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## Archaeometallurgical residues from Dunnyneill Island

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## Abstract

*Excavations on Dunnyneill Island yielded a total of 1.75kg of residues from pyrotechnological processes (of which 1.1kg was contributed by just two pieces of smithing hearth slag). Despite the small size of the assemblage, over half of which came from topsoil or disturbed contexts, there was a strong relationship between residue type and both site phase and geographical location.*

*Ferrous metalworking is represented mainly in the lower part of the site, where the low earthwork yielded a significant assemblage of iron-working (smithing) slags from the ditch fill and a small amount from the bank construction. The same area yielded a large collection of iron-working slag from disturbed contexts. A single small piece of iron-working slag was recovered from a Phase 3 context in Trench 1.*

*Non-ferrous metallurgical processes are represented by a number of sherds from shallow crucibles, which probably functioned as ceramic cupels, used in the assaying of silver, from both Phase 2 and Phase 4 contexts. A single tiny slag fragment from Phase 4 may suggest the working of zinc-bearing copper alloy.*

*The occurrence of several glazed pebbles in Phase 2 indicate high temperature processes in which metal did not enter the hearth. They may have been produced in a hearth in which crucibles were heated, but they are not diagnostic of process, and may not necessarily have been produced in a metallurgical hearth. The high-sodium, low-calcium glaze may suggest that they were produced during the burning of kelp.*

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## Methods

All material was examined under a low-magnification stereo microscope. Material was selected for further analysis as appropriate.

Crucible material was examined to determine the chemical composition of surficial slag phases using the Energy Dispersive X-Ray Fluorescence (ED-XRF) Eagle II instrument at English Heritage, Fort Cumberland, Portsmouth, with the kind assistance of Dr Justine Bayley. The samples were analysed in a normal atmosphere to produce only qualitative indications of metal presence.

Whole-specimen chemical analysis for major elements was undertaken using fused beads on the Open University Earth Science Department's Wavelength-Dispersive X-Ray Fluorescence (WD-XRF) system. Whole-specimen chemical analysis for minor and trace elements was undertaken on the Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) in the School of Earth, Ocean and Planetary Sciences, Cardiff University.

Scanning electron microscope imaging and microanalysis was undertaken on the Cambridge Instruments (LEO) S360 analytical SEM, equipped with an Oxford Instruments INCA ENERGY energy-dispersive x-ray analysis system (EDX).

This report includes and updates the information contain in the evaluation report for the assemblage.

## Results

### Crucibles

#### Description

##### Dish-like ceramic cupel

#18 (c107) Figure 1a. A small sherd, 21 x 14 x 6mm, apparently from a thin dish-shaped vessel, approximately 60mm in diameter, in a pale grey fabric. There is thick dark maroon glaze on the upper surface. The lower face does not show significant vitrification except on the outer face of the rim. The analyses show the slag to be lead-rich and silver bearing, and the vessel is likely to have been used as a cupel.

##### Flat-bottomed ceramic cupels

#206 (c404). A tiny sherd (9mm along the rim, with 9mm of the vertical outer face preserved) from the rim of vessel very similar to #700 (see below). The outer vertical face is lightly vitrified, becoming slightly green onto the rim. On the inner surface the uppermost 3mm has a pale green glaze, but below this the glaze thickens and darkens abruptly. The lower part of the glaze has a strong golden yellow colour. The fabric is mid-grey in colour and extremely quartz-rich. The vessel appears to have been 50-60mm in diameter. Analyses suggest that this vessel was a cupel used in silver assaying.

#700 (c424) Figure 1b. A 28 x 23 x 20mm sherd from a vessel with a flat base, steep sides with a slightly out-turned curved rim, and a gently concave upper surface. The vessel is somewhat irregular, but would have been 50-55mm in diameter, the rim stands 20mm above the base and it is made of a grey quartz-rich fabric. The base is lightly vitrified and strongly fissured, with the fissures extending onto the outer wall, where they locally show a slag fill. The inner surface has a dark vitreous deposit extending up to the rim. Analyses suggest that this vessel was a cupel used in silver assaying. On the more central part of the upper face a slight pale upstanding ridge may correspond to the limit of an original metal pellet.

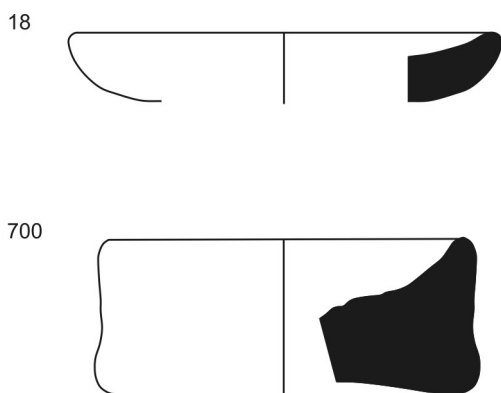


Figure 1. Cupels: #18 (dish-shaped) and #700 (flat-bottomed).

