A typology of lead-bale slags based on their physico-chemical properties

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ABSTRACT: A typology of lead bale smelting slags for descriptive purposes and for recognition in the field is proposed. Extensive SEM/EDX studies of bale slags from Yorkshire, and from Cumbria and Derbyshire, are used to illustrate the typology. The melting points of 23 slags have been determined and experiments with synthetic slags conducted. This has led to an understanding of some of the mechanisms involved in slag formation, and of the temperatures which were developed in typical bales. This in turn has led to an explanation of different types of bale which have been encountered by this author and others.

Introduction

Lead smelting in England and Wales in the medieval period was carried out on carefully-constructed bonfires known in the Mendips and Derbyshire as *boles* and further north as *bales*; in this paper the spelling *bale* will be used, regardless of area. The open fire had to be situated in a position where there was exposure to wind of a consistent direction and strength. Therefore, many were placed with an aspect ranging from south through to west, although this was not always the case. Bales were superseded in England around AD 1570 by the ore hearth, which was powered by foot or water driven bellows and resembled a blacksmith's hearth. The change from bale to ore hearth is described in detail by Kiernan (1989).

Excavations have been carried out at Beeley and Totley, Derbyshire (Kiernan and van de Noort 1992) with a reconstruction of a later bale from a contemporary description. More recently, a bale site has been excavated at Linch Clough, Derbyshire (Bevan *et al* 2004). In Yorkshire and the North Pennines, Raistrick (1927) described a bale at Winterings, Swaledale, and more recent discoveries of bales have been reported by Beadle (1980), Fairbairn (1994) and Pickin (1992). Work specifically in Swaledale is reported by Barker (1978), who assigned a radiocarbon date of AD 1439–69 to material from a bale at Calver, and by Barker and White (1992). Sites at Calver Hill have been described in more detail by Smith and Murphy (2003).

Slag studies using a scanning electron microscope with an energy dispersive X-ray detector (SEM/EDX) have been reported for sites at Fell End, Arkengarthdale, and Spout Gill, Swaledale (Murphy 1992). A more recent paper (Murphy and Baldwin 2001) has described bales in Swaledale and neighbouring Wensleydale together with brief descriptions of SEM studies.

Bale smelting technology is poorly understood, although it is known that various forms of hearth existed. In the course of the investigations referred to above, it became apparent that different types of slag are found at bale sites, but the relationships between slag types, compositions and their conditions of formation have not been addressed in detail. The present work set out to examine a substantial body of bale-smelting residues, characterising them by determining their chemistry and melting points and, by inferring the conditions under which the slags were formed, understanding the processes used.

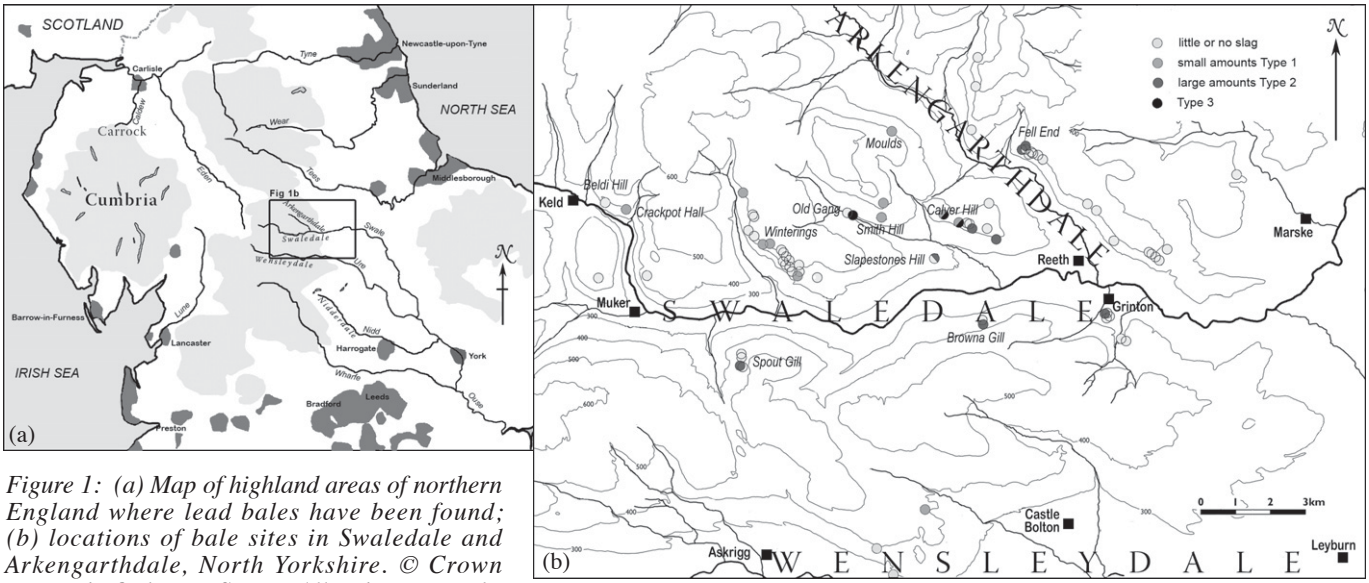

Figure 1: (a) Map of highland areas of northern England where lead bales have been found; (b) locations of bale sites in Swaledale and Arkengarthdale, North Yorkshire. © Crown copyright Ordnance Survey. All rights reserved.

To do this, over 200 slag samples have been examined by SEM/EDX. Although the majority of samples have come from Swaledale, Arkengarthdale and Wensleydale in North Yorkshire, others are from Derbyshire, Cumbria and the North Pennines, and show similar structures and characteristics to those reported here. Figure 1(a) shows the upland lead mining areas of northern England from which samples were collected, and Figure 1(b) the locations of bale sites in Swaledale and Arkengarthdale.

The sites reported here have been generically termed 'bale sites'. It must be emphasised that the exact technology used has not been established, although it can be stated with a high degree of certainty that the smelting of lead ores was carried out.

Location and identification of sites

Bales have been found by field walking and from reports of bare patches of ground or signs of local pollution. Some bales in Swaledale and Wensleydale were found by prediction, on the basis that ore would be smelted on an exposed edge if one were available, on routes downhill from mines, and uphill from sources of fuel (Murphy and Baldwin 2001). In the majority of cases, bales were not found on limestone (calcium carbonate, $CaCO_3$), presumably because of the difficulties arising from fissures in the rock and the generation of quicklime (calcium oxide, CaO) during smelting. In predominantly limestone country, bales were situated on small exposures of sandstone (mainly silica, SiO_2) or on heavy soil overburden.

At the larger bales there are quantities of smelting slags, which have to be distinguished from residues of fuels used in other activities, either industrial or domestic. More difficult to identify are sites with no more than a scattering of pieces of fire-reddened sandstone which can be the first indication of a bale. Closer examination may identify sparse surface residues such as glazed stones or tiny droplets of yellow/cream lead silicate slag on stones, sometimes with streaks or inclusions of bluish-grey lead or matte (melted sulphides), and prills of lead metal 1–3mm in diameter. Occurrences of pieces of galena (lead sulphide, PbS) can arise from mining or ore dressing and on their own should not be accepted as evidence for smelting. Some of the larger sites at Calver (Smith and Murphy 2003) have detached dumps of slag, and are perhaps sorting areas where lead prills were recovered. The occurrence of slag can be misleading due to the transport of old bale slags to post-medieval smelters for reprocessing, as has been reported for Marrick Mill (Tyson 1989).

Typology of bale smelting slags

There are common characteristics among the slags encountered, and a general basis for classification is proposed, providing a typology useful for recognition of slags in the field and for interpretation of sites. With some practice, it is possible to fit slags into the classes proposed, using only a geological hammer and, for some, a magnifying glass, although the typology has been drawn up on the basis of chemical analysis of the slags. At some sites, most slags will fit into one or other of the classes, at others there will be slags of different types. There are examples of several classes in the same piece.

Lead silicate slags (Type 1)

One of the most common signs of a bale site is the presence of reddened sandstones which have been splashed

Figure 2: Type 1 light-coloured slag coating on a piece of sandstone (below and left of coin), from Calver 72A.

with yellow or cream lead silicate (Fig 2). In some cases, this may show as a green or almost transparent glaze. Slags of this type are never abundant; they are fairly brittle and shatter fairly easily when samples are being cut for microscopy. When examined by SEM/EDX, Type 1 slags show a plain matrix of lead silicate with occasional inclusions of unreacted material.

