Metallurgical Residues by Dr. T.P. Young

Summary

Metallurgical residues from Hartshill Copse include a small number of macroscopic slags. These are dominated by slags from iron smelting. Slag morphology indicates smelting in a non-slag tapping furnace, probably with a shallow slag-pit. Chemical analysis of the slags suggests that they were produced from the smelting of an iron oxide-rich ore, perhaps a weathered sedimentary iron ore. Dating of features bearing a rich assemblage of smelting residues suggests smelting was undertaken on the site at a point in the 6th – 5th centuries BC. The small quantity of such slags retrieved strongly suggests that the smelting activity lay outside the excavated area.

Micro-residues, including both spheroidal and flake hammerscale, were recovered from a wide variety of contexts in the EIA enclosure (Fig. xx). Seventeen contexts from Roundhouse B yielded hammerscale, but in very small quantities and not enough to suggest a direct relationship between the context and metallurgical process. Larger quantities of scale derive from features to the south and east of the roundhouse. In all, nine contexts within the enclosure yielded in excess of 10 pieces of scale. A single sample from the enclosure ditch and two probable EIA contexts outside the enclosure also yielded more than 10 pieces of scale. Chemical analysis of spheroidal hammerscale from an assemblage yielding both macro- and micro-residues is broadly similar in composition to the smelting slags, so an origin during bloomsmithing is likely.

Hammerscale was also recovered from almost all postholes within roundhouses C and D (contexts apparently securely dated to the LBA 10th century BC), as well as structure A. Nine contexts within Roundhouse D yielded more than 150 pieces of hammerscale, as did one each from Roundhouse C and structure A. In total, structure A yielded 344 pieces (at moderate densities of up to almost 4 pieces per litre of sample), Roundhouse C yielded a total of approximately 780 pieces (at up to 2.3 pieces per litre), whereas Roundhouse D yielded over 4500 pieces of hammerscale (including 1200 from the hearth, context 1374/1644/1669), with six samples from Roundhouse D exceeding 10 pieces per litre of sample.

Samples of the two hammerscale classes from Roundhouse D were subjected to chemical analysis. The flake hammerscale had a chemical composition similar to that of comparative material from other iron-working sites. In contrast, the spheroidal hammerscale composition

was unlike the comparative material, but similar to the Iron Age material from the site interpreted as from bloomsmithing.

The micro-residue evidence for iron-making or iron-working is therefore apparently even stronger from roundhouses C and D than from Roundhouse B. None of the contexts with extremely high hammerscale densities was amongst those dated by ^{14}C, but two of the dated contexts from Roundhouse D yielded over 100 pieces of hammerscale. None of the contexts yielding hammerscale from roundhouses C and D or structure A yielded any macroscopic slag. There are therefore two possible interpretations of these data: firstly the assemblages can be taken at face value to suggest a phase of iron-working, and probably of iron-making, dating to about the 10th century BC, alternatively it is conceivable that the LBA contexts have been contaminated by downward movement of hammerscale from a, now removed, overlying deposit, perhaps dating to the 5th-6th century BC iron-making phase. The abundance of the hammerscale in some of the LBA contexts must be seen as a strong argument in favour of their genuine attribution to this period. The extremely early date means that caution must be exercised in accepting this interpretation, particularly in the lack of any macroscopic slag from LBA contexts.

In conclusion it is suggested that iron-making was undertaken on the site in the 6th to 5th centuries BC. The focus of this smelting activity is unknown. The ore employed was probably an iron oxide-rich ore derived from the weathering of a sedimentary ironstone. Microresidue evidence also suggests that iron-making was undertaken on the site some four hundred years earlier, but this is not yet supported by macroscopic slag or structural evidence.

Description

Macroscopic slags

Macroscopic slag weighing 2208g was recovered from nine individual contexts. In summary, the assemblage included at least six fragments believed to come from a non-slag tapping iron smelting furnace, together with two smithing hearth cakes. A coal/coke-fired piece which included shale fragments, recovered from the surface of LBA dated pit fill 020 (Group 88), can be regarded as a modern intrusion and has been omitted from the descriptive catalogue, below.

A particularly important collection of both micro- and macro-residues was retrieved from posthole 322, contexts 422 and 323, within the EIA enclosure. This material included a large block of iron smelting slag, a second probably from iron smelting, together with a large collection of small debris including prills, flows, lining fragments and rusty slags. A radiocarbon determination obtained from charcoal associated with this material suggests a date of cal BC 550-360 (93% probability; GrA-24524).