#### Undiagnostic crucible fragments and slag

#40 (c203). This fragment (26 x 18 x 11mm) is probably from the lip of a crucible. It has only a very thin layer of quartz-rich material on the concave surface, covered in an irregular layer reddish coloured vesicular glassy slag forming the bulk of the fragment and convex (external?) surface, which appears to show dimples from contact with fuel. The analyses of the slag show similarity with those from the cupels (see above), but the slag is apparently on the external surface. However, given the extremely thin layer of crucible-like material it is possible that this piece has been strongly deformed by heat.

#26 (c104). A piece of flown slag, 17 x 14 x 7mm. One side is formed of partially melted quartz-rich material, approximately 0.5mm thick. The quartz grains are set in a groundmass of pale reddish-brown glass, which also extends as a layer over the quartz-rich material, of variable thickness but up to 3mm. This red glass is overlain by darker brown to black glass, with an apparently iron-rich surface layer. It is not clear whether this material represents a melted surficial layer (and attached slag) from a crucible, or tuyere, or indeed whether the quartz-rich material represents hearth lining. The analyses (see below) suggest that slag was associated with the melting of a zinc-bearing copper alloy.

#224 (c404). A small fragment of crucible, with a vitrified surface 7 x 5mm and approximately 11mm thick. It is not clear whether the unvitrified end is an original surface. The vitrified surface is probably slightly concave. The fabric is pale grey, quartz-rich, becoming vesicular towards the vitrified surface. A brownish glassy phase has penetrated in to the crucible up to 4mm below the vitrified surface. The slag phase was analysed and shown to be lead-rich, but dominated by copper. The form of the fragment suggests, but does not prove, that it may be from a flat-bottomed crucible as #206 and #700.

#197 (c404). A small piece of glassy slag with a rich brown colour, attached at one end to some green glass bearing quartz grains. The piece is suggestive of a crucible slag with at least a 7mm thickness of brown slag attached to vitrified crucible material. Analysis shows the slag to be lead-rich.

#### Analysis

The analysed material falls into two groups: firstly a group (#18, #206, #700, #40, #197) with lead-rich slags, with variable copper contents, and bearing silver; and secondly a smaller group of material (#224, #26) where copper is more important, lead is frequently at significantly lower concentrations, silver is at very low levels or absent, and in #26 zinc is locally above trace element levels.

|                                     | Cu           | Zn    | Pb           | Sn    | Ag           |   |
|-------------------------------------|--------------|-------|--------------|-------|--------------|---|
| <b>Dish-shaped crucible #18</b>     |              |       |              |       |              |   |
| Low upper                           | minor        | tr    | <b>Major</b> | tr    | tr           |   |
| High upper                          | minor        | tr    | <b>Major</b> | minor | tr           |   |
| <b>Flat-bottomed crucible #206</b>  |              |       |              |       |              |   |
| Yellow glass                        | major        | tr    | <b>Major</b> | tr    | minor        | Comparative examples for flat-bottomed cupels from Britain and Ireland include examples from:   |
| Near rim                            | major        | tr    | <b>Major</b> | tr    | minor        |   |
| <b>Flat-bottomed crucible #700</b>  |              |       |              |       |              |   |
| High upper                          | major        | minor | <b>Major</b> | tr    | tr           | <i>Clatchard Craig</i> , where an irregular vessel approximately 41mm in diameter (Close-Brooks 1986) has a thick internal lead and tin bearing glaze.  |
| Low upper                           | major        | tr    | minor        | tr    | <b>Major</b> |   |
| <b>Deformed crucible sherd? #40</b> |              |       |              |       |              |   |
| Convex 1                            | major        | tr    | <b>Major</b> | tr    | tr           | <i>Lagore Crannog</i> , where 23 examples of flat-bottomed crucibles were found (Hencken 1950; Craddock 1989, no 171; Comber 1997, 2004) the vitreous residues indicate heating from above, but there are no published modern analyses. All the material has recently been redescribed by Comber (2004). Some of the examples (E14:439, E14:522 contain a central circular depression, attributed by previous authors to the use of these vessels as supports (e.g. Craddock 1989; Comber 1997), but which might be the scar from metal button removal. Some of the vessels are taller and less vitrified, and these may be parting vessels rather than cupels. |
| Convex 2                            | minor        | tr    | <b>Major</b> | tr    | tr?          |   |
| Concave                             | minor        | tr    | <b>Major</b> | tr    | tr           |   |
| <b>Slag fragment #197</b>           |              |       |              |       |              |   |
| Spot 1                              | major        | tr    | <b>Major</b> | tr    | tr?          |   |
| <b>Crucible fragment #224</b>       |              |       |              |       |              |   |
| Spot 1                              | <b>Major</b> | tr    | major        | tr    | -            |   |
| <b>Slag fragment #26</b>            |              |       |              |       |              |   |
| Pale side s1                        | <b>Major</b> | tr    | minor        | tr    | tr           | <i>Clogher</i> , Warner (1986) comments that the flat-bottomed crucibles appear at Clogher after the yellow layer (following Warner 1979) i.e. 7-9th century. The Clogher material is unpublished, but was described by Quinn (1981). She listed 10 examples of "B2" crucibles, at least 6 of which were shallow. Five of the specimens were described in detail (Quinn, 1981, p. 64-65, nos. 3727, 3531, 3362, 3790, 3388) and the vessel shape and pattern of vitrification seem very similar to the present material.  |
| Pale side s2                        | <b>Major</b> | tr    | minor        | tr    | tr           |   |
| Pale side s3                        | <b>Major</b> | minor | major        | minor | tr           |   |
| Dark side s3                        | <b>Major</b> | minor | minor        | tr    | tr?          |   |