Mixed silicate black slags (Type 2)

Black, vitreous slags were found to contain lead and silica, but other elements such as calcium, iron and barium were also present. Traces (0–2%) of sodium, potassium, zinc, aluminium and fluorine may also be found. Gas vesicles are generally common and vary from 0–20% by volume. These slags often have a white or grey external coating of lead carbonate or sulphate. They are harder than lead-rich silicate slags and take a good polish. They vary in appearance and physical properties, from glassy, bright brittle to dull and tough; this variation has been used as the basis for sub-division into Types 2a and 2b as it is related to the slag structure as determined by SEM/EDX.

Type 2a are characterised by a homogeneous glass of mixed metal silicates which appear to have the general molecular formula $MO.SiO_2$ (where M is the sum total of divalent metal atoms). This must be taken with the usual caveats concerning semi-quantitative analysis by SEM/EDX, but appears to be general with virtually all of the samples examined. These slags are shiny, black, very brittle and very hard. They take a very good polish after which they resemble polished jet. When examined by SEM/EDX, they appear as a featureless plain matrix, often with minor amounts of unchanged silica (SiO_2) (Fig 3).

Calebrack A, Calebrack B and Long Hill slags were hard

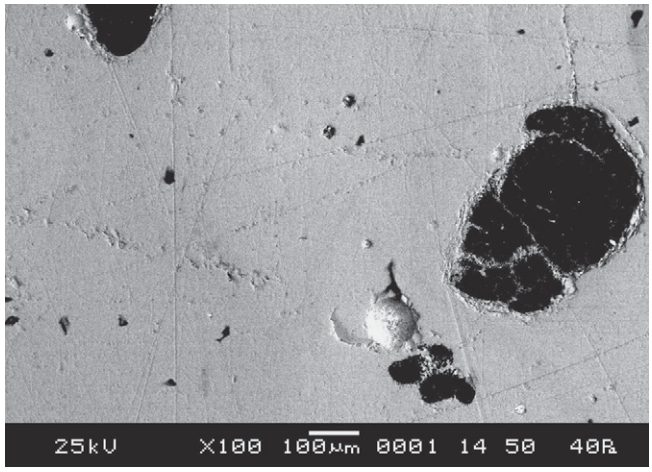

Figure 3: BSE image of Calebrack B slag showing matrix of lead silicate (light) and inclusions of unreacted SiO_2 (black).

black and vitreous, having only Pb and SiO_2 present, although with a low Pb/SiO_2 ratio. They have been classified as Type 2a on the basis of their appearance.

Type 2b slags have a matrix of mixed metal silicates (as Type 2a) but also contain precipitated species of high melting compounds, which have clearly separated from the molten slag and in many cases have fairly well-defined crystal forms. These samples were very dull, dark grey to black, hard, and took a good polish but less so than Type 2a slags. It is fairly clear that it is the precipitated crystals that confer dullness, toughness and overcome the brittleness which is evident in Type 2a slags.

The most common species in Type 2b slags was Ca_2SiO_4, which showed as long laths with a hexagonal cross-section (Fig 4). CaF_2 appeared in the samples as unchanged fragments of fluorite or as fine fern-like dendrites, leaves or round spots (Fig 5). Fern-like precipitations of BaF_2 were found in some samples having high barium

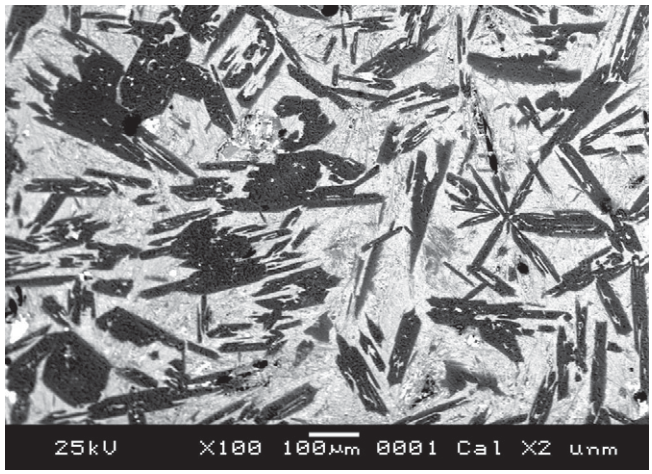

Figure 4: BSE image of Calver X2 slag showing crystals of Ca_2SiO_4 (black) in a matrix of mixed Ca/Ba silicate.

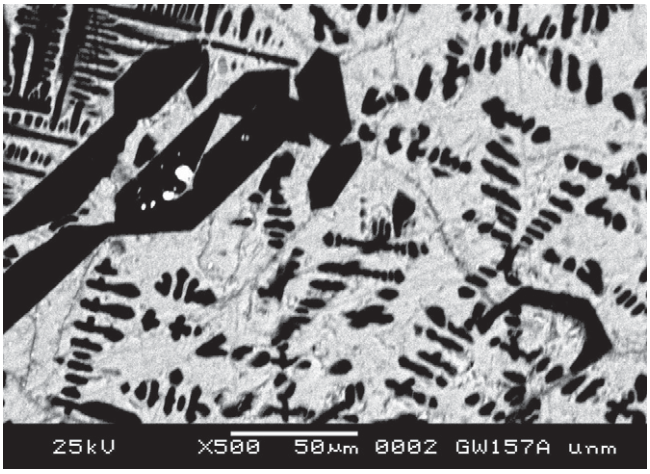

Figure 5: BSE image of Grinton West 157A slag showing hexagonal crystals of Ca_2SiO_4 with fern-like dendrites of precipitated CaF_2 (both black) in a matrix of mixed Ca/Ba silicate.

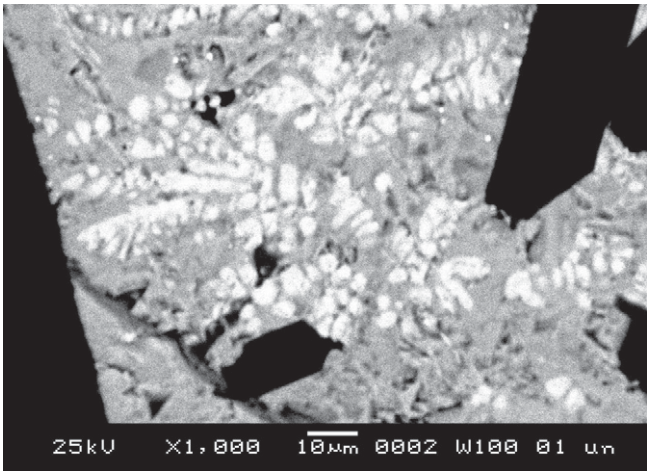

Figure 6: BSE image of Winterings 100 slag showing fern-like crystals of BaF_2 (white) with large hexagonal crystals of Ca_2SiO_4 (black) in a matrix of Ca/Ba silicate (with high Ba – mid grey).

contents (Fig 6). Other precipitated species were $CaSiO_3$, calcium phosphate (Fig 7), Zn_2SiO_4 (Fig 8), barium/calcium silicates having the general formula $((CaO)_2.BaO.(SiO_2)_3)$ or $(CaO.(BaO)_2.(SiO_2)_3)$ (Fig 9), barium aluminosilicate, and various spinels (high-melting point mixed oxides of divalent and trivalent metals, such as barium aluminate).

In some instances, segregation of complex mixed silicates may take place, particularly if the zinc or aluminium content is high and also where relatively small amounts of magnesium are present. The segregated species may have a variable non-stoichiometric composition. The abundance of the precipitated species varied considerably both within samples and between samples. In some cases, the precipitated species was predominant with only a small volume of mixed silicate matrix.

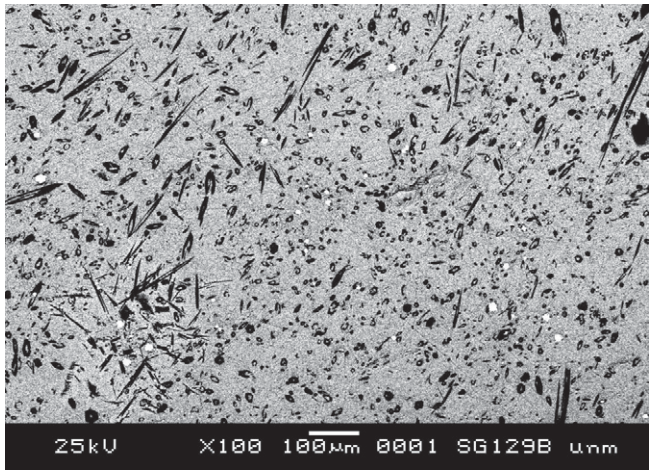

Figure 7: BSE image of Spout Gill 129B slag showing a matrix of Ca/Ba/Fe/Pb silicate (light grey) with needle-like crystals of calcium phosphate/silicate (black).

