5.4 Appendix 2: The Metallographic investigation of metalwork and industrial waste found at Leckie Broch by E. Photos-Jones, Scottish Analytical Services for Art and Archaeology (Ltd), Glasgow, UK

5.4.1 Abstract

The collection of iron objects from Leckie Broch comprising of tools, knives and weapons and bars as well as iron making waste products (metallurgical slag) presents a well-rounded picture of the iron metalwork in use at a 1st-2nd C AD broch site. The presence of two pieces of slag among the finds suggests that iron was probably manufactured locally. This brief account aims to establish the level of iron 'making' expertise at Leckie Broch. It does not attempt to establish whether individual objects were made locally or were imported. The analysis suggests a very good level of understanding of iron making and an ability to manipulate different types of ores in order to give the tool/weapon the desired properties. Given the plethora of objects, the ready availability of natural resources, the long tradition in bloomery iron making and the presence of slag, it is highly likely that Leckie Broch and its associated domain were self-sufficient in iron manufacturing. A few pieces stand out and these may have been imported.

5.4.2 A brief summary of the composition, properties and treatment of carbon-rich and phosphoric iron, in reference to the Leckie Broch artefacts

There is no comprehensive published account of early iron metallurgy in Scotland although the present author has gone some way in undertaking analyses of metallurgical waste from numerous sites around the country in the 1990s and early 2000s (see list of select references and also www.sasaa.co.uk for a complete list of SASAA Reports). This appendix focuses on metallographic analysis as a means of assessing the ability/expertise of the Leckie Broch smith(s) in dealing with their material. Whether the smiths were procuring their metal locally (or made their own) or worked with 'imported' metal remains a matter of conjecture. It is a fact that the composition of a metal object and the history of its manufacture can be clearly reconstructed from the study of its metallographic structure. The collection of iron objects from Leckie Broch includes iron spearheads and projectile points, knives, rings, iron plates, hammers, fragments of iron rods, bars and straps, pointed objects and spikes, nails, awls, share or spade, ring-headed pins, swords, hooks, iron slags and blooms, shears, chisels, wedge shape chisels, iron bridle bits and styli (Table 1).

5.4.2.1 About the bloomery

Bloomery iron making has been the main method used for the making of wrought iron (iron with very low amount of carbon) until the 17th-18th centuries, certainly in Scotland (Hall and Photos-Jones 1998; Photos-Jones *et al* 1998; Photos-Jones and Atkinson 1999; Johnson *et al* 2006; Photos-Jones and Hall 2001). Although this date varies considerably according to geographical region it nevertheless reflects the continuity of this practice in Europe from the first millennium BC. In the bloomery, iron is never molten, but rather it is produced by the solid state reduction of iron from its oxide ore (magnetite, hematite, limonite etc.) in a reducing or oxygen-starved environment. In Ireland and the Scottish Highlands the ore used was almost certainly consisted of iron oxy-hydroxides. The method has been called the direct process since the transition from ore to metal takes place in one step. The reducing agent is the carbon monoxide produced by the burning of charcoal. Carbon in the charcoal reacts with the oxygen from the ore to produce iron and releases carbon dioxide as gas. Although bloomery furnaces produce primarily iron with minimal amount of carbon (*c.* 0.1-0.2% carbon) iron with higher carbon content is also present. This is because the amount of carbon absorbed by the iron varies depending on the local reducing conditions (ie the amount of carbon monoxide present), the diffusion rate of carbon monoxide into the iron being relatively slow. If the conditions are exceptionally reducing and the ore is allowed to reside within the furnace for sufficiently long times then iron with more than 2% carbon can be formed. This amount of carbon allows the iron to melt in the temperature operated by the bloomery furnace, namely *c.* 1200°C, so it can be tapped out of the furnace and cast, hence its name, cast iron.

5.4.2.2 About the iron-carbon alloy

A few lines are necessary here to describe the different metallographic phases mentioned in the results below. The iron-carbon alloys worked in antiquity demonstrate only a small number of phases given the conditions under which the metal was made. Ferrite is a magnetic form of iron, almost devoid of carbon, less than 0.01%, but capable of containing various amounts of other elements, such as phosphorus. Cementite, on the other hand, is iron carbide, Fe_3C, very hard and brittle. Pearlite is a mixture of ferrite and cementite with carbon in excess of *c.* 0.02%. If the total content of carbon within the iron is 0.4%, then the section will appear to contain equal amounts of ferrite and pearlite. At 0.8% carbon the entire section will consist of pearlite only. Pearlite is usually laminated in form but spheroidized. Speroidization occurs when lamellar pearlite is heated for a prolonged period near or below 700°C. Martensite is a phase resulting from the quenching of carbon-rich iron from temperatures above 720°C. Since this phase is very brittle, it is usually necessary to soften it by heating the object for a short time at temperatures between 100°C and 650°C. This operation is called tempering. Usually, and for each functional object made, a combination of two properties would be sought: hardness (the ability to withstand indentation) and toughness (the ability to withstand cracking).

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5.4.2.3 About phosphoric iron

Apart from carbon-rich iron, a number of Leckie iron work samples appear to have been made with phosphoric iron. Phosphorus is a common impurity in many iron tools and weapons dating to the pre-Roman and Roman Iron Age (600 BC to 300 AD). The presence of phosphorus in the steel gives the object greater hardness and tensile strength but reduced ductility and shock resistance. In tool steels the maximum P allowed is 0.04%.