Table 1. results of ED-XRF analysis of crucible sherds and related slag. Results are classified as major components (bold indicates the most abundant element), minor components, trace components (tr) where doubtful indicated by a query and absent (-).

## Discussion

Open dish-shaped "crucibles" like #18 are not a common component of most early assemblages, although the general type is found on Roman sites, where they have been recognised as heating trays or cupels for purifying silver (e.g. Zienkiewicz 1993, figure 46, 4-9). In an early medieval context, the most similar material is the Dunadd type B2 crucible (Lane & Campbell 2000; not the same as a Tylecote 1986 type B2, see below), although the present material is much smaller than the single example from Dunadd. Dish-shaped ceramic cupels were recorded by Bayley (1992; fig. 318) from Coppergate, York.

The Dunnyneill Island specimens #206 and #700 derive from a vessel form that occurs widely, but has rarely been recognised as being separate from other flat-bottom "crucibles", and therefore which has no simple name or classification. This group has disk-like shape (though not always circular in plan), with a diameter of 30-60mm and a height of 10-20mm. The upper surface is concave and usually vitrified, the lower surface unvitified and flat (ranging from slightly convex to slightly concave). Commonly-employed terminology for material similar to #206 and #700 includes *flat-bottomed crucible*, *dog-bowl crucible* and *heating tray*. They do not feature in the illustration of Tylecote's (1986) classification of crucibles, but the text assigns type B2 to a cylindrical, flat-bottomed crucible type represented at Lagore. It seems likely, through the use of the term cylindrical, that Tylecote

was particularly referring to the published material like Lagore find no. 1371 (Hencken 1950, figure 117). This crucible does not appear on Comber's (2004) list of the surviving Lagore material, but no. 1371 appears similar to the tall flat-bottomed crucible E14:523, which from the description given by Comber as lightly reddened, may be similar to vessels ascribed to a use in parting elsewhere (e.g. Bayley 1991).

Comparative examples for flat-bottomed cupels from Britain and Ireland include examples from:

*Clatchard Craig*, where an irregular vessel approximately 41mm in diameter (Close-Brooks 1986) has a thick internal lead and tin bearing glaze.

*Lagore Crannog*, where 23 examples of flat-bottomed crucibles were found (Hencken 1950; Craddock 1989, no 171; Comber 1997, 2004) the vitreous residues indicate heating from above, but there are no published modern analyses. All the material has recently been redescribed by Comber (2004). Some of the examples (E14:439, E14:522 contain a central circular depression, attributed by previous authors to the use of these vessels as supports (e.g. Craddock 1989; Comber 1997), but which might be the scar from metal button removal. Some of the vessels are taller and less vitrified, and these may be parting vessels rather than cupels.

*Clogher*, Warner (1986) comments that the flat-bottomed crucibles appear at Clogher after the yellow layer (following Warner 1979) i.e. 7-9th century. The Clogher material is unpublished, but was described by Quinn (1981). She listed 10 examples of "B2" crucibles, at least 6 of which were shallow. Five of the specimens were described in detail (Quinn, 1981, p. 64-65, nos. 3727, 3531, 3362, 3790, 3388) and the vessel shape and pattern of vitrification seem very similar to the present material.

*Brough of Birsay* (Curle 1982, 410 and 411; Craddock 1989, no 179b 410;), two examples (classified as flat bottomed oval containers) rather doubtfully included here, from Pictish, late 8<sup>th</sup> century deposits. They are of rather different form to the present material, and are described as "showing signs of firing".