Ditch fill 005 (EIA Group 22). The larger piece appears to be corrosion around a piece of iron, rather than slag. The smaller piece of slag is small nub of vesicular, dense slag, but is too small to be certain whether this piece of iron slag is derived from smelting or smithing.

Posthole fill 323 (EIA Group 165). Two broken slag pieces: first with flow lobes of dense in right angle between two original contact surfaces. Some slight lineation on the contact surfaces creates strong impression that these are charcoal/wood contacts, so that this is a piece of slag within a hearth rather than a runner. Such a form could be interpreted as forming close to the blowing wall, below the hotzone of a non-tapping iron smelting furnace. The other piece is a rusty slag, probably, but not certainly, from iron smelting. Finer-grained material from the same context is dominated by fired wall material, but also including some dense flow lobes of fayalitic slag. Material labelled from the equivalent context 422 (sample 23) comprises fired clay, prills and blebs as well as more corroded material. The entire assemblage is likely to have been derived from iron smelting.

Posthole fill 325 (EIA Group 165). A highly irregular crudely plano-convex slag cake. The lower part includes a lobe of flowed slag, but the upper part is dominated by melted wall material, with abundant gravelly inclusions and vitrified upper surface. A small plano-convex cake of this type is likely to be from blacksmithing.

Context 407 (EIA Group 48). Dense slag, locally with rusty surface. Includes small area of wall contact and interaction, suggesting orientation of the piece is approximately 100m along the wall, extending 55mm into furnace and up to 50mm thick. Upper (?) surface is irregularly broken; lower surface comprises impressions of large charcoal fragments. Charcoal ranges up to at least 40 x 40x 30mm. The most likely interpretation of this piece is that it derives from close to the blowing wall of a non-tapping iron smelting furnace. The open texture of the dense slag, with large charcoal voids and areas of wall attachment would be typical features of material from Irish sites recently examined by the author (particularly that at Tullyallen 6, unpublished).

Posthole fill 588 (EIA Group 48). Two small pieces of grey slag with large charcoal impressions. One of the pieces has some original lobate surface. These are almost certainly slags from within an iron smelting furnace.

Pit fill 821 (RB Group 102). A complexly lobed mass, probably from just in front of the burr area in a non-tapping iron smelting furnace. One side of the specimen shows slag with a coarsely equant texture, a common feature of the burr area (the zone of interaction between the iron-rich furnace contents and the wall immediately beneath the blow hole). The slag has flown around very large wood or charcoal pieces, ranging up to at least 80mm long.

Pit fill 1030. (LBA Group 122). The larger slag piece is a small smithing cake with very fine charcoal impressions, the smaller slag piece is melted furnace/hearth wall. 25g of the sample comprises corroded iron pieces, including nails.

Ditch fill 1076 (EIA Group 16). This is a large piece (90 x 80 x 55mm thick) of plano-convex slag cake. The piece is extremely dense, and has little internal vesicularity. The upper surface is marked by rather rusty impressions of small charcoal pieces. The upper part of the cake has a dense slag layer some 30mm thick, with an equant granular, crystalline texture distally, with a more radial, lath texture proximally, where the cake shows adhering altered lining. This burr region is marked by the development of flow lobes in the lower part of the cake. Suggesting a high mobility of slag close to the furnace wall. The lower surface shows flow lobes proximally, becoming replaced by charcoal impressions distally. This is a difficult slag piece to identify, with no certain indicators of origin. It shows some features which would be unusual an a plano-convex bloomsmithing cake, particularly the lack of a smooth upper surface and the presence of flow lobes, so an origin within a non-slag tapping smelting furnace appears likely, but is by no means certain.

Micro-residues

Recovery was variously by means of magnetic and visual sorting of soil sample residues. The microscopic residues hand picked as “slag” are dominated by dark, vitreous, vesicular, non-magnetic material, which cannot be identified precisely by optical methods. It is likely indeed, that this class covers various types of material and that the majority of these materials are not of metallurgical origin. It may include some slag-like materials, particularly the dark glass, that may be derived from the melting of the lining of a furnace or hearth at temperatures in excess of about 1000℃. Most of the material is probably highly coked organic matter, particularly wood charcoal, but possibly also including a small proportion of burnt bone.