Phosphoric iron behaves differently from carbon-rich iron. Cold hammering of low phosphorus iron increases the hardness of the metal as Gilmour and Tylecote (1986) have shown. Phosphorus, from the ore, distributes unevenly between the metal and the slag. Given the small amount of phosphorus that enters the metal, (less than 0.05% P), phosphoric iron is difficult to measure analytically. This amount is well below the limit of detection of the SEM-EDAX so its presence is deduced metallographically from its hardness rather than from analysis. However, it can be carried in slag inclusions in metal artefacts in amounts of up to 12% P_2O_5 as has been found in one particular "currency" bar from Arran (Photos-Jones 2001); this amount is highly unusual (Atkinson and Photos-Jones forthcoming). More sophisticated techniques like SIMS (Secondary Ionisation Mass Spectrometry) can easily measure such very small amounts but, of course, are not widely available. Using a number of different instrumental techniques, Kaloyeros and Ehrenreich (1991) tried to establish the distribution of phosphorus within the iron and from that deduce the properties displayed by Romano-British tools and weapons which appear to have been largely made of this type of material.

Ehrenreich (1985) has shown that contrary to what perhaps was widely believed of the 850 or so objects analysed metallographically and with the SEM, more than half (66%) had less than 0.1% C, 22% had 0.1%-0.5% C and only 12% had more than 0.5% C. This means that two thirds of the total collection was wrought iron with alloying elements which would have imparted naturally (as the result of the bloomery making) hardness to the object and not via the carburisation process. According to Ehrenreich, high C iron was not always established during the Iron Age to enhance properties of specific tools. Opting for phosphoric iron may have been an easy solution to the problems inherent in carburisation and steel making generally. Quenching was of limited use. Rather than being deleterious to the object phosphorus was actively sought where good iron was required.

Forge welding involves the welding of two pieces of metal together so that they can become one while hot, but not molten. When iron is heated an oxide layer is formed on the surface. For the forge welding to take place this oxide layer needs to be removed. The presence of slag inclusions serves that purpose since slag is a good deoxidant. Metals which are free of slag inclusions, like for example, crucible steel are difficult to weld. The interface of these steels need to be covered by borax or crushed slag before welding. Forging both deforms and shapes the object, as well as expels excess slag trapped within the metal. Apart from producing composite structures, forge welding also produces heterogeneous structures, in this particular case high and low carbon irons, each bringing into the resulting object their composite properties.

Piling, consisting of folding and welding iron plates together is useful if the sheets welded together are a combination of iron and low carbon steel (steel with 0.3% carbon). Because the solid state diffusion of carbon is slow, one way of making good quality steel is to sandwich high carbon sheets with low carbon ones "subsequent heating will distribute the carbon more uniformly".

5.4.3 Methodology

Seventeen objects and two pieces of slag have been sectioned in preparation for metallographic and /or scanning electron microscopy with energy-dispersive X-ray (SEM-EDAX) analysis. A wedge or minute "slice of a pie" shaped section was removed with a diamond saw from the edge of each sample and mounted on fast-setting metallographic resin. It was ground with a series of silicon carbide papers and then polished with diamond paste of 6 micron, 3 micron and 1 micron size. It was subsequently etched with Nital (4%). Micro hardness testing took place using a 100g load. The scale of hardness used was the diamond pyramid (H_v). Two samples of slag (LBB1=A1980.829, LBB2=A1980.149) were also sectioned, polished and prepared in the same manner as the objects. Table 1 presents the list of all objects analysed, together with information regarding their context, dimensions and results of analyses. Table 2 presents the results of the SEM-EDAX. The results are presented below according to sample typology, namely tools, iron bars, knives and weapons, unspecified material and slags/blooms.

5.4.4 Results

LB17 A1980. 621, bent nail? Fig. 1

Optical Examination: the metallographic structure consists of ferrite and pearlite. Carbon content: *c.* 0.3-0.4% C. Two grain sizes are observed: a finer grain size (at the edges of the section) denoting a faster rate of cooling; a larger grain size (at the core) denoting the opposite. Pearlite is not lamellar but partly spheroidised (globular) suggesting a prolonged period of heating or holding this steel for a period of time under the transformation temperature. This is the temperature, *c.* 700°C, at which

austenite transforms into ferrite. This prolonged heating must have been followed by fast cooling of only the edge of the object, resulting in the small grain size visible in that area. Slag inclusions are elongated along the line of working. **Remarks**: this object has a nearly uniform carbon composition throughout, differing only in the grain size which is the result of differing rates of cooling between the edges and the core. It is a rather carefully prepared object to classify as merely a nail.

LB19: A1980.570, large amorphous lump, Fig. 2

Optical Examination: The sample shows extensive corrosion with only a relatively small amount of metallic phase still remaining. Very uniform distribution of nearly eutectoid steel corresponding to a total carbon content in the iron of 0.8%. The hardness at 100% pearlite is Hv= 264. Fine ferrite is observed at the grain boundaries of only some areas Hv(F+P) =209 where presumably some decarburisation must have taken place. The ferrite remained at the grain boundaries instead of forming full grown ferrite grains because of fairly rapid cooling. It is suggested that the 'object' may have been thrown in water to cool rapidly since practically only one phase is obvious, ie that corresponding to pearlite. No slag inclusions are visible.

LB20: A1980.612, chisel, Fig.3

Optical Examination: large equi-axial ferrite crystals. The hardness values suggest that the ferrite must contain small amounts of alloying elements, perhaps phosphorus; it is also possible that it may contain small amount of carbides or nitrides. Phosphorus at levels c.0.05% can make plain wrought iron as hard as a medium carbon steel. Since phosphorus-rich iron hardens as it is worked, it is particularly suitable for tools. Slag inclusions: only a small number is visible.

LB22: A1980.552, chisel, Fig. 5

Optical Examination: extensively corroded section but with large ferritic areas. Hardness values are high (Hv=256 and 282) suggesting ferrite with perhaps phosphorus and/or other inclusions. There are numerous slag inclusions present. Since phosphorus partitions preferentially in the slag rather than the metal it was decided to carry out SEM-EDAX analysis of slag inclusions with the aim of establishing the possible presence and amount of phosphorus within. One slag inclusion seen in Fig. 5 shows globular iron oxide (wustite) in a glassy phase. SEM-EDAX analysis of the glassy phase showed c. 3% P_2O_5 This suggests that phosphorus might well be present in the metal. **Remarks**: this tool (chisel) is similar in composition to that shown in Fig. 3, namely ferrite with inclusions like phosphorus and/or cementite which give the object its increased micro-hardness. However the increased microhardness of LB22, compared to LB20, might be more consistent with either ferrite plus dissolved cementite or elevated amounts of phosphorus.