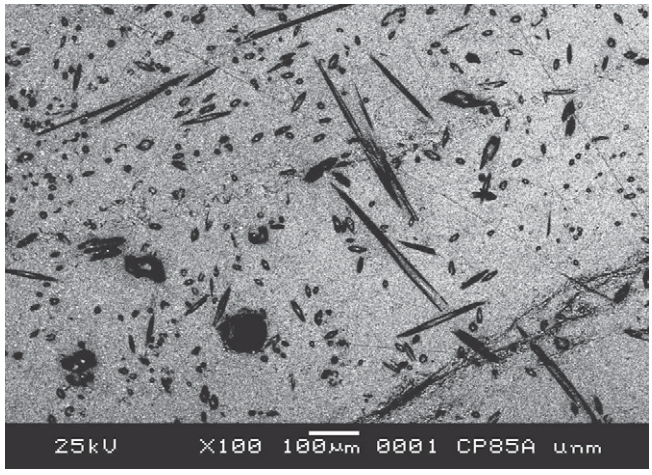

Figure 8: BSE image of Crackpot Hall 85A slag showing a matrix of principally Pb silicate (light grey) with prominent hexagonal crystals of Zn_2SiO_4 (black).

Grey slags (Type 3)

These are chemically unchanged gangue minerals, usually barytes (barite, $BaSO_4$) or fluorspar (fluorite, CaF_2), which may have been physically altered to a greater or lesser extent by the action of fire. They are often heterogeneous, and cut surfaces are usually grey or light brown. It is common for Type 3 slags to have a white or grey external coating of lead carbonate or sulphate. In some instances the mineral is held together by a minor matrix of mixed metal silicates, where Pb is generally predominant, or by Pb silicate. Very often galena and other lead residues are present. Although these could be regarded as a mixture of gangue and a Type 1 or Type 2 slag, their common occurrence and distinctive appearance make it convenient to treat them as a separate class. These slags have first and second melting points (see below) based on the matrix but will never have been fully molten. Their appearance is typified by Figures 10 and 11 which demonstrate this.

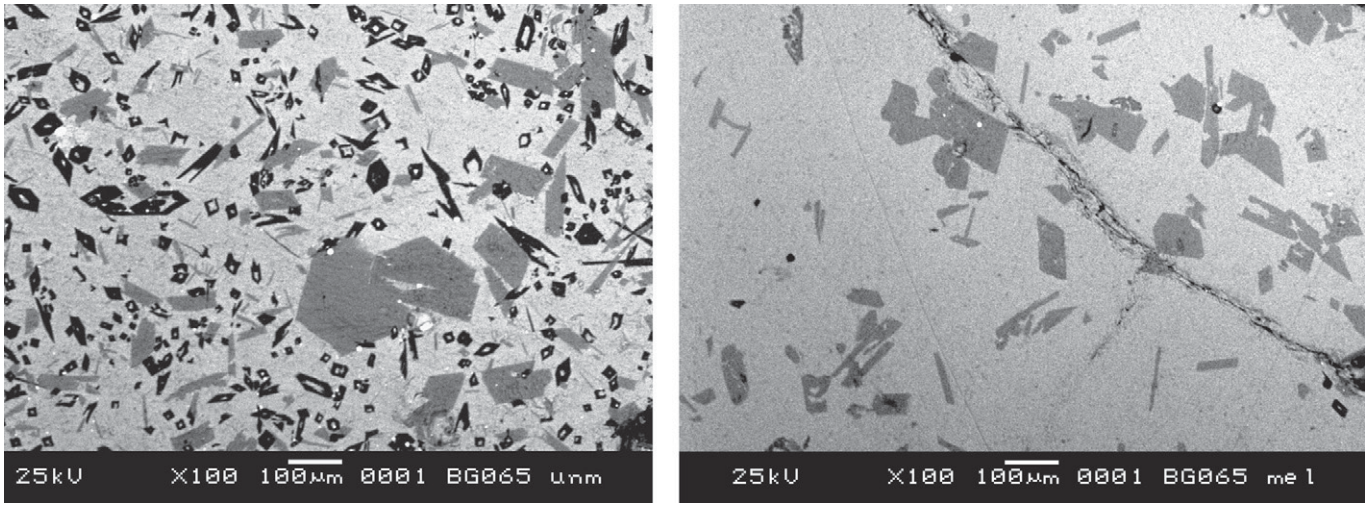

Figure 9: BSE images of Browna Gill 065 slag. Unmelted (left) and melted (right) samples show a matrix of Ca/Ba silicate (light). There are prominent crystals of Ca_2SiO_4 (black) in the unmelted sample, which are virtually absent in the melted sample. Both samples contain Ba/Ca silicate crystals (mid grey) having a general formula $(Ca.Ba)_2.SiO_4$, where the Ca:Ba ratio is 2:1 in both samples.

Galena, matte and lead residues

A fairly common residue on many sites is lead sulphide, which varies from unchanged galena through melted matte to metallic lead. Other lead residues are white secondary compounds such as lead carbonate ($PbCO_3$), basic carbonates (hydrated $PbCO_3$), sulphates ($PbSO_4$), and hydrated sulphates; these are the forms which are generally present on the surface of the piece. Residues of this type may be the predominant species present at a site or (more usually) will be present as inclusions in other slags. Their outward appearance is similar to Type 3 slags but they can be easily distinguished when broken.

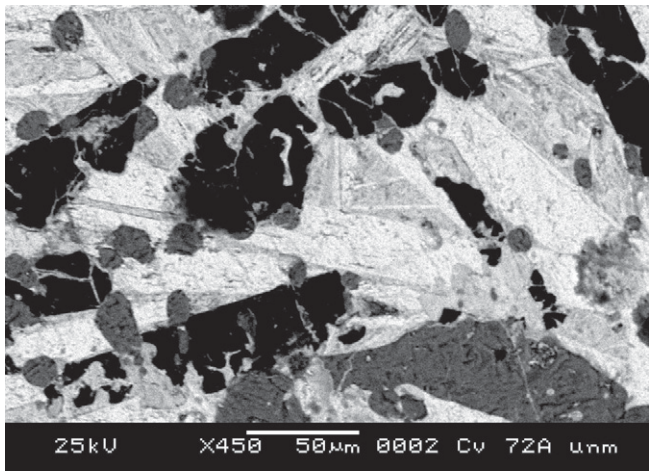

Figure 10: BSE image of Calver 72A slag showing a matrix of lead silicate and lead oxide crystals (light grey) with considerable amounts of $BaSO_4$ (dark grey) and crystals of Ca_2SiO_4 (black).

Unchanged minerals

Pieces of silica, fluorspar and barytes occur fairly commonly as inclusions and as heterogeneous mixtures with lead or lead compounds. Their appearance is quite different from Type 3 slags, where the unchanged mineral is only recognisable under the microscope. Limestone and calcite ($CaCO_3$) are calcined in the bale to quicklime (CaO), which dissolves on exposure to water and for this reason calcium species are relatively uncommon. In surviving cases, the quicklime has reacted further to calcium carbonate and is preserved, but such instances are rare and can only be recognised as smelted material by identifying inclusions.

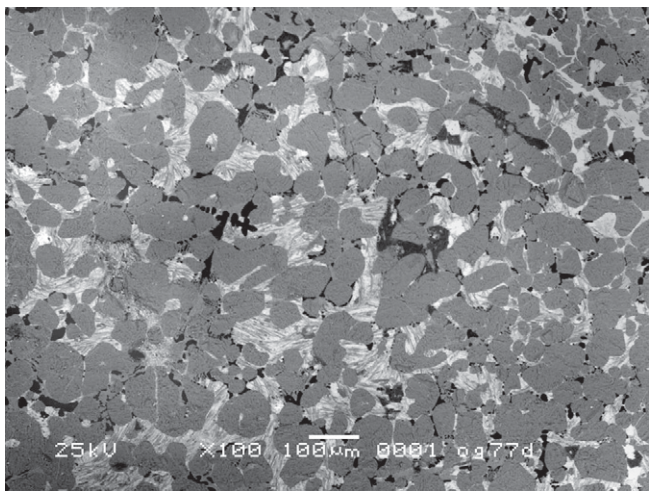

Figure 11: BSE image of Type 3 slag from Old Gang 077D showing $BaSO_4$ (mid grey) in a matrix of crystals of lead silicate and lead oxide (pale grey) with CaF_2 (black), some of which is present as a precipitated species.