Some non-magnetic slag-like materials are more certainly identified, and these are dominated by glassy materials, mainly of a pale colour, but there are also some darker crystalline non-magnetic slag particles which may be small fragments of iron-smelting slags. There are rare examples of large non-magnetic slag spheroids, and these are likely to be slag droplets from the base of an iron smelting furnace.

Amongst samples picked by magnet, the dominant materials are burnt stone (including flint and ironstone particles), fired clay and metallurgical residues, including small slag fragments and hammerscale. Only the hammerscale has been systematically quantified.

The quantity of hammerscale of both flake and spheroidal types is relatively small when the enormous quantities of such material generated by metallurgical processes are considered. In total 6144 fragments of flake hammerscale and 475 spheres were retrieved. The sampled spheroidal hammerscale from contexts 1402/1667 (LBA Group 44) had a size range of 100 – 1900μm, with a mean of 660μm, that from 1543/1669 had a range of 200 – 1000μm, with a mean of 480μm. The spheroidal hammerscale from other contexts appears broadly similar, although no detailed measurements of size distribution have been made. The one exception is the deposit rich in smelting debris 422/323 (EIA Group 22) in which a proportion of significantly larger spheroids were present; it is possible these may have a separate origin with the smelting furnace.

Flake hammerscale assemblages were all rather degraded. It is possible however, that coarser materials were not retrieved by the sampling regime; the samples investigated were dominantly those from the 0.5 to 1.0 mm size fraction.

Distribution

The macroscopic slags were widely distributed across the site, with no clear focus.

Micro-residues, including both spheroidal and flake hammerscale, were recovered from a wide variety of contexts in the EIA enclosure. Seventeen contexts from Roundhouse B yielded hammerscale, but in very small quantities (total 123 pieces, maximum density 1.9 pieces per litre of sample) and not enough to suggest a direct relationship between the context and metallurgical process. Only three of those contexts exceeded 10 pieces of scale. Larger quantities of scale derive from features to the south and east of the roundhouse. In all, nine contexts within the enclosure yielded in excess of 10 pieces of scale (total approximately 700 pieces); three of these, two postholes and a pit, each yielded more than 150 pieces of hammerscale, with scale density up to almost 10 pieces per litre of sample. A single sample from the enclosure ditch and two probable EIA contexts outside the enclosure also yielded more than 10 pieces of scale.

Hammerscale was also recovered from almost all postholes within roundhouses C and D (contexts apparently securely dated to the LBA, approximately 10th century BC), as well as structure A. Nine contexts within Roundhouse D yielded more than 150 pieces of hammerscale, as did one each from Roundhouse C and structure A. The processing of the microresidue samples was variable and it cannot be guaranteed that full recovery of hammerscale from roundhouse C and D contexts was achieved. For this reason comparison of the hammerscale type ratios is slightly problematic. However, structure A yielded four assemblages of more than 10 pieces (total 344 pieces at densities of up to almost 4 pieces per litre of sample), with an overall the flake:spheroidal hammerscale ratio was 43:1. Roundhouse C yielded a total of approximately 780 pieces, whereas Roundhouse D yielded over 4500 pieces. The flake:spheroidal hammerscale ratios for these two roundhouses was approximately 10:1 and 12:1 respectively. The maximum densities of hammerscale was 2.3 pieces per litre in Roundhouse C, but six samples from Roundhouse D exceeded 10 pieces per litre of sample. The close association of hammerscale with Roundhouse D is particularly noteworthy, and the approximately 1150 pieces from the hearth is extremely significant.

One odd feature of the distribution of the hammerscale within roundhouses C and D is that apparent inhomogeneity of the posthole fills. The replicate samples from the two halves of the posthole often show strongly contrasting densities of hammerscale. One possible explanation for this might be that hammerscale is intrusive within quite small structures, such as worm holes, roots or mammal burrows.

Investigation of the variation in the ratio of flake:spheroidal hammerscale across the site (Fig.. c and d) shows a rather variable pattern amongst the samples with only a small number of hammerscale pieces, however, the samples with more than 1 piece of hammerscale per litre of soil show a more structured pattern, with the samples with the highest density of hammerscale (particularly the eastern side of Roundhouse D and posthole 322 in the enclosure) showing a slightly lower flake:spheroid ratio (range 8 – 14) than the samples with a slightly lower density (roundhouses B and C, structure A, enclosure G; typically 15 and above). This provides a suggestion that these samples with the moderate flake:spheroidal hammerscale ratio may be indicative of bloomsmithing residues. Samples with a higher ratio might be from blacksmithing.