*Ballinderry No2 Crannog* (Hencken 1942) Crucible no. 313 provides a single example of the type at this site.

*Moyneagh Lough*, a thinner example of "heating tray" of early 8<sup>th</sup> century date (Bradley 1991) is known from this site (Craddock 1989, no. 160). The slag is confined to the centre of the disc.

*Dunmisk*, where there is a possibly related subrectangular flat-bottomed vessel with internal glaze. (Ivens 1979, Figure 19, 2)

*Armagh*, where there are several broadly similar vessels, although some examples do not have any vitrification (Gaskell Brown and Harper, 1984, Figure 19, numbers 114, 117, 120, 122a, 124, 126). Quinn (1981) described some examples, with nos 114, 112, 117, 120 and 132 having patterns of vitrification close to that of the Dunnyneill specimens.

Additional examples have been widely recorded in Scandinavia (Fyrkat, Roesdahl 1977; Sigtuna, Söderberg 2004; Birka, Söderberg 2004; Viborg, Krøngaard Kristensen 1990). The example from Birka illustrated by Söderberg (2004) and its experimental analogue provide a good illustration of the likely use of the Dunnyneill examples.

Although two quite separate vessel forms appear to be represented in the Dunnyneill Island material, they are linked by a similarity of use, with vitreous deposits on their upper, shallowly concave surfaces, with residues characterised by high lead contents and significant, locally high, silver contents.

Interpretation of the purpose of such vessels has generally been somewhat speculative in the past. The low degree of heating evident on many flat-bottomed crucibles and the commonly oxidised fabric led to speculation that the vessels may have been used as metallurgical heating trays (for instance during soldering or filigree work), or indeed as heating trays for use in glasswork or enamelling. One group of these vessels does show a reduced fabric and vitrification indicating heating from above (as opposed to heating from below as seen in most crucibles). The observation of a sub-circular depression in the upper vitrified surface of some examples helped to give rise to the interpretation of some examples as crucible stands (e.g. Craddock 1989; Comber 1997).

Increased understanding of metallurgical processing of the precious metals has led to recognition of the flat-bottomed vessels as being implicated in at least two separate processes (although these are probably not the only purposes for which the flat-bottomed vessels were employed):

1. the taller flat bottomed vessels, which have oxidised fabrics and no evidence for very high temperatures can now be identified as often being used in parting; a process in which silver is separated from gold by heating thin sheets of the mixed alloy interleaved with a salt-containing material (Bayley 1991, 1995). A substantial group of parting vessels is represented by the taller classes within Type B crucibles from Dunadd (Lane & Campbell 2000; Bayley 2001)

2. the shorter flat bottomed vessels, as in the Dunnyneill Island material, with only a slightly dished, vitrified, upper surface. The vitreous deposit on the upper surface has been demonstrated, as in the Dunnyneill Island examples, to be rich in lead, with a measurable content of silver in many cases (e.g. Clatchard Craig, Close-Brooks 1986; Fyrkat, Roesdahl 1977; Sigtuna, Söderberg 2004; Birka, Söderberg 2004; Viborg, Krongaard Kristensen 1990).

Bayley and Eckstein (1997) have discussed the significance of these finds and argued that they represent use of the vessels as cupels. A small quantity of silver alloy would have been placed on the vessel and melted in the presence of an excess of lead. The lead would have oxidised to litharge, which would then react with the vessel to produce a lead-rich silicate slag. In later medieval and post-medieval assaying, a process of this type is known as scorification and produces an argentiferous lead metal "button", which can then be refined to silver by cupellation in a bone ash or other porous cupel. However, Bayley and Eckstein suggest that before the introduction of bone ash cupels, the entire process would be undertaken in a single step with the production of a silver button within a "normal" silicate vessel.

In either case, cupellation or scorification, the product is a metal button in the centre of the vessel, and removal of this button leaves a circular scar, similar to those previously taken as evidence for the use of the flat-bottomed "crucibles" as crucible stands.

## Interpretation

The use of cupels, such as those from Dunnyneill Island, is not entirely clear. It would seem most likely that these small cupels are for assaying silver, rather than for purifying silver for use. Söderberg (2004) has suggested that they assaying of silver may have been particularly significant at before the general acceptance of coinage in Scandinavia (pre-late 10<sup>th</sup> century, but that assaying continued to be significant within the mint, with similar ceramic cupels appearing through until at least the 13<sup>th</sup> century.

## Glazed pebbles

### Description

The collections include five small specimens in which stone chips have become glazed. Four of these were stratified in Phase 2 deposits (three from 421, one from 110) and the fifth was from topsoil (301). The pieces contained different geological substrates: two were sandstone, one was probably calcareous mudstone, one was a fossiliferous shale and one was probably a tuff.