LB23 A1980.576, awl or chisel, Fig.6

Optical Examination: the structure suggests martensite uniformly distributed throughout. This observation is corroborated by the high micro-hardness readings.

LB30 A1980.575, iron shaft with head/nail, Fig. 4

Optical Examination: the metallographic structure consists of ferrite with spheroidized pearlite at the grain boundaries. Globular pearlite is formed when iron/steel with lamellar pearlite is heated for a prolonged period of time near or below 700°C and allowed to cool slowly. Grain size is slightly larger at the two edges but smaller at the interior. There is even carburisation throughout (0.3%-0.4% carbon). Slag inclusions are limited.

LB32a and b A1980.694a and 694b chisel, Fig. 7

Optical Examination: two samples were removed from the object at either end. Equi-axial ferrite which may or may not contain phosphorus. Few slag inclusions are evident. Ferrite has been cold-worked to enhance hardness. This would have been necessary for the cutting edge of the chisel to be functional. The slag inclusions present are also elongated along the line of working.

Bars

LB13 A1980.564: flat strip/bar, Fig. 9

Optical examination: evenly distributed ferritic iron with finely dispersed cementite within the ferrite grain boundaries, but only in places. Micro-hardness is uniform at the two points where measurements were taken (Hv= 114 Hv and Hv=115) and suggests ferrite. However, at the upper right hand corner of the section an additional phase, Fe_3-P (steadite), can be seen at the ferrite grain boundaries. Although these grains resemble pearlite they stain a darker yellow (with 4% Nital). Phosphide is a hard phase and hardness measurements should reflect that (none were taken). Slag inclusions: well worked metal with only sparse presence of slag inclusions. **Conclusions:** the shape of the object (a bar) and the even distribution of ferrite may suggest raw material, namely a currency bar" to be traded or worked into shape.

LB14a A1980.551 square section hook

Optical examination: the section showed a very uniform distribution of ferrite with long nitride needles. The grains are clearly defined but some of them contain what appears to be carbides (wavy structure within the grains). **Hardness readings** were taken at two places.

One (120Hv) is consistent with ferrite, the other (154Hv) is higher suggesting that other alloying elements may be present, (excess carbides/nitrides?).

LB14b A1980.551 wedge section hook, Fig. 10

Optical examination: the section displays ferrite with elongated slag stringers. The ferrite grain boundaries are not immediately obvious. They contain nitride needles or "specs" presumably of unresolved cementite. **Hardness readings** were taken at two places. One (116Hv) is consistent with ferrite, the other (132Hv) is slightly higher suggesting that other alloying elements may be present, (excess carbides/nitrides?).

Remarks: both sections of this object show the same ferritic structure. However, there are areas of high and low hardness which can only be associated with the presence/absence of carbides and/or nitrides. The bloom out of which this object was made was good quality wrought iron. The presence of nitride needles suggests that the object was exposed to the reducing environment of the hearth at a high temperature followed by slow cooling.

LB16 A1980:701 Fig. 11

Optical examination: the section consists of six layers of alternating high and low carbon areas. The high carbon areas are primarily pearlite at *c*. 0.8% with fine ferrite. In between the three layers of pearlite are two areas of fine-grained pearlite and ferrite at *c*. 0.4% carbon. Finally, a coarser grained ferrite with small amounts of pearlite is also visible in the composite photograph.

Remarks: this is a particularly long bar of iron which appears to have been manufactured from the piling of a strip of 0.8% C (pearlitic) iron with a strip of 0.4% C. The first folding would produce the following sequence: P/F+P, F+P/P+P/F+P, F+P/P which is the effect shown in the section of Fig. 11.

LB18 A1980.623, Fig. 12

Optical examination: the bar is made from the welding of two strips of iron differing in their carbon content only by a small amount. One is primarily wrought iron, the second is *c*. 0.1-0.2% C. The welding line is outlined by the presence of the slag stringers. **Remarks: t**his is a bar of iron or a currency bar.

Knives and Weapons

LB11a and LB11b A1980.669 (larger bit): tanged blade

Optical examination: both sections are severely corroded and no metal was detected.

LB12 A1980.661 spearhead, Fig. 13

Optical examination: the section was largely corroded with only one small metallic area remaining and consisting of ferrite grains with lamellar (or partly spheroidized) pearlite at the grain boundaries. Micro-hardness on the ferrite is Hv=154. This value suggests the presence of some phosphorus and/or carbon as cementite. Remarks: little can be said about the metallographic structure of this object on account of the small amount of metal left.

LB15 A1980.730 tanged blade, Fig. 14

Optical examination: this is an unusual specimen characterised by a series of "ghost banded" ferrite and martensite with very high hardness readings: a) at the ferrite end Hv= 266 and the martensite end Hv=454. This blade was produced as a result of piling of strips of ferrite and high carbon iron and subsequent quenching. The alternating layers of high and low carbon and the subsequent heat treatment would have provided a very good cutting edge, indeed, for such a small object.

LB21 A1980.697, knife blade, Fig. 15

Optical examination: the section shows large ferritic grains. The microhardness measurements (Hv=209 and 220) suggest ferrite in the presence of phosphorus. There is very fine pearlite at the ferrite grain boundaries.

LB34a A1980.650a, knife blade, Fig. 16

The surface of all three sections appears "pitted". This is characteristic of the presence of small slag inclusions and small amounts of cementite which is not dissolved into the ferritic matrix. The metal does not contain carbon in sufficiently large amounts (*c*. 0.1%) to form a separate phase, i.e. pearlite, at the grain boundaries.