Chemical analysis

Chemical analyses were undertaken by the laboratories of the School of Earth, Ocean and Planetary Science, Cardiff University. Major element analysis was undertaken using induction-coupled plasma optical emission spectrometry (ICP-OES) and trace elements by induction-coupled plasma mass spectrometry (ICP-MS). Unfortunately the system was not able to measure Si in the samples, and for some samples rich in magnetite the acid dissolution was incomplete and the iron measured is a minimum content.

Macroscopic slags

Five specimens of slags interpreted as smelting slags were analysed. The samples were derived from contexts 323 (EIA Group 165), 407 (EIA Group 48), 588 (LBA Group 154), 821 (RB Group 102) and 1076 (EIA ditch Group 16). The chemical analyses are presented in Table 1. The analyses are all very similar, supporting the proposition that these are slags produced from a common process. Total iron, quoted as FeO varies from 62.8% to 74.0%. The slags are only moderately aluminous (Al_2O_3 varying from 3.2% to 4.4%), have low CaO

(0.6% to 1.1%), low MgO (0.3% to 0.5%), moderate TiO_2 (0.2% to 0.3%) and moderate P_2O_5 (0.6% to 0.8%).

The trace element contents are also fairly tightly grouped. Elements worthy of comment include fairly low contents of Pb (7-10ppm), Ba (180-250ppm) and U (1.3-2.4ppm). Contents of some of the "immobile" elements are moderate, with Y at 40-56ppm, Nb at 4.7-5.4ppm, Th at 3.1-3.8ppm and total rare earth elements (ΣREE) of 140-210ppm.

The upper-crust normalised (after Taylor and McLennan 1981) REE profiles are mainly humped, with Gd the most enriched (1.6 – 2.4 times upper crust). The heavy REE (HREE) are slightly less enriched (1.4 to 1.8 times upper crust for Lu, but slightly higher than the light REE (LREE) with 0.9 –1.4 times upper crust for La, with a very slight negative Ce anomaly.

In detail, the REE profiles show a spread from examples with a MREE "hump" through to examples with depletion of the LREE, which imparts an overall slope to the profile. The sample from (1076) is the most humped, with those from (323), (821) and (407) showing slightly lower LREE values, but with that from (588) showing a marked slope down to the LREE. A degree of variability is to be expected, even within slags from a single smelt, because of the non-homogenous nature of slag in a non-tapping furnace.

Micro-residues

Three samples of micro-residues were selected for analysis, together with five samples of comparative material, since there are no published chemical analytical studies of hammerscale. For all of the samples the analytical technique required sample sizes greater than single particles. In order to attain a suitable bulk samples size the sample of spheroidal hammerscale from an EIA context contained eight spheroids from context 422 (Group 165), the sample of spheroidal hammerscale from LBA contexts contained 33 spheroids from contexts 1402/1667 (Group 44) and 1543/1660 (Group 45), and the sample of flake hammerscale from LBA contexts contained 23 pieces from contexts 1402/1667, 1543/1660 and 1425/1665 (Group 42). All the LBA contexts from which the samples were drawn are postholes within roundhouse D.

The analyses of the two sets of spheroidal hammerscale are rather similar, and strongly dissimilar to the flake hammerscale. The flake hammerscale shows low concentrations of all elements (except iron).

The upper-crust normalised REE profile of the flake hammerscale is fairly flat, but those of the two spheroidal samples show relative deletion of the LREE, giving a profile close to that of the macroscopic smelting slags.

Comparative material

Hammerscale of each of the two classes was sampled from existing collections from two sites. Firstly the 4th century smithy within the basilica at Caerwent, Gwent, context CWT2835 (more than200µm fraction), and secondly material from an early medieval (probably 8th century) smithy at Abernant, Gwent, context ANC099A (1-2mm fraction of magnetic residues). In addition, magnetic spheroids produced in a corn-drying kiln in the Iron Age settlement of Bornish, South Uist (context 269, samples 5967 and 5991), were analysed as an example of non-metallurgical magnetic spheroids.