The glaze in most cases was thin, even and fairly clear, sometimes with a pale greenish colour. One piece (sf #485) was rather more complicated, and showed a colour change from clear or slightly green where attached to the stone, but becoming darker towards the top of the piece and almost black where it is contact with some ashy material.

### Analysis

Small pieces were removed from three of the specimens (#83, #111, #482) by miniature diamond saw and mounted for examination on the analytical SEM. The samples were mounted on a stub and carbon coated for analysis. The analyses are at best semi-quantitative.

The results show a strong enrichment in sodium and potassium in the glaze with respect to the underlying stone, but a much weaker enrichment in calcium (only seen in #111 and #482, but not in #83).

|  | n | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO | MgO | K <sub>2</sub> O | Na <sub>2</sub> O |
|--|---|--------------------------------|------------------|--------------------------------|-----|-----|------------------|-------------------|
| <i>average glaze composition glaze</i> |   |                                |                  |                                |     |     |                  |                   |
| #83                                    | 2 | 4.0                            | 59.4             | 3.0                            | 0.4 | 1.3 | 7.6              | 5.1               |
| #111                                   | 4 | 3.9                            | 67.7             | 3.1                            | 0.7 | 1.3 | 6.9              | 3.7               |
| #482                                   | 3 | 5.8                            | 54.5             | 5.9                            | 1.0 | 2.4 | 6.3              | 8.7               |
| <i>average rock composition</i>        |   |                                |                  |                                |     |     |                  |                   |
| #83                                    | 2 | 7.4                            | 61.5             | 5.5                            | 1.0 | 2.0 | 1.9              | 0.7               |
| #111                                   | 4 | 5.9                            | 69.2             | 2.7                            | 0.0 | 1.3 | 1.4              | 0.1               |
| #482                                   | 1 | 5.8                            | 61.5             | 4.3                            | 0.4 | 1.4 | 1.8              | 2.1               |

Table 2. Partial semi-quantitative EDS analyses for the glaze and underlying rock for three selected glazed pebbles.

## Discussion

Glazed stones like those reported here are not normally considered diagnostic of any particular pyrotechnological process, and indeed might arise during transient high temperatures in domestic hearths and other fires. The glazes would normally be expected to be formed by fluxing of the rock surface by the alkalis in the wood ash, and therefore for the glazes to show elevated calcium and potassium contents. In this case the glazes are enriched in potassium and sodium. Sodium is an element which is not particularly abundant in wood ash, but which is abundant in seaweed ash.

## Iron slag and associated residues

### Description

Slags from iron-working were abundant in Trench 7, with only a small quantity being found higher on the mound.

#### Low density glassy lining slags

These materials derive entirely from Trench 7 and are all certainly or probably associated with vitrified hearth lining. They included the group of sf #590 – 605 (context 712) which may comprise just one or two original, now fragmented pieces (possibly one with and one without attached lining material). Part of this group shows the slag forming a thin sheet with large crystals of ?olivine showing on one side. Similar material was recovered from context 706 (Sf #547, 548), also showing large crystals on one side of a dimpled sheet. Sf #548 also showed some accreted flake hammerscale.

Context 713 yielded a specimen that appears to show several small sandstone pebbles, or pieces of sandy lining, fused together by a glassy slag.

#### Plano-convex smithing hearth slag cakes

The upper part of the site yielded a substantial piece (105g) of a plano-convex smithing hearth slag cake (SHC) from Phase 4 (context 407, sf #306). This piece appears on general morphological grounds to be a smithing hearth cake, but the broken face shows bladed olivine crystals up to 17mm long. Such a large crystal size indicates a substantial pool of molten slag, which was allowed to cool slowly. This piece was further investigated (see analysis section below) because of the textural differences between this piece, the only SHC from the upper part of the site, and the SHC pieces from the lower part of the site. The analysis indicated that the iron content of SHC # 306 was rather low, but whether the enhanced fluxing of the iron was deliberate or accidental it is not possible to determine.

A small piece (29.8g, broken in two) of vesicular grey iron slag was recovered from Phase 3 (context 106), and this is very likely to be a smithing hearth slag.

From the lower part of the site, Trench 7 produced a much larger assemblage of iron-working slags, although much of the material came from disturbed contexts within the tree throw. Substantial fragments of plano-convex smithing hearth cakes came from context 704 (sf #514, 125g), context 712 (#487, 500g)

and context 714 (#582 690g). These pieces indicate total cake weights in the range of 500-1000g, consistent with an origin in blacksmithing. Various smaller pieces of iron slag from the same trench can be identified as small pieces of smithing hearth cakes.