Slags

LBB1 A1980.829, slag sample 1

SEM examination and analysis: area analyses at three different regions of the sample revealed an iron silicate, (fayalite-rich) composition and the presence of four distinct phases (Table 2). These consisted of a) small fine dendrites of wustite (bright in the SEM photograph) b) long needles of fayalite (light grey), c) an alumina-rich glassy phase (black), d) a second glassy phase rich in calcium, e) unreacted silica grains and f) charcoal impregnated with iron and phosphorus. This type of slag mineralogy reflects a typical bloomery slag.

LBB2 A1980.149, slag sample 2

SEM examination and analysis: area analyses at three different regions of the sample revealed a glassy slag,

high in silica (55%) and low in iron (30%) with up to 15% in Al_2O_3 + CaO + K_2O (Table 2). Round metallic iron inclusions were present as well as potassium aluminosilicate inclusions. **Remarks**: this is not a typical bloomery slag like LLB1. Nevertheless, similar slags have been encountered in medieval contexts at Perth (Photos-Jones and Atkinson 1999). Such slags can indeed form within a bloomery furnace although they fit better in the high bloomery, a later development using primarily water power as an energy source and run more efficiently. Typical bloomery slags of the early periods (Iron Age / Roman) were very inefficient in the loss of iron in the slag.

5.4.5 Discussion

The Leckie objects have been broadly classified on the basis of typology in the following groups: a) tools, b) knives and weapons, c) bars and c) slag/ metallurgical waste. A summary of the metallographic structures is seen in Table 1. Metallographically speaking, from a total of twenty objects, 15% (or 3/20) (LB13, LB14a and LB14b) were made of ferritic iron or iron with nitride needles, 40% (or 8/20) (LB20, LB22, LB32a, LB32b, LB33, LB12, LB34a, LB34b and LB34c) were made from phosphorus-rich ferrite on account of their relatively high(er) hardness values and another 45% (or 9/20) were made from carbon-rich (0.2-0.8% C) iron (LB17, LB18, LB23, LB30, LB33, LB16, LB21, LB19 and LB15). Clear evidence of heat treatment appears in only two objects (LB23, LB15). Good understanding of forging and piling is seen in another two objects (LB16 and LB15). The above results suggest that there appeared to be no particular preference in the making of individual groups of objects with one type of metal or the other, such as for example tools with phosphoric iron and weapons with carbon-rich iron. A possible exception to this rule might be the chisels but the number of samples analysed is too small to draw any meaningful conclusions.

The evidence for martensite on two samples suggests that the smith who manufactured these objects was very well versed in the principles of heat treatment and in the even carburisation of the objects. Assessing the correct temperature, based on the colour of the iron when hot, from which to cool the object rapidly (quenching) would have been the result of experience. Opting for high phosphoric iron for some tools/weapons would have minimised the need for relying on such valuable expertise while still procuring a well-functioning cutting edge. Certainly the objects (LB23, LB15 and LB16) showing heat treatment, forging and piling or a combination thereof, appear to have been made by an "expert" smith.

Two samples of slag recovered from the vicinity of Leckie Broch have been analysed with the SEM-EDAX (LBB1 and LBB2). They contain phosphorus and manganese; their make up matches that of slag inclusions in two objects also analysed with SEM-EDAX. On the basis of these two slag samples, it can be argued that at least these two Leckie objects had been produced locally. It is likely that the same also applies to the majority of the rest of the objects.

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Glossary of Technical Terms

Annealing The process of softening a metal hardened by cold working, ie hammering. The lowest temperature at which a metal will soften varies with the degree of cold working, greater amounts tending to reduce the temperature.

Austenite A non-magnetic form of iron normally existing only at high temperatures (above 720 C). Carbon can dissolve in it up to about 1.8% at 1150 C and diffuse readily.

Bloom or bloomer Iron that has been produced in a solid condition as the result of the reduction (smelting) of iron ore. Pure iron melts at 1535 C, but bloomer is not usually heated above 1250 C. The carbon content varies but is usually low.

Cast iron An impure iron containing more than 1.9% C and other elements like silicon, phosphorus, formed in the liquid. Not malleable, hot or cold, and very brittle. It exists in two forms, white and grey, which describes the appearance of the surface exposed when it is fractured.

Cementite Iron carbide, Fe_3C, very hard and brittle, forming one of the constituents of pearlite (qv).

Cold working When hammered at low temperatures, metals increase in hardness and strength.

Decarburization The loss of carbon from the surface of a ferrous allow as a result of heating it in the presence of a medium such as oxygen which reacts with the carbon.

Direct process The iron-making process by which wrought iron is reduced directly from ore.

Ferrite A magnetic form of iron, almost devoid of carbon but capable of containing various amounts of other elements, such as phosphorus.

Flux Lime or other material added to the smelting charge to render a slag easy flowing.

Free-running temperature The temperature at which the viscosity of a metal is low enough for it to be poured.

Eutectic The allow composition that freezes at the lowest constant temperature, causing a discrete mixture to form in definite proportions.

Graphite The form of carbon occurring in cast iron containing more than c. 1% silicon and slowly cooked.

Hammer scale The scale removed from iron during forging. This consists of metal which has reacted with air and which has thereby been converted mainly to iron oxides.

Hardness Of metals is usually measured by indentation tests. Two popular scale of hardness are the diamond pyramid (HV) and the Brinell (HB).

Hot short Brittleness in hot metal. The presence of excess amounts of sulphur in steel causes hot-shortness.

Inclusions Particles of impurities that are usually formed during solidification and are usually in the form of silicates, sulphides and oxides.

Martensite A hard produce of quenching iron containing carbon from temperatures above 720 C.

Mild steel Modern equivalent of wrought iron but without the slag which gives the latter its fibrous structure.