Secondary minerals

These are produced by weathering of primary slags or unchanged raw materials, but are rarely sufficiently common to merit consideration as an additional group. Basic lead carbonate commonly occurs on the surface of smelted residues and is one of the signs used in the initial recognition of a site.

Other slags

Other types of slag may be confused with bale slags; the most frequent occurrences are:

- Coal or coke slags from smithies, lodging shops, braziers, portable engines, reverberatory furnace fire-boxes etc. These are fairly common in North Yorkshire where seams of low grade coal with a high ash content are encountered. These slags are black or brown, with a low bulk density and low particle density and have many gas vesicles. They are often contorted and can show well-developed flow lines.
- Smithy slags which are similar to the above, but are often more compact and have inclusions of iron oxides and irony hearth accretions.
- Iron smelting slags from bloomery furnaces and other forms of iron processing. These are usually brown, with many gas vesicles but in fairly large pieces and are heavier than coal slags; they usually show flow lines.
- Lead smelting slags from smelting mills. Some forms are indistinguishable from bale slags and recognition is often based on the known existence of furnace smelting on the site.

Experimental Procedures

The samples examined came from the sites listed in Table 1, most of which are shown in Figure 1b. One of the main reasons for carrying out the experiments described below was to correlate melting point and microstructure/composition with bale temperatures and to use them as indicators of differences in smelting technology.

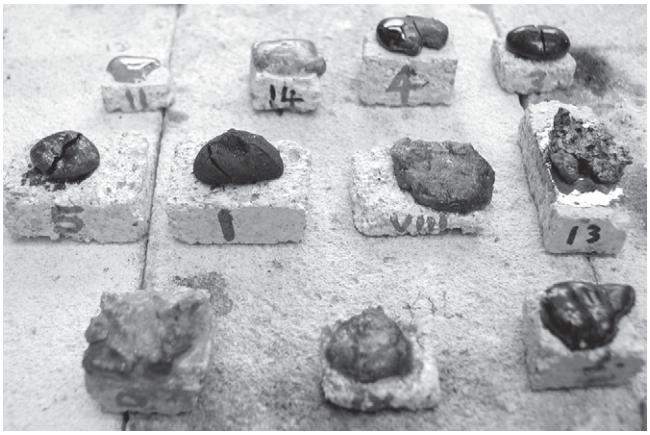

Figure 12: Samples removed from the furnace after melting point determination. Image width ca *200mm.*

Melting point determinations

Each piece of bale slag was cut in half using a diamond wheel and placed on a 15mm thick slice of firebrick; up to ten samples could be tested at any one time. The samples were placed in an electric furnace, the temperature was increased, and the door opened at intervals of 10°C after 700°C. Each sample was prodded with a thin steel rod. The first temperature (T1) was recorded when the surface of the sample became sticky, the second (T2) when the rod could easily be pushed through the sample and the third (T3) when the slag was fully molten and ran into a ball or lens. Slags were removed from the furnace when they had fully melted and were allowed to cool in air. Figure 12 shows a range of slag samples after removal from the furnace.

The furnace temperature was monitored with two thermocouples inserted through the rear. One, the controller, was in a ceramic sheath in one of the top corners; the

Table 1: Bale sites mentioned in the text

Site	Location (NGR)	Site size	Site description	Main slag types
Browna Gill 065	SE 01025 97498	medium	small hillock	2b: dull dark grey
Calebrack	NY 34428 35456	large	flat open moor	1: black vitreous
Calver 25	NZ 00906 00343	(several bales)	shoulder of hill	1 and 3: grey
Calver 72	NZ 00038 00595	large	crest of hill	1 and 3: grey
Calver X	SE 01400 99846	very large	gentle slope	2a and 2b: black
Calver Z	SE 00949 99984	very large	gentle slope	2a and 2b: black
Crackpot Hall 085	NY 90883 00817	medium	gently sloping moorland	2b: black
Crackpot Hall 086	NY 90894 00845	medium	extension of Crackpot Hall 085	2b: black
Grinton West 157	SE 04576 97697	extensive	small hillock	2a and 2b: black
Long Hill	NY 35428 34562	large	flat common	1: black vitreous
Moulds 202	NY 98335 02930	large	flat upland at head of hushes	2a and 2b: black; 3: grey
Old Gang 077D	NY 97311 00626	small	sloping fellside at E end of peat house	3: (see Fig 11)
Slapestones Hill 143	SD 99667 99325	large	flat, partly covered with grass	2a and 2b: black
Smith's Hill 083	NY 98140 00511	medium	at side of track from top of Helaugh Crag	1: on sandstone (rare)
Spout Gill 129	SD 94062 96343	large	sloping moorland	2a and 2b: black
Winterings 100	SD 95210 99661	large (several bales)	SW-facing edge of Winterings High Scar	2a and 2b: black

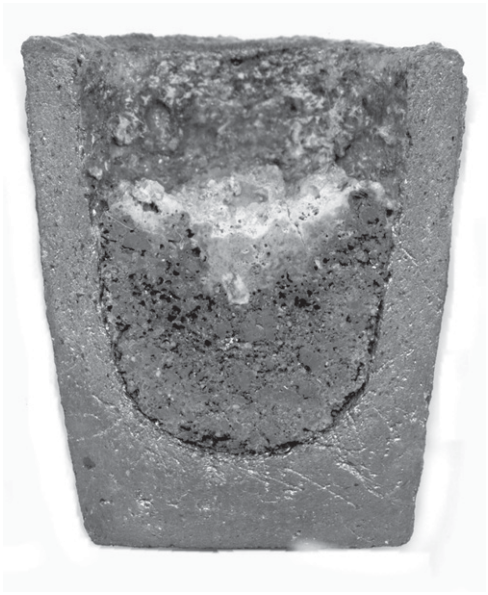

Figure 13: 35ml crucible containing synthetic slag from experiment 2. The lighter-coloured layer on the surface of the melt is litharge.

other was placed in the centre, surrounded by the samples. The latter had a digital readout and was used for the determination of melting points. The rate of temperature rise was restricted so that both thermocouples gave concordant readings.

The results of the melting point determinations are summarised in Table 2. Initial softening points (T1) ranged from 770–1060°C. In a few cases, the sample started to melt, then hardened as reactions took place within it. In others, a complete melt was not obtained at 1150°C, although in some cases low-melting silicates separated.

Analyses

Slag was prepared for the SEM/EDX either by removing the melted piece, where this was possible, or by cutting away most of the firebrick support. A cross-section was then cut and polished. Unmelted samples were taken from the other half of the same piece of slag.

A JEOL 636 OLV SEM with backscattered electron (BSE) detector was used for obtaining images. Elemental analysis was conducted with an energy dispersive X-ray detector. Samples were not coated but were run under low vacuum conditions with an air pressure of 30–50Pa, which was sufficient to prevent charging. An accelerating voltage of 25kV was used throughout. The accuracy was sufficient to be able to determine atomic ratios in standards such as $CaCO_3$, CaF_2, PbS and $BaSO_4$. However, there was a tendency to overstate the amounts of light elements (C, O and F) and to understate heavy elements (Pb) when these were present in small amounts. Lead was determined at the higher-energy Lα line and sulphur at the Kα line, which is coincident with the strong Pb Mα line. Despite this, the peak resolution software was able to give good atomic ratios for PbS but much less good results when the two elements were present in dissimilar amounts.

Where a definite chemical species has been identified, this is referred to using either the chemical formula (*eg* Ca_2SiO_4, CaF_2) or the name of a mineral (*eg* galena, calcite). Where the formula can not be established a descriptive name is given (*eg* lead silicate, Ca/Ba/Fe silicate, lead basic carbonate).