#### Iron slag films

Two small pieces from trench 7 (sf# 509 and 524, both from context 705) were from thin films of crystalline iron slag. Such films may be the result of slag solidifying against an object (such as a stone) within the hearth, but are sometimes indicative of processes outside the hearth. They may arise from slag on the workpiece being detached during hammering, or they may arise from slag sticking to a tool, such as a poker.

### Analysis

A full chemical analysis (Table 3) was prepared by XRF (major elements) and ICP-MS (minor and trace elements) to examine the slag bearing extremely coarse-grained fayalite in sample #306. This texture was not observed in other iron slag material from the site. The analysis reveals that the iron content of this part of the slag cake is quite low (41.1% FeO), with high silica (43.91%) and relatively high calcium and potassium (4.2% CaO and 3.6% K<sub>2</sub>O), compared with typical smithing hearth slag bulk analyses. However, compositions close to this analysis are often seen in the well-fluxed upper layers of smithing hearth cakes (with high contributions from the hearth lining and/or added flux). In this case the high calcium, potassium and fairly high phosphorus values suggest that the contribution from the fuel ash is significant too. The contents of the non-ferrous metallic elements lead, tin and zinc are all low. The upper-crust normalised rare earth element profile is fairly flat, and shows that the REE are relatively depleted, with a slight fractionation, such that the light REE occur at about 0.32 upper crust levels with the heavy REE depleted, such that Lu occurs at about 0.16 upper crust levels (upper crust normalisation factors after Taylor and McLennan 1981).

The analysis supports the contention that this slag was a particularly well-fluxed smithing slag. The nature of the fluxing material is uncertain, and probably significant contributions from both clay-rich materials (hearth lining, tuyère, deliberate flux...) and the fuel ash were involved. However, the slag shows isolated quartz inclusions in the upper part, and these are suggestive, although not conclusive, evidence for a deliberate use of quartz sand flux.

### Discussion

The evidence for iron-working from Dunnyneill Island suggests that it was focused on the lower part of the site. As with many early medieval sites in Ireland the SHCs are slightly larger than is typical in Britain (pers. obs.) and many other areas. The relatively small size, for Ireland, of the SHCs (500-1000g) is apparently consistent with general purpose blacksmithing; there are no fragments from the larger 2-13kg SHCs found on other Irish early medieval sites which were involved with the production of iron.

The site has not produced any material from tuyères, which is unusual for Irish early medieval iron-working sites.

## Summary

Metalworking at Dunnyneill Island includes iron smithing on the lower part of the site. The SHCs range between 500g and 1000g, which is consistent with assemblages from other Irish early medieval sites where smithing was undertaken.

The upper part of the site yielded several sherds and slag fragments that are associated with the assaying of silver in ceramic cupels. The cupels are of two forms; one flat-bottomed and one dish-shaped. The flat-bottomed form occurs widely in Ireland, as well as in Scotland and Scandinavia. The dish-shaped form, unfortunately represented only by a single sherd, is paralleled by material from Anglo-Scandinavian York, but is apparently a form not previously recorded from Ireland.

A single small slag fragment was suggestive of the working of a zinc-bearing copper alloy.

Glazed pebbles were also recovered from the upper part of the site. These pebbles are not indicative of any particular pyrotechnological process, but the relatively high-sodium low-calcium glazes may suggest that seaweed, rather than wood ash, is implicated in their formation.

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| (a)       |                  |                                |       |       |      |      |                   |                  |                  |                               |       |       |      |      |      |       |
|-----------|------------------|--------------------------------|-------|-------|------|------|-------------------|------------------|------------------|-------------------------------|-------|-------|------|------|------|-------|
| sample    | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | FeO   | MnO   | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | LOI   | total |      |      |      |       |
| DN03 #306 | 43.91            | 2.54                           | 41.13 | 0.11  | 0.75 | 4.20 | 0.71              | 3.64             | 0.13             | 0.75                          | 1.14  | 99.01 |      |      |      |       |
| (a)       |                  |                                |       |       |      |      |                   |                  |                  |                               |       |       |      |      |      |       |
| sample    | Be               | V                              | Cr    | Co    | Ni   | Zn   | Ga                | Rb               | Sr               | Y                             | Zr    | Nb    | Mo   | Sn   | Cs   | Ba    |
| DN03 #306 | 0.16             | 10.16                          | 10.3  | 98.72 | 54.2 | 36.1 | 3.47              | 15.28            | 201.2            | 5.7                           | 353.8 | 2.46  | 0.93 | 1.64 | 1.31 | 392.0 |
| (c)       |                  |                                |       |       |      |      |                   |                  |                  |                               |       |       |      |      |      |       |
| sample    | La               | Ce                             | Pr    | Nd    | Sm   | Eu   | Gd                | Tb               | Dy               | Ho                            | Er    | Tm    | Yb   | Lu   |      |       |
| DN03 #306 | 9.82             | 18.96                          | 2.30  | 8.18  | 1.43 | 0.33 | 1.22              | 0.17             | 0.94             | 0.17                          | 0.47  | 0.07  | 0.47 | 0.05 |      |       |
| (d)       |                  |                                |       |       |      |      |                   |                  |                  |                               |       |       |      |      |      |       |
| sample    | Hf               | Ta                             | Pb    | Th    | U    |      |                   |                  |                  |                               |       |       |      |      |      |       |
| DN03 #306 | 8.92             | 0.24                           | 8.05  | 2.00  | 0.69 |      |                   |                  |                  |                               |       |       |      |      |      |       |