The flake hammerscale from Caerwent contains over 96% iron expressed as magnetite. For the Hartshill and Abernant specimens the laboratory reported problems in getting all the magnetite into solution, so those iron totals are too low. For other elements the flake hammerscale shows lower concentrations than found in the spheroidal hammerscale. The upper-crust normalised REE profiles for the samples from Abernant and Caerwent are approximately parallel, with the REE relatively enriched by 1.5 to 2 times in the spheroidal scale.

The material from the corn-drier at Bornish showed a surprisingly low iron content given its strongly magnetic properties. The material was markedly different from the iron-working residues in many aspects of its composition, and it will not be discussed further here.

Interpretation

Chemical analyses suggest that the macroscopic smelting slags were the product of smelting quite a rich iron ore. The contents of CaO and MgO are low, suggesting it was not a carbonate ore, The P_2O_5 is moderate, suggesting a sedimentary ore. The most likely solution is that the ore was a sedimentary iron oxide, probably goethite. Iron oxide pellets were present in the magnetic residues, suggesting they had been heated – so smelting of a highly weathered greensand is possible.

The chemical analyses of the microresidues from the LBA contexts leaves no room for doubt that they indeed from iron-making or –working. The match between the REE profiles of the spheroidal hammerscale and the macroscopic slags suggests that they were likely to have been derived during bloomsmithing, and the expulsion of residual smelting slags from the raw bloom. Some spheroids may be produced in the smelting furnace too, but the context of much of the Hartshill material suggests against that in this case.

Discussion

The volume of metallurgical residue from the site is very small, but indicates that both iron smelting and iron working took place somewhere on the site. However, determination of the scale of that activity must await the discovery of its focus. The amount of iron smelting slag recovered represents the equivalent of perhaps one tenth of one smelt.

One of the most remarkable features of this site is the extremely widespread nature of the micro- and macro- residues. The mechanism for their dispersal across the site from the original focus of activity remains unknown.

The iron smelting appears to be reasonably closely tied to the prehistoric structures recognised, with microscopic residues occurring widely in their postholes and macroscopic slags occurring within pits and postholes within the enclosure and within the fill of its ditch G. The small number of slag pieces does not permit much comment on the technology and scale of operation, but do point to the use of non-slag tapping furnaces. Such furnaces are widely presumed to have been in use in the Early Iron Age, but direct evidence for them has not generally been forthcoming in southern England. Identification of the ore involved in the smelting operation would be very important. The best known iron-smelting site in the area is the Saxon site at Ramsbury (Haslam 1980), some 27km further up the Kennet Valley, but still within a broadly similar geological setting.

Until recently it had been assumed that most of the iron being employed in Early Iron Age Wessex was sourced from outside the region (e.g. Ehrenreich 1994), but a number of smelting sites within the area have started to be recognised. The technology of iron smelting appears to be very close to that on several unpublished sites of this period in Ireland for which the author has undertaken review of the metallurgical residues.

Although there is doubt over the proper collection of hammerscale from the earlier-processed residues, the certain LBA contexts appear to yield a hammerscale assemblage broadly comparable with that from the EIA contexts. The extremely early proposed date of this material is remarkable. Iron smelting of 10th century BC age has not yet been recognised in western Europe, although the process may have been undertaken in Eastern Europe at this time (Pleiner 2000). Iron artefacts become relatively widespread in Britain in the latest Bronze Age "Llyn Fawr Phase", usually attributed to a period around the 8^{th}

century BC, but there is so far little evidence for smelting sites or slags before the 6th century BC. If the hammerscale from roundhouses C and D is genuinely of 10th century age, then it is a remarkable discovery.

Given these extremely early proposed age for the hammerscale assemblage from Roundhouses C and D, together with the absence of macroscopic slag from this part of the site, caution is urged in taking the assemblage at face value. It is possible that the "LBA" assemblage has arisen by a different route, perhaps by downward percolation of the microresidues from an overlying (now removed) deposit. An alternative explanation might be that there are superimposed structures on the site of Roundhouse D; the postholes with extremely high hammerscale contents appear to have a more rectilinear distribution than circular.

Acknowledgements

Niall Sharples kindly supplied the residues from Bornish, Anne Leaver those from Abernant and the National Museums and Galleries of Wales the material from Caerwent. David Dungworth kindly supplied unprovenanced hammerscale for development of the analytical technique.

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