Synthetic slag preparation

Experiments (discussed on p.126) suggest that temperatures of 900°C could only be obtained with difficulty in an open fire such as a bale. Nevertheless, slags collected from bale sites show that partial or substantial melting had taken place and that these slags contained refractory calcium or barium silicates, or barium sulphate. The melting point determinations suggested that a wide range of temperatures was achieved. Therefore, experiments making synthetic slags were conducted to give an insight into the conditions which were necessary to form a slag and to determine the silicate species which would form preferentially.

Three experiments were carried out. For the first, powdered limestone, silica sand and barytes were washed repeatedly with cold water, dried at 150°C, and then weighed into a 35 ml A5/0 salamander crucible. The mix used was 3g sand, 7.5g limestone and 6g barytes. The weights were 1/40th of the gram molecular weight corresponding to $3CaCO_3$, $BaSO_4$, $2SiO_2$ which is equivalent to a molecular formula of $2MO.SiO_2$ with CaO as the principal base. The crucible was heated gradually to 1100°C and held at that temperature for 1 hour. It was withdrawn from the furnace, but little reaction appeared to have taken place, although $CaCO_3$ would have been calcined to quicklime. No reaction appeared to have taken place.

The second experiment followed using this crucible and its contents. 2g of galena was added to the top of the crucible and it was returned to the furnace for 30 minutes. The galena could be seen burning soon after placing it in the furnace. The crucible was withdrawn and tested with a thin steel rod. Some reaction seemed to have taken place. A further 15g of galena was added to the top of crucible contents and the crucible heated

Table 2: Summary of experimental results

Sample	T1 (°C)	T2 (°C)	T3 (°C)	Appearance on melting	Slag type, appearance in SEM and composition	MO:SiO_2 unmelted	Ca:Ba (atomic) unmelted	Ca:Ba (atomic) melted
Smith's Hill 083 A	770	780	790	Clear transparent yellow glass, wets brick.	1: yellow $PbSiO_3$, single phase, no change on melting.	–	–	–
Calver 72A	780	790	960)	Clear orange glaze runs out from sintered grey mass. Removed at 960°C.	3: complex multi phase with inclusions, does not melt completely but $PbSiO_3$ glaze runs at low temp. (Fig 10)	–	–	–
Calver 25A	780	800	810	Dull patchy orange brown with bits, wets brick.	1: two phases of Pb silicate, high Pb.	–	–	–
Spout Gill 129 A	790	880	1000	Black ball, dull interior.	2a: featureless matrix of Al/Ca/Fe/Ba/Pb silicate.	1.1	1.4	1.5, 1.6, 1.7
Grinton West 157 B	860	870	880	Back ball, shiny top and interior, cracks on cooling.	2a: featureless matrix of Ca/Ba silicate with traces of Al, Pb, Fe and Zn.	0.9, 1.0	0.8, 0.9	0.8, 0.9
Calebrack B	860	900	950	Lens, wetted substrate, shiny glass, removed 1060°C.	1: uniform matrix of Pb silicate with traces of Al, Ca and Fe and inclusions of SiO_2. (Fig 3)	–	–	–
Calebrack A	860	930	950	Lens, wetted substrate, shiny glass, removed 1060°C.	1: uniform matrix of Pb silicate with traces of Al, Ca and Fe and inclusions of SiO_2.	–	–	–
Slapestones Hill 143	870	870	880	Black ball, shiny top and interior, cracks on cooling.	2a: featureless matrix of Ca/Ba/Fe/Pb silicate with a trace of Al and K.	1.0, 0.8	1.6, 1.4	1.4, 1.4
Calver X1	900	950	970	Flat thin lens on melting, wetted substrate, semi-shiny, removed 1120°C.	2a: featureless matrix of Ca/Ba silicate with traces of Fe and Pb.	1.1	2.1	2.2, 2.2
Long Hill LH2	900	980	1060	Peaked lens, did not wet substrate, both dull and shiny parts, heterogeneous, removed 1060°C.	2a: featureless matrix of Pb silicate with traces of K, Ca, Ba, Fe and Zn with inclusions of silica.	–	–	–
Calver X5	900	1100	>1120	Became hard at 1020°C then sticky again at 1050°C. Stayed as soft sticky piece, dull, removed 1120°C.	2b: mixed Ca/Ba silicate with traces of Fe and Pb and having many crystals of Ca_2SiO_4, $(Ca,Ba)_2SiO_4$ with a Ca:Ba ratio of 1.2, and some inclusions of $BaSO_4$. (Fig 14)	>2	0.6	1.5, 1.5
Moulds 202 3	910	1020	1070	Flat ball, did not wet substrate, dull, removed 1080°C.	2b: Ca/Ba silicate with crystals of Ca_2SiO_4.	1.0	1.9	2.2, 2.5
Winterings 100	920	1020	1140	Melted to light sandy-brown patchy lumpy mass which wets brick.	2b: matrix of Ca/Ba silicate (with high Ba) with traces of Pb, Al, K, and Fe with considerable deposition of Ca_2SiO_4 crystals. (Fig 6)	1.6	0.7	1.2, 0.9
Crackpot Hall 085 A	930	950	1000	Black ball, dull top and interior.	2b: matrix of mixed Pb silicate with Al, K, Ca, Fe, Zn and Ba with prominent crystals of Zn_2SiO_4. (Fig 8)	0.9, 0.9	1.8, 2.0	1.8, 2.3
Moulds 202 5	930	1040	1070	Lens, wetted substrate, dull glass, removed 1080°C.	2b: matrix of Ca/Ba/Pb/Fe/Al silicate with large crystals of Ca_2SiO_4 and fine fern-like crystals of CaF_2.	1.2, 1.2, 1.3	1.3, 1.3, 1.2	1.4, 1.8
Calver Z3	970	980	1060	Never became fully molten but fully softened, dull, heterogeneous, removed 1060°C.	2b: matrix of mixed Ca/Ba silicate with traces of Al, Pb, Fe and Zn with prominent crystals of Ca_2SiO_4.	1.2	0.8, 0.8	1.4
Grinton West 157 A	970	1020	1150	Melts to brown patchy blob which wets brick.	2b: matrix of mixed Ca/Ba/Pb silicate with traces of K and Fe, with crystals of Ca_2SiO_4 and fine fern-like leaves of CaF_2. (Fig 5)	2.0	0.5	1.2, 1.6, 1.6, 2.3
Crackpot Hall 086 B	970	1090	1140	Melts to orange-brown heterogeneous patchy ball.	2b: matrix of Pb/Zn silicate with traces of Al, K, Ca, Fe and Ba, with crystals of Zn_2SiO_4.	1.1, 1.1	–	–
Moulds 202 4	1000	1040	1060	Lens, wetted substrate, dull glass, removed 1080°C.	2b: matrix of Ca/Ba silicates with traces of Al, K, Fe and Pb, a few large crystals of Ca_2SiO_4 and a fine pattern of fern-like CaF_2/silicate crystals.	1.2	1.90	1.6
Calver X2	1030	1080	>1120	Did not melt, some glaze ran, dull, removed 1120°C.	2b: matrix of mixed Ca/Ba silicate with traces of Al/K/Fe and Zn. Dense occurrences of Ca_2SiO_4 throughout. (Fig 4)	2.2, 2.4	0.7, 0.6	1.6
Browna Gill 065	1050	1080	1090	Lens on melting, semi shiny, removed 1120°C.	2b: matrix of Ca/Ba silicate with low amounts of Al, Fe, K, Pb and Zn. Prominent crystals of Ca_2SiO_4 and of Ba/Ca silicate. (Fig 9)	1.2	0.9	1.3
Spout Gill 129 B	1060	1080	1150	Melts to black lumpy mass which just wets brick but main form is a ball. Fairly shiny on top.	2b: matrix of Ca/Ba/Fe/Pb silicate with traces of Al, K and Zn. A significant feature of both Spout Gill samples was the presence of long crystals of calcium phosphate having possible Si/Pb/Fe. (Fig 7)	1.2	0.8	1.2, 1.6
Calver X6	Lost	Lost	>1120	Residue in furnace was particle with some molten glaze, removed after cooling from 1120°C.	2b: matrix of mixed Ca/Ba silicate with traces of Al, Pb, Fe and Zn. Prominent crystals of Ca_2SiO_4 and inclusions of $BaSO_4$.	~0.7	0.6	0.5

Notes: Phase names in the Slag type column are assigned as set out on p.121; Analyses; T1 = sample surface sticky, T2 = steel rod able to penetrate sample, T3 = sample fully molten; data for oxide/atomic ratios in last three columns are individual measurements on the mixed silicate matrix in different areas of a sample.

at 1100°C for a further hour. On withdrawal and cooling, there was a surface layer of brown litharge and the contents appeared uniformly hard. The crucible was sawn lengthwise with a diamond saw and one of the two halves polished for examination by SEM/EDX (Fig 13).