Neuman lines or bands Markings on ferrite which occur as a result of great shock at low temperatures (below 500 C). They disappear when the metal is heated above c. 600 C.

Pearlite One of the constituents of iron containing carbon in excess of c. 0.02%; a mixture of ferrite and cementite, usually laminated in form.

Phase A portion of an alloy, physically homogeneous throughout, which is separated from the rest of the allow by distinct bounding surfaces.

Quenching The process of rapid cooling of metal alloys for the purpose of hardening.

Recrystallisation A process in which the distorted grain structure of metals that are subjected to mechanical deformation is replaced by a new strain-free grain structure during annealing.

Scale The surface oxidation on metals caused by heating in air or in other oxidising atmospheres. It is produced at all stages in iron making including smelting and smithing (see *hammer scale*), and constitutes one of the most common wastes at a metallurgical site.

Smelting Involves a chemical reaction between the ore and the fuel, or between a heated sulphide ore and the atmosphere.

Speiss A residue of lead or copper smelting containing a high proportion of metallic arsenic compounds.

Sorbite Spheroidised structure of iron carbide in ferrite formed by tempering martensite between 500 and 700 C.

Sorbitic pearlite Unresolvable pearlite formed during rapid cooling in the range 500-600 C.

Spheroidised pearlite Globular cementite particles formed when iron/steel with lamellar pearlite is heated for a prolonged period near or below 700 C.

Stringer (slag) Aligned silicate (slag) inclusions following the direction of working.

Tempering The operation of softening the hard and brittle constituent, martensite, by heating it for a short time at temperatures between 100 and 650 C.

Widmanstaetten structure occurs in steels which have been fairly rapidly cooled from high temperatures, c. 1000 C.

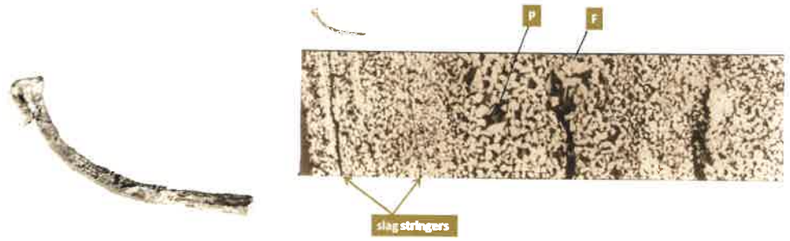

Figure 1. LB17 A1980. 621. P=pearlite; F=ferrite; slag inclusions elongated along the line of working. Hardness values for the two areas and at the pearlite phase are: small grains Hv=234, large grains Hv=243.

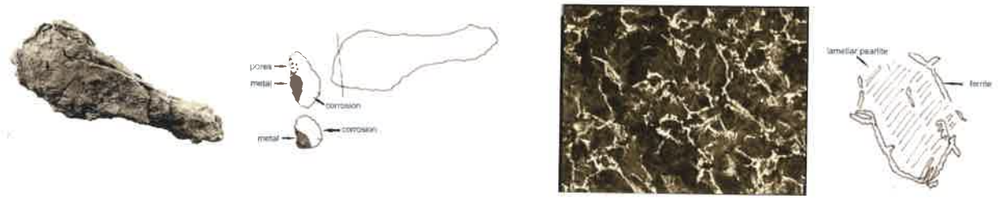

Figure 2. LB19. A1980.570. This is an object of unidentified typology. Although in an advanced state of corrosion, the remaining metallic parts consist of steel with 0.8% carbon. If this object were part of a bloom, it would have been unworkable and it would have probably been discarded.

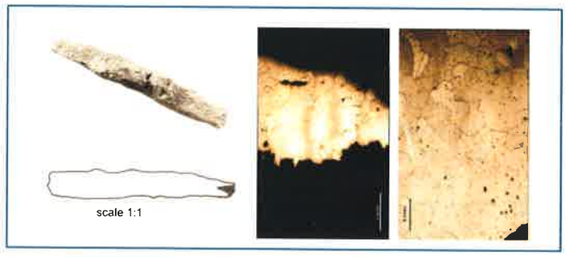

Figure 3. LB20. A1980.612 This is ferrite with small amounts of carbides or nitrides to account for the registered hardness of Hv=141 or 125. Tools made exclusively of ferrite would be too soft to use and so undesirable.

Figure 4. LB30 A1980.575 Ferrite with spheroidised pearlite. The object has been well and evenly carburised throughout.

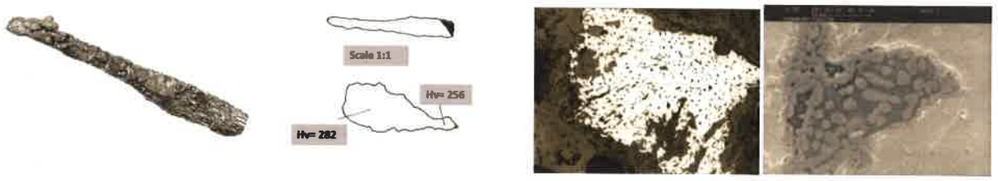

Figure 5. LB22 A1980.552 Tool (chisel) displaying substantial hardness which derives, either from an elevated phosphorus content within the ferrite matrix and/or cementite. Both phosphorus and carbon were at the time of the analysis, and with the instrumentation used, not possible to detect. From left to right: object; place of section removed; micro-hardness measurements at two different spots on the section; image of section (ferrite=bright phase; corrosion areas = dark phase); slag inclusion showing globular wustite in a phosphorus rich glassy matrix; area surrounding the slag inclusion is the metal.