Table 3. Chemical analysis of iron slag #306

(a) major elements, expressed as weight% oxide. Iron is expressed as the Fe<sup>II</sup> oxide. LOI = loss on ignition. Analysis determined by XRF on fused bead.  
 (b) – (d) trace elements, expressed in parts per million (ppm). Analysis determined by ICP-MS.

nd = not determined, < = below detection

| Context                   | Phase                   | SF# | weight<br>Fe        | Cu   | ?     | natural/other | description   |
|---------------------------|-------------------------|-----|---------------------|------|-------|---------------|---|
| <b>Upper part of site</b> |                         |     |                     |      |       |               |   |
| 110                       | 2 loam                  | 83  |                     |      | 0.69  |               | glazed chip of fossiliferous shale  |
| 416                       | 2 bank                  | 495 |                     |      |       | 11.3          | bone  |
| 421                       | 2 fill of curvilinear   | 482 |                     |      | 8.12  |               | glazed piece of sandstone   |
| 421                       | 2 fill of curvilinear   | 485 |                     |      | 2.13  |               | complex piece centred on part melted stone chip - gives clear/slightly green glass. Darkens near ?top where become black near ash   |
| 421                       | 2 fill of curvilinear   | 491 |                     |      | 0.39  |               | small glazed sandstone pebble   |
| 424                       | 2 Fill of curvilinear   | 700 |                     | 7.88 |       |               | Piece of flat-bottomed cupel  |
|                           |                         |     | <b>0 7.88 11.33</b> |      |       |               |   |
| 106                       | 3 loam                  | 20  |                     | 29.8 |       |               | piece of vesicular iron-rich slag broken in two - probably from a smithing cake   |
|                           |                         |     | <b>29.8 0 0</b>     |      |       |               |   |
| 104                       | 4 levelling             | 26  |                     | 1.57 |       |               | dark glassy lining slag - red colouration looks like influence of Cu oxides   |
| 107                       | 4 slumped/slighted bank | 18  |                     | 1.68 |       |               | small piece of sandy rim of dish-shaped cupel, very widely splayed, glazed internally   |
| 203                       | 4 ditch fill            | 40  |                     | 2.46 |       |               | highly vitrified and vesicular piece of sandy material, probably crucible, with red glaze   |
| 404                       | 4 levelling             | 197 |                     | 0.45 |       |               | small fragment of flow-banded chestnut glass with small amount of attached lining/crucible slag   |
| 404                       | 4 levelling             | 206 |                     | 0.85 |       |               | fragment of wide-splayed crucible rim with orange glassy residue  |
| 404                       | 4 levelling             | 224 |                     | 0.58 |       |               | vitrified sandy material, blending into glassy brown slag, probably crucible  |
| 407                       | 4 loam                  | 306 |                     | 150  |       |               | unusual SHC fragment. Upper vesicular, glassy, greenish, with patches of ?quartz in clear glass (flux?), interior dense - locally bladed olivine to 17mm forming smooth brown surface |
|                           |                         |     | <b>150 7.59 0</b>   |      |       |               |   |
| 301                       | topsoil                 | 111 |                     |      | 2.91  |               | glazed piece of ?tuff   |
| 605                       | topsoil                 | 457 |                     |      | 30.65 |               | clinker   |
|                           |                         |     | <b>0 0 33.56</b>    |      |       |               |   |