The third experiment was a repeat of the first, with no galena but with 2g of coal added to the mix of sand, limestone and barytes. No reaction, other than superficial burning of the coal, was noted after 1 hour at 1100°C and the mixture was removed from the crucible as a free-flowing powder.

Results of investigations of archaeological slags

The following observations were made:

- The lowest-melting slags were lead silicates (Type 1 slags). When Pb and SiO_2 were the only species present, very high Pb/SiO_2 ratios were normal, as with the samples from Smith's Hill and Calver 25A.
- Type 1 and Type 2a slags with simple featureless matrices (*eg* Fig 3) had sharp melting ranges (*ie* T1, T2 and T3 were typically separated by <50°C. Slags with only a few high-melting inclusions or crystals were similar. For example, Moulds 202/4 had relatively few crystals of Ca_2SiO_4 and had a fairly limited melting range.
- Slags with high frequencies of crystalline Ca_2SiO_4 had wide melting ranges and there is clear evidence that these arose from dissolution of the suspended crystals. As the dissolution progressed, the melting point of the matrix increased. Evidence for the dissolution of Ca_2SiO_4 comes from changes in the Ca:Ba atomic ratio of the slag matrix (see Table 2). This is fairly conclusive, and is most apparent with slags that have been heated for extended periods when determining their melting points. The Ca_2SiO_4 crystals in the Browna Gill 065 sample disappeared completely on melting, although crystals of Ca/Ba silicate which represented the equilibrium condition were unchanged (Fig 9). The complex structure of the unmelted sample from Calver X5 simplified considerably on melting (Fig 14). Slags with no precipitated Ca_2SiO_4 showed no significant change in the Ca:Ba ratio of the matrix; this included Type 2a slags and the Crackpot Hall slags, where the precipitated species was Zn_2SiO_4.
- Most slags had other phases present. In nearly all cases, despite heating, the mineral inclusions such as SiO_2, $BaSO_4$, CaF_2, $CaCO_3$ and PbS or precipitated species such as BaF_2, CaF_2, Zn_2SiO_4 and various spinels were unchanged. Even at the final melting point (T3) it is most unlikely that these crystals would have dissolved completely and the final product would have been a 'slush' of molten matrix containing suspended crystals.
- The matrix $MO:SiO_2$ ratio in the lowest-melting Type 2 slags was around 1.0 and increased to 1.2–1.6 in the higher melting slags (as measured by T1), although

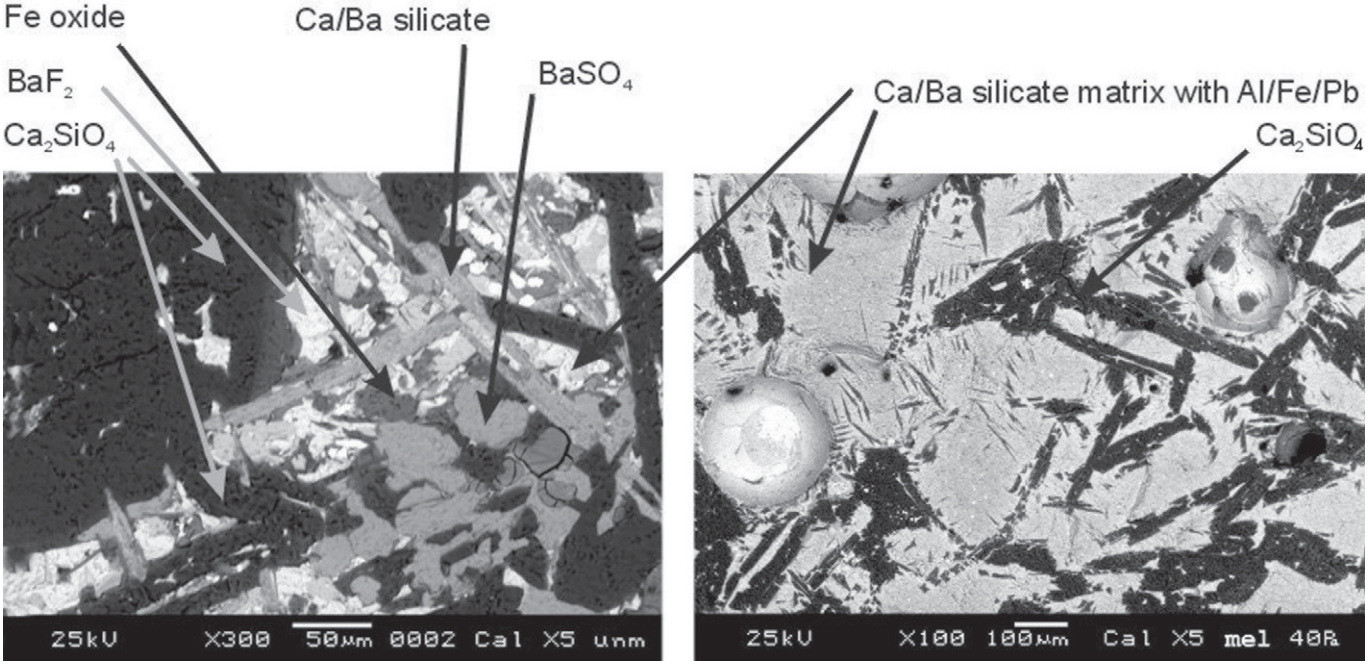

Figure 14: BSE image of Calver X5 slag. The unmelted sample (left) has a complex structure with a matrix of mixed Ca/Ba silicate (light grey). There are many large crystals of Ca_2SiO_4 (black) and inclusions of $BaSO_4$ (mid grey). The round pieces (dark grey) appear to be iron oxide and the needles (lighter grey) are $(Ca.Ba)_2SiO_4$ with a Ca:Ba ratio of 1:2. The melted sample (right) is much less complex with a Ca/Ba silicate matrix (light grey) and crystals of Ca_2SiO_4 (black).

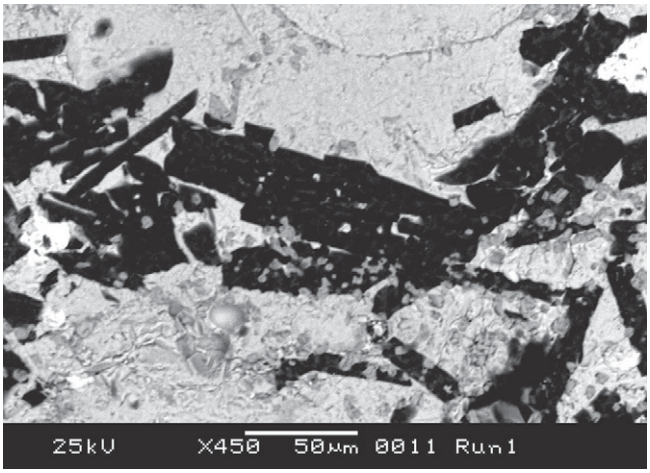

Figure 15: BSE image of synthetic slag with crystals of $CaSiO_3$ (black) in a matrix of Pb/Ca silicate (light). The grey fragments in the white matrix are $BaSO_4$.

some had ratios well in excess of 2.0. More accurate analyses would have to be carried out to confirm this but it could give an indication of bale temperature.