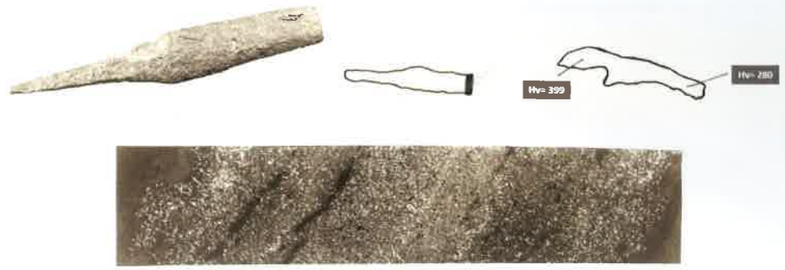

Figure 6. LB23 A1980.576, awl or chisel Matensite uniformly distributed throughout. From left to right: top: object; place of section removed; micro-hardness measurements at two different spots on the section; below image of section (martensite).

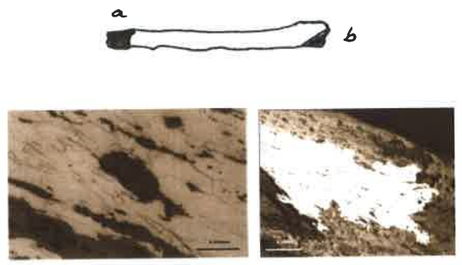

Figure 7. LB32a (right) and LB32b (left) A1980.694 Cold worked ferrite showing elongated ferrite grains as well as slag inclusions at both ends of the chisel sampled (a and b)

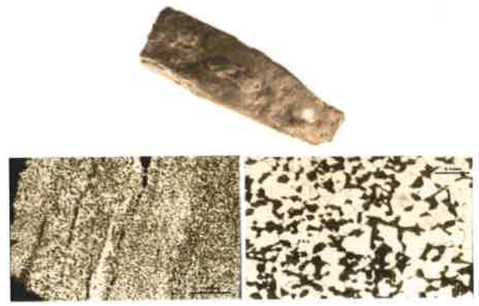

Figure 8. LB33 A1980. 718. Bottom: two images at low and high magnification of the section showing Ferrite (light areas) and Pearlite (dark areas) well distributed throughout the sample. Carbon content= 0.3-0.4%.

Figure 9. L13 1980.564 flat strip/bar Hardness measurements on polished section: Hv= 114 and Hv=115. This is consistent with a ferrite. Left to right: object; section taken from one end; metallographic section showing large ferrite grains.

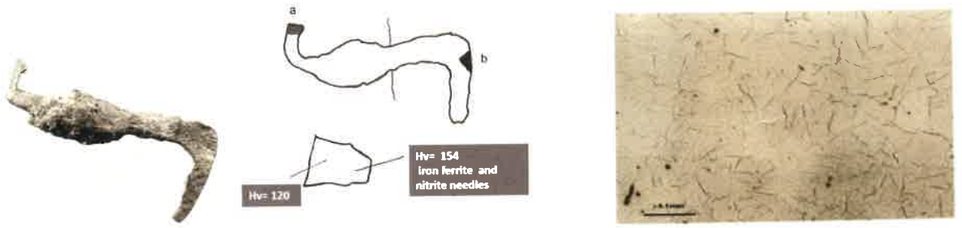

Figure 10 L14 A1980.551 hook. Left to right: object; two places (a) and (b) where sections have been obtained; micro-hardness testing on section (a); nitrite needles shown in the area of Hv=154

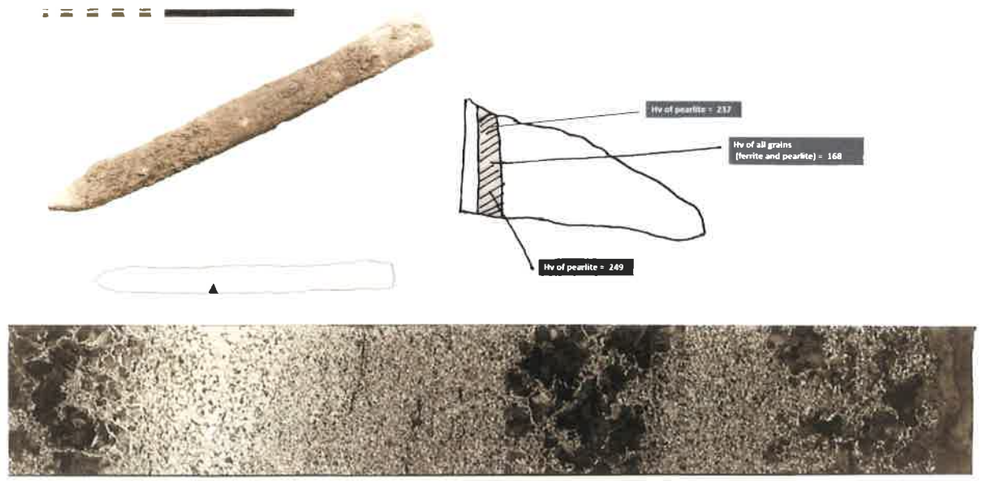

Figure 11. LB16 A1980:701 from left to right: object; area of section removed; various spots were micro-hardness measurements were taken; composite metallographic section showing the effect of piling and the formation of area of dark pearlite and light ferrite.

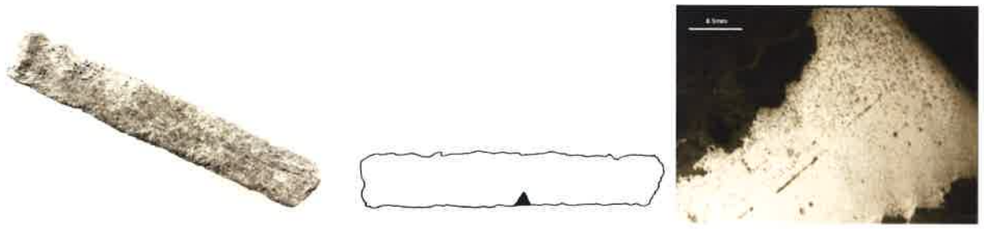

Figure 12. LB18 A1980:623 From left to right: object; place of sectioning; Hardness measurements: area of the ferrite grains Hv =118; hardness of the area containing ferrite and pearlite Hv=168.