| Context                   | Phase              | SF# | weight<br>Fe   | Cu          | ? | natural | description   |
|---------------------------|--------------------|-----|----------------|-------------|---|---------|---|
| <b>Lower part of site</b> |                    |     |                |             |   |         |   |
| 707                       | bank               | 550 |                |             |   |         | 8.01 irregular bleb of lining slag - internal variable grey - blue, externally variable cream - chocolate, vesicular                                |
| 707                       | bank               | 565 |                |             |   |         | 5.63 irregular lining slag, mainly dark but some blue streaks   |
|                           |                    |     | <b>0</b>       | <b>0</b>    |   |         | <b>13.64</b>  |
| 702                       | fill upper fill    | 487 | 500            |             |   |         | SHC   |
| 712                       | fill primary fill  | 586 | 26.36          |             |   |         | dense rusty SHC fragment. Lower face dimpled, upper in rounded lumps with lining melted in  |
| 712                       | fill primary fill  | 589 |                |             |   | 2.4     | small piece of vitrified hearth/furnace lining  |
| 712                       | fill primary fill  | 590 | 9.04           |             |   |         | dimpled lining slag sheet, glassy with v large ?olivines on one side, dark surface, patches of green glass & lining, rusty charcoal in some dimples |
| 712                       | fill primary fill  | 591 | 5.94           |             |   |         | as 590  |
| 712                       | fill primary fill  | 592 |                |             |   | 0.6     | vitrified lining  |
| 712                       | fill primary fill  | 593 |                |             |   | 0.01    | vitrified lining (2 pieces)   |
| 712                       | fill primary fill  | 594 |                |             |   | 1.03    | natural crinoidal limestone   |
| 712                       | fill primary fill  | 595 | 3.37           |             |   |         | dark lining slag with charcoal incl. V heterogeneous  |
| 712                       | fill primary fill  | 596 | 0.14           |             |   |         | glassy  |
| 712                       | fill primary fill  | 597 |                |             |   | 0.19    | vitrified lining  |
| 712                       | fill primary fill  | 598 |                |             |   | 0.09    | vitrified lining  |
| 712                       | fill primary fill  | 599 |                |             |   | 0.19    | vitrified lining  |
| 712                       | fill primary fill  | 600 | 0.36           |             |   |         | dark glass with lining and rusty surface  |
| 712                       | fill primary fill  | 601 |                |             |   | 0.14    | rotten igneous rock?  |
| 712                       | fill primary fill  | 602 | 0.24           |             |   |         | glassy slag   |
| 712                       | fill primary fill  | 603 | 10.2           |             |   |         | irregular ?contorted glassy iron slag with lining etc.  |
| 712                       | fill primary fill  | 604 | 5.41           |             |   |         | as 603  |
| 712                       | fill primary fill  | 605 | 1.38           |             |   |         | glassy with lining  |
| 712                       | fill primary fill  | 609 |                |             |   | 0.19    | small chip of bluish-grey vesicular glassy lining slag  |
|                           |                    |     | <b>562.44</b>  | <b>0</b>    |   |         | <b>3.67</b>   |
| 701                       | topsoil            | 483 |                |             |   | 13.12   | broken nub of dark glassy lining slag rich in sediment and small sandstone clasts   |
| 704                       | topsoil            | 514 | 125            |             |   |         | fragment of probable smithing slag, contains piece of fired white rock  |
| 704                       | topsoil            | 553 |                |             |   | 3.93    | small lobe of dark glassy lining slag   |
| 705                       | hillwash           | 509 | 1.74           |             |   |         | thin film of well flowed iron slag, max 4mm thick   |
| 705                       | hillwash           | 515 |                |             |   | 9.5     | irregular piece of lining slag with fused and slagged lining or pebble blebs in dark glassy slag  |
| 705                       | hillwash           | 524 | 1.58           |             |   |         | thin double layer cf. 509. Good crystalline slag - could be from anvil or other hard face   |
| 706                       | fill of tree throw | 546 |                |             |   | 20.39   | part fired piece of organic material with charcoal, bone chips and snails   |
| 706                       | fill of tree throw | 547 | 20.6           |             |   |         | small piece of rusty iron slag, slab, lower face dimpled, rusty charcoal, v coarse olivine, upper face very vesicular                               |
| 706                       | fill of tree throw | 548 | 40.41          |             |   |         | cf. 547 - but larger slab, lower face coarse olivine, but mainly green/cream vesicular glass, smooth upper surface. ? accreted flake scale.         |
| 713                       | fill of tree throw | 576 |                |             |   | 0.61    | 3 small ?sandstone grains fused together with vitrified glaze   |
| 714                       | fill of tree throw | 582 | 690            |             |   |         | p-c cake (part)   |
| 714                       | fill of tree throw | 585 | 5.19           |             |   |         | dense dark crystalline iron slag with pendent blebs. Slightly vesicular   |
| 714                       | fill of tree throw | 608 | 6.27           |             |   |         | small fragment of dense dark slag with dimpled surface and accreted rusty material with charcoal  |
| 714                       | fill of tree throw | 610 | 0.5            |             |   |         | irregular piece of vesicular iron slag - possibly from margin of thin sheet   |
|                           |                    |     | <b>891.29</b>  | <b>0</b>    |   |         | <b>47.55</b>  |
| <b>overall total</b>      |                    |     | <b>1633.53</b> | <b>7.59</b> |   |         | <b>109.75</b>   |

# GeoArch



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