Results of production of synthetic slags

The following observations were made:

- As expected, the three main gangue components: sand, limestone and barytes did not form a slag at 1100°C in the absence of a liquid phase.
- Galena (PbS), which oxidised to molten PbO (m.p. 900°C), appeared to be essential for slag formation at 1100°C.
- From the SEM/EDX analysis of the residue it was apparent that only a small amount of slag had formed after two hours and that most of the hard residue was a mixture of unreacted components and lead oxide. Nevertheless, some significant areas of slag were found and it is probable that once some liquid silicate had formed then further reaction would become more rapid.
- The first slag reaction appeared to be between molten PbO and solid SiO_2 to form a lead-rich silicate, which melts at around 750°C and is then available for further reaction. Reaction with limestone appeared to be fairly easy with most of the slag being Pb/Ca silicate with some Pb/Ca/Ba silicate. As the reaction proceeds Ca and Ba will gradually displace PbO from the silicate matrix, this will result in the melting point of the slag being raised and PbO being available for further reaction or reduction to metallic lead.
- The experiments showed that $CaSiO_3$ could be produced at moderate temperatures, well below its melting point (1600°C), provided there was a local excess of Ca (Fig 15). This was deposited from Pb/Ca silicate slag areas. This observation is important as it demonstrates that species such as $CaSiO_3$ can be formed at temperatures well below their melting point by crystal growth.
- Ca_2SiO_4 crystals are common in the slags from North Yorkshire but were not produced in the synthetic slags which had relatively low Ca/Pb ratios. It is very probable that Ca_2SiO_4 would form in situations where more Ca was available, but may require a longer reaction time.
- Reaction between lead silicate and calcium oxide appeared to be more common than between lead silicate and barium sulphate. Although there were occurrences of Pb/Ca silicates in the synthetic slags, no examples of Pb/Ba silicates were found, only Pb/Ca/Ba silicates.

Mechanism of slag formation

The experimental work on synthetic slags showed that the three main gangue elements, silica, limestone and barytes, did not form a slag when heated to 1100°C and remained as an unreacted mixture. The result was expected, and demonstrates a well-known aspect of chemical kinetics, which requires a liquid or gas phase to be present for a reaction to take place at a reasonable speed. When liquid lead oxide, formed by the oxidation of galena, was present a liquid lead silicate slag was produced and this was then able to react further with other species present in the mixture. It is possible that other low melting species such as alkali metal silicates or chlorides from the fuel might also initiate a reaction.

Lead silicate slags (Type 1 slags)

A temperature of 890°C is required to produce molten litharge, although in practice the presence of impurities may reduce this. It can be seen from the PbO/SiO_2 phase diagram (Fig 16) that once formed, different lead silicates will remain molten and active down to approximately 715°C. Initially a mixture of PbO and Pb_4SiO_6 is formed, and other lead silicates having progressively lower Pb/SiO_2 ratios are produced as more silica is dissolved. When the SiO_2 content reaches 30wt%, the liquidus temperature increases sharply and rises to over 1000°C. Once the lead silicate has solidified then further reaction with solid materials will cease. The silicate-forming reaction will be countered by reduction of lead silicate to lead in the lower, reducing parts of the fire. The simple lead silicate slags tested showed narrow melting ranges with initial softening points (T1) of 770–790°C.

Examination of the phase diagram shows that PbO, $PbSiO_3$, Pb_2SiO_4, Pb_4SiO_6 and quartz can be expected to occur in lead silicate slags. Mixed lead silicate phases can therefore be expected in the range 5–21wt% lead

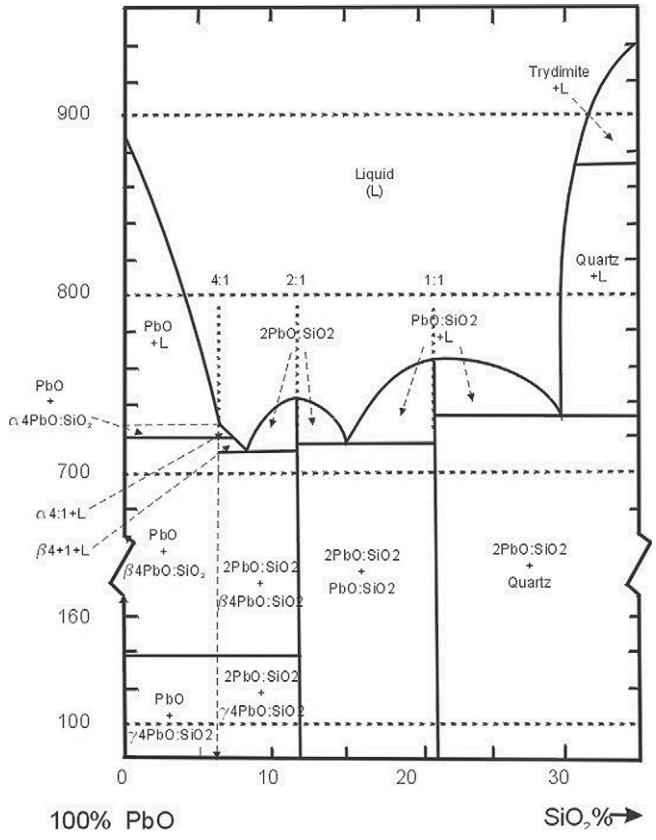

Figure 16: Phase diagram for the system PbO-SiO_2.

oxide and should be detectable in the SEM/EDX. In practice, needle-like crystals have been detected, although these are easily overlooked. When other elements are absorbed into the slag any crystallinity is destroyed and a featureless glass is formed.

Comparisons of experimentally determined slag softening/melting points with those predicted from the phase diagram (Fig 16) are in reasonably good agreement, given the relative unsophistication of the method of determination (see Table 3).

Mixed silicate black slags (Type 2a and 2b slags)

Type 1 lead silicates will react with other gangue materials, generally with a progressively increasing melting point until solidification takes place. Unfortunately phase diagrams or melting point data are not available for multi-component silicate mixtures. Generally speaking, small amounts of alkali metals (Na, K) will favour low-melting slags—ordinary window glass is a good example. In contrast, calcium and barium silicates have very high melting points, with temperatures of the order of 1800°C (see Fig 17) and large quantities of these elements generally increase the melting point of silicate slags. The melting point troughs in Figure 17 are around 1200°C. However, only one of the archaeological slags

Table 3: Experimentally determined and predicted melting points for Type 1 slags

	Temperature (°C)			
Sample	T1	T2	T3	Predicted m.p.
Smith's Hill 083A	770	780	790	725–745
Calver 25A	780	800	810	728
Calebrack B	860	900	950	950
Calebrack A	860	930	950	940

Note: T1 = sample surface sticky, T2 = steel rod able to penetrate sample, T3 = sample fully molten.

consisted only of these three elements (see below). All the other samples also contained small amounts of iron, lead, potassium and other elements which would depress the melting points to around 1000°C.

Crystallisation in black slags (Type 2b slags)

Because few of the field slags were simple mixtures, it has not been possible to compare their behaviour on melting with that predicted from Figure 17; growth of the high-melting species Ca_2SiO_4 is clearly a non-equilibrium process when the overall composition of the slag is taken into account. This is clearly shown by the behaviour of the sample from Browna Gill 065. After melting, the slag matrix has the composition 46.1wt%SiO_2, 17.7wt% CaO and 36.2wt% BaO, corresponding to the point A on Figure 17. The diagram suggests that the species 2CaO.BaO.3SiO_2 would precipitate from the melt and that it would not redissolve at the melting point. On the other hand, the Ca_2SiO_4 which is present must be in a state of non-equilibrium; it would require a matrix having much higher Ca, lower Ba and slightly lower SiO_2 contents for equilibrium. The predicted result is therefore that Ca_2SiO_4 will tend to

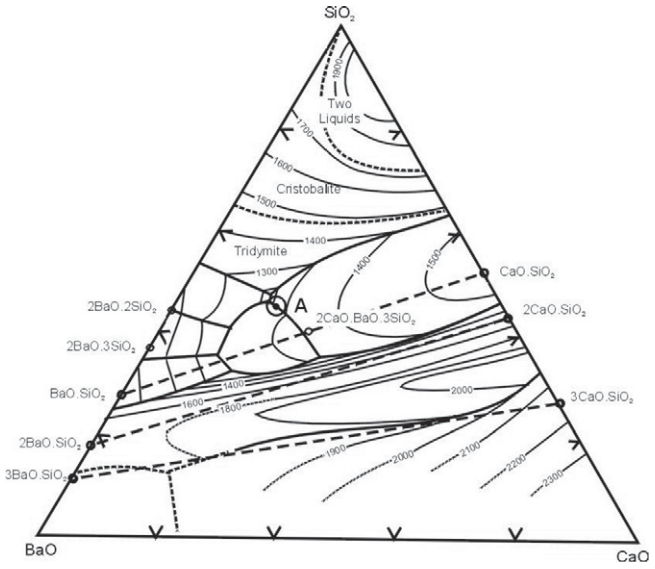

Figure 17: Ternary phase diagram for the system BaO-CaO-SiO_2.

dissolve and that $2CaO.BaO.3SiO_2$ will remain; this is what happened experimentally (see Fig 9).