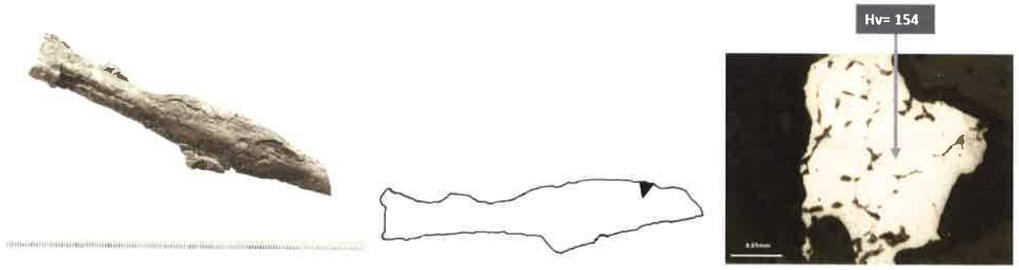

Figure 13. LB12 A1980.661 From left to right: object; place of sectioning; small area showing remnant ferrite with possible phosphorus /cementite

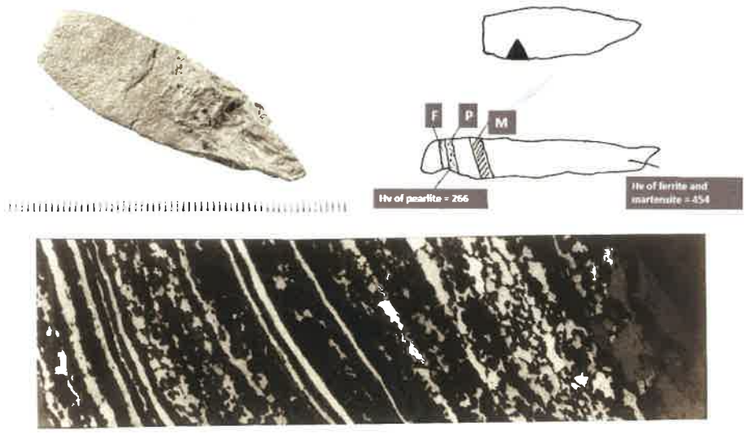

Figure. 14. LB15 A1980.730 From left to right: object; area of sectioning; bands of ferrite, peralite and martensite with corresponding microhardness testing. This is an unusual piece and would have provided a very good cutting edge.

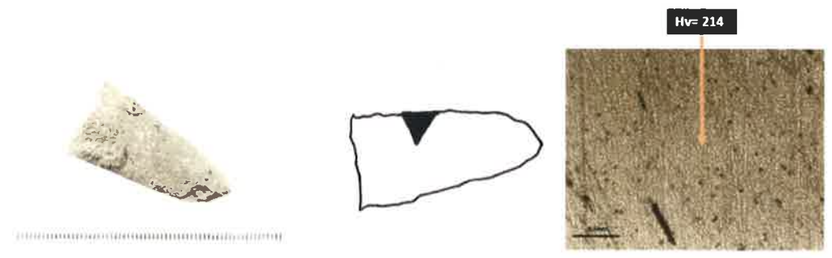

Figure 15 LB21 A1980.697 From left to right : object; area of sectioning; single area of harness testing, Hv=214

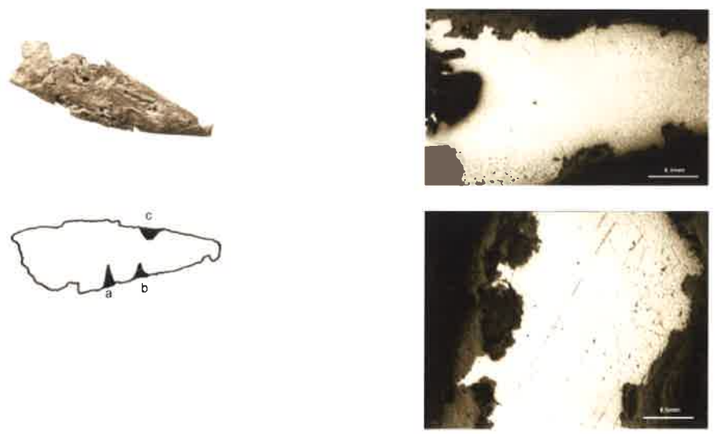

Figure 16 LB34 A1980.650a. from left to right: object; and areas (3x) of sectioning; ferrite in (c) with hardness Hv=118; and in (b)Hv=115. This is a soft material to have worked effectively as a cutting edge.

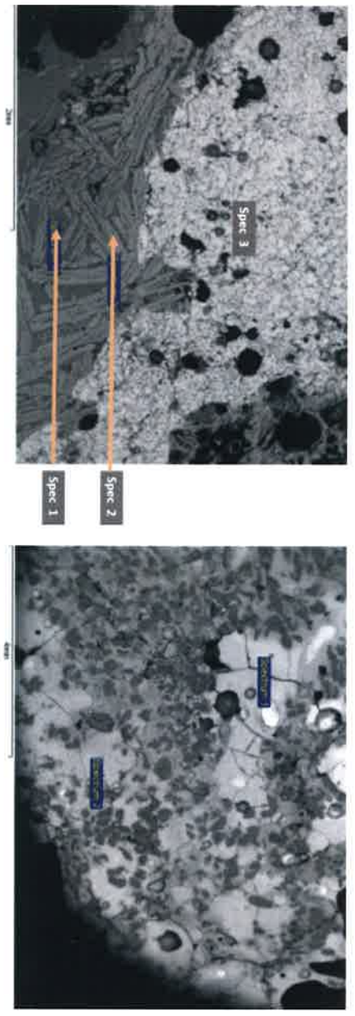

Figure 17. LBB1=A1980.829, typical bloomery slag showing iron oxide (wustite) (spectrum 3), long needles of fayalite (spectrum 2) and interstitial glass (spectrum 1).

