standard deviation (StDev) of EDS analyses of early post-medieval slag, normalised, no. of analyses in brackets, bd = below detection limit.

Sample		**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**FeO**	**CuO**	**ZnO**	**Sb_2O_5**	**PbO**
CC2Fa	Average	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
(3)	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
CC2Ga	Average	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
(3)	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
CC2Gb (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
CC2I	Average	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
(4)	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
Mn1Oa	Average	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
(3)	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
Mn1Ob	Average	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
(3)	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
Mn1Oc	Average	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
(3)	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
Mn1Ta	Average	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
(3)	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
Mn1Tc	Average	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
(3)	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
Mn1Ua	Average	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
(3)	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
Mn1Ub	Average	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
(3)	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
Mn1Uc	Average	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
(3)	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
Mn1Va	Average	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
(3)	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
Mn1Vb	Average	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
(3)	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
Mn1Vc	Average	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
(3)	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

Table A6: Average and standard deviation (StDev) of EDS analyses of late post-medieval (19th century) slag, number of analyses in brackets, normalised. Sb_2O_5, PbO, ZnO and CuO all below detectable limits therefore not included.

Sample		**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**FeO**	**BaO**
19th CA (5)	Average	0.94	2.61	30.63	37.49	2.02	0.12	1.30	7.34	0.71	0.28	15.67	0.87
	StDev	0.35	0.33	3.17	2.58	0.47	0.15	0.24	2.00	0.23	0.06	2.36	0.54
19th CB (2)	Average	1.56	2.80	27.98	35.02	2.20	0.23	1.09	9.89	0.48	0.38	17.61	0.59
	StDev	0.04	0.11	0.52	0.13	0.10	0.00	0.00	0.01	0.01	0.01	0.60	0.03