Bale temperature, slag typology and bale design

There appears to be little information on the temperatures which can be obtained in open wood fires. Some experimental work has been carried out in connection with a study on fire-setting technology for mining (Willies 1994). The temperature of a 5th November bonfire was measured and found to reach 573°C after 12.5 minutes and a maximum temperature of 709°C after 26 minutes. The fire then collapsed on itself and the temperature of the embers stayed at or over 690°C for a considerable period of time. As the thermocouple was situated at the windward end of the fire, it is possible that higher temperatures may have been reached elsewhere in the fire. A second experiment, using dry wooden sticks, took over an hour to reach 573°C, but when substantial quantities of wood were added, a maximum temperature of 779°C was obtained. A metal sheet was then placed in front of the fire, causing it to draw very strongly to the point where a distinct roar was produced, though a temperature of only 785°C was reached. Other experiments by Doonan (1994) produced temperatures up to nearly 900°C in a wood fire used for ore roasting; the fire was in a pit 2.0 by 0.9 by 0.2m deep.

This work suggests that an open fire exposed to wind and with no protective construction can reach 800°C, but that some experience is needed to achieve this. This would probably be sufficient to produce molten litharge (theoretically 890°C is necessary), which is necessary for the slagging reaction with silica. It is reasonable to suppose that the additional heat of the roast reaction would make up the difference, even though the temperature of the fire itself was slightly lower. Therefore, Type 1 and Type 3 slags could be formed in simple open fires, but some form of protection, such as a wall, would be necessary to obtain the higher temperatures necessary for Type 2 slags.

From the slags examined here, temperatures of over 1050°C must have been encountered at least at some sites and the most obvious ways of achieving these would be by packing the wood closely, to restrict the flow of entrained air, while leaving sufficient exposure to air at the surface for oxidation to take place. Even in carefully controlled furnaces, such as those in industrial boilers, a heat loss of 15–20% is fairly common. In the case of an open bale fire, the induced draught and consequent heat loss would be very large indeed, and the heat wasted in the off-gases enormous.

Surrounding the fire with a wall, perhaps on three sides, would restrict air flow and also reduce heat losses. Similar protection might be afforded by a suitably designed pit. These approaches seem to have been used in the later medieval bales reported in Derbyshire, the circular wall reported at Winterings in Swaledale (Raistrick 1927) or the pit bales suggested in Swaledale (Murphy and Baldwin 2001). Partially-enclosed bales could be expected to produce slags of Type 2a, 2b or 3. It is unlikely that they would give rise to Type 1 slags, as further reactions with gangue materials would take place, leading to the production of Type 2 slags.

Higher temperatures would also be promoted by the use of a fuel of higher calorific value than wood. The most obvious way of achieving this would be by using charcoal, or thicker wood which subsequently formed charcoal. Kiernan's reconstruction of a late-medieval bale describes the use of wood grading from brushwood at the top to branch wood lower down the fire, supported on a bed of tree trunks covered with slag (Kiernan 1989; Kiernan and van de Noort 1992). Charcoal was used on open bales in some countries (Agricola 1556) and this possibility has been discussed in more detail elsewhere (Smith and Murphy 2003).

High temperatures in excess of 1300°C can also be obtained in enclosed, induced-draught furnaces or blast furnaces supplied with forced draught from a bellows. The former have been well-documented for iron and tin smelting; the latter are known from historical references from the 14th century onwards. Blast furnaces for re-working bale slags have been referred to as 'blackwork ovens' (Kiernan 1989; Kiernan and van de Noort 1992) and have been used for smelting lead in County Durham (Drury 1992) and Yorkshire (Jennings 1967). One imagines these were cylindrical furnaces about 0.3–0.5m in diameter and about 0.5m in height. They would be somewhat similar to the rectangular slag hearths used to work up grey slags from the late 16th to the 20th century. Although ideal for extracting lead from slags, they would be less efficient for smelting ores, simply because they were poorly suited to produce the oxidising conditions necessary for the elimination of sulphur from galena. Even these furnaces would have been unable to achieve the temperatures necessary to melt Type 3 slags with high $BaSO_4$ contents, and would have had difficulty in achieving the 1418°C needed to melt CaF_2. They would produce Type 2a or Type 2b black slags.

Bale locations and typology

In their paper on the Calver Hill bale sites, Smith and Murphy (2003) noted that Type 1 slags tended to be on smaller bale sites, often associated with small-scale mining and where the miners had possibly brought fuel to the site on their way to work. The paucity of residues suggests that smelting was not conducted over a sustained period and that the ores were well dressed. The presence of mainly Type 1 with some Type 3 slags suggests that maximum temperatures of less than 900°C, and probably around 800°C, were obtained.

Many of the Type 3 slags were associated with bales which were more distant from mine workings and were generally larger than those having Type 1 slags. They appeared to be at sites that had exposed positions but were not optimal for the transport of fuel; Calver 25 and Calver 72 had slags of this type. The Type 3 slags found were accretions of $BaSO_4$, with smaller amounts of CaF_2, held together by lead silicate, oxide and basic carbonate.

On Calver there were two sites where slags of Type 2a and 2b predominated (samples Calver X1–X6 and Z3). These were at relatively low altitude, were very large, and were associated with charcoal dumps. They were the sites most remote from mines on Calver and may have been used for smelting ores from further away. They were the nearest practicable sites for easy transportation of wood, consistent with keeping a reasonable distance from pastures. Both of these sites have been carbon-dated to the later medieval period and have median dates of AD 1439–69 (Barker 1978) and AD 1420 (Smith 2006). The scale of activity is huge by comparison with the higher sites, both in terms of the area over which the slags are scattered and the amount of slag present. Similar sites occur on Fell End in Arkengarthdale and at Spout Gill in Swaledale. Their scale suggests that smelting may have been carried on under the sponsorship of gentlemen landowners having more resources than the miners, and at a time when a division of labour between mining and smelting had became established. The slag compositions, melting points of the examples tested, and appearance, all suggest that they have experienced temperatures of the order of 1100°C but have not been sufficiently molten to have easily run from a furnace. It is possible that these large sites also re-processed slags from earlier workings; if so, silica must have been added to account for the differences in composition between Type 2 and Type 3 slags.

Conclusions

- Slags have been classified according to a typology based on their chemical composition but which also reflects their appearance. The typology has been found convenient for describing different types of bale site and possible differences in smelting technology.
- Some bale slags, principally Types 1, 3 and 2a, have melting points which are consistent with temperatures which can be obtained in open bonfires.
- Other slags, Type 2b and some Type 2a, have melting points in the range 950–1150°C. These temperatures imply a different technology, for example the use of a pit or enclosure to restrict air flow and heat loss, or the use of charcoal as fuel.
- The presence of high-melting phases in the slags, such as $CaSiO_3$ (1600°C) and Ca_2SiO_4 (2130°C), cannot be taken as an indication that temperatures of this order have been obtained. Experiments show that these phases may be generated at temperatures much lower than their melting points.
- Experiments showed that at 1100°C no reaction took place between common gangue constituents ($CaCO_3$, $BaSO_4$ and SiO_2). The presence of a liquid phase, in this case PbO, was necessary before slag reactions could take place, and a mechanism for slag formation has been proposed. Other mechanisms, *eg* involving low-melting fuel ash slags, are possible but have not been investigated here.

Further work

This work has been conducted as part of a wider study designed to understand the processes involved in medieval lead production. Radiocarbon dating of bale charcoal has been undertaken by the author as part of a project funded by the Northern Mine Research Society (NMRS); at present this is very much a range-finding exercise but it is hoped to correlate dates with bale types and possibly with slag types. Other members of NMRS have applied geophysical techniques to the location of lead smelting sites. Difficulties encountered, particularly on the larger sites, are that slags are scattered over a very wide area and that the bales cannot be located. Therefore, before any excavation is carried out, non-destructive surveying should be undertaken. Medieval mining sites are being surveyed, and a better understanding of how these can be identified is also being developed. The socio-economic changes which have occurred throughout the bale-smelting period (*ie* up to about 1570), and the way in which these have influenced the lead industry, are also being studied. Physico-chemical studies of lead slags may seem a long way from these wider concerns, but this

paper has already shown that differences in slag types appear to relate to different ways in which mining and smelting was carried out and possibly indicate changes in the structure of the industry.

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