Figure 18. LBB2=A1980.149

SASAAA Number	Museum Number	Context	Typology	Description	Dimensions	Metallographic observations
Tools						
LB17	A1980.621	Field no. SF374.DK: Context 5 (destruction layer 3A/3B): Phase 3 (end).	Bent nail?	Probable bent nail with square-sectioned shaft and flat discoid head, also partly bent downwards along shaft.	Length along shaft = 45mm.	F+P, throughout, small F grains at edges, larger at centre
LB19	A1980.570	Field no. 201.CH: Context 6 (layer 3A): Phase 4, post-broch.	Wedge-shaped object, 'bloom'	Curved, wedge-shaped iron object and a thick tang-like projection with an oval cross section.	Length 9.2cm, thickness 1.0-3.0cm, width 0.2-1.4cm.	P, throughout (0.8% C), slight decarburisation at edges
LB20	A1980.612	Field no. 350.DI: Context 9 (layer 1), Phase 5a.	Chisel	Small chisel, the shaft having a rectangular cross section.	Length 8cm, max width 1cm.	F+P (Hv=125-141)
LB22	A1980.552	Field no. 71.BP: Context 7 (layer 3A, top): Phase 4, post-broch (end).	Small hammer	Possible small chisel, the shaft having a rectangular cross section (a lump associated with weathering during burial has adhered on the surface at the narrow end).	6cm long, 1cm wide (functional end), 0.5cm wide (opposite end). Lump associated with weathering during burial has adhered on the surface at the narrow end.	
LB23	A1980.576	Field no. 214.CT: Context 5 (destruction layer 3A/3B): Phase 3 (end).	Awl?	Small tanged knife blade.	Length 4.7cm, max width 0.7cm, blade thickness (excluding corrosion) 1mm.	P (Hv=280), P+M (Hv=399)
LB30	A1980.575	Field no. 209.CH: Context 6 (layer 3B): Phase 4, post-broch.	Iron shaft with head/nail?	Iron shaft with head. Shaft has a rectangular section slightly expanding towards the head. The head is rectangular and flat, flush with the shaft. Iron masons wedge. Complete.	Length 7.2cm, thickness (shaft) 0.2cm-1.2cm, width 0.2cm-0.4cm, length (head) 1.6cm, thickness (head) 0.8cm.	F+P (0.3-0.4% C)
LB31	A1980.522	Field no. 105.BD: Context 6 (layer 3A): Phase 4, post-broch.	Small hammer	Small shaft-hole hammer or wedge, with rectangular cross section.	Length 9.2cm, width at "butt" 1.1cm, thickness at "butt" 0.8cm.	
LB32a	A1980.694	Missing	Chisel	Chisel	Missing	F probably with Ph, equiaxial grains
LB32b	A1980.694	Missing	Chisel	Chisel	Missing	F probably with Ph, cold worked elongated grains
LB33	A1980.718	Field no. 840.FT: Context 4 (layer 3B), Phase 3, primary broch.	Hammer	Leaf-shaped blade, parallel sides, pointed at one end; possibly rivetted flat blade of iron knife or even a hammerhead with a rectangular shaft-hole; the top is wedge-shaped (and was perhaps a different form of hammerhead). The hammerhead itself is blunt with a rectangular cross-section.	Length 9.2cm, max. thickness 1.9cm, max. width 2.8cm.	F+P (0.3% C)

Table 1 (1)

SASAAA Number	Museum Number	Context	Typology	Description	Dimensions	Metallographic observations
Bars						
LB13	A1980.564	Field no. 153.BH, Context 4 (layer 3B), Phase 3, primary broch.	Flat stip/bar pointed at one end	Iron bar, square in section; uncertain whether this is a complete object.	Length 10.4cm, width 0.7cm, thickness 0.7cm.	F (Hv=114-115)
LB14a	A1980.551	Field no. 68.BD, Context 6 (layer 3A), Phase 4, post-broch.	Two right angle pointed bar	Hammered iron bar tapering to a flattened right-angled point on one end and another right angle with an angled point on the other to form a Z-shape. Possibly a cranked tang.	Length (total) 6.7cm, thickness (bar maximum) 0.7cm, width (bar, maximum) 0.7cm.	F (Hv=119), F+nitride needles (Hv=154)
LB14b	A1980.551	Field no. 68.BD, Context 6 (layer 3A), Phase 4, post-broch.	Two right angle pointed bar	Hammered iron bar tapering to a flattened right-angled point on one end and another right angle with an angled point on the other to form a Z-shape. Possibly a cranked tang.	Length (total) 6.7cm, thickness (bar maximum) 0.7cm, width (bar, maximum) 0.7cm.	F (Hv=116-132), some nitride needles
LB16	A1980.701	Field no. 614.DL, Context 4 (layer 3B, base), Phase 3, primary broch, early.	Flat strip/bar, pointed at one end	Iron bar in the form of a flat strip with a slight curved cross section, pointed at one end and expanding slightly at the other; the bar is riveted, one rivet being clearly visible, the other only detectable by X-ray. It does not look like a sword blade and could be an iron currency bar.	Missing	P (Hv=237-249), F+P (Hv=168), P/F+P/P/F+P/P, piled
LB18	A1980.623	Field no. 386.DK, Context 5 (destruction layer 3A/3B), Phase 3, end.	Flat strip/bar	Flat strip of iron, slightly curved; one end is rounded, the other is straight. Iron strap. Uncertain if complete (may have been longer).	Length 12.4cm, thickness 2.1cm, width 0.2cm.	F (Hv=118), F+P (Hv=168) (0.1% C)

TABLE 1 (2)

SASAAA Number	Museum Number	Context	Typology	Description	Dimensions	Metallographic observations
Knives/ weapons						
LB11a	A1980.669	Field no. 230.CU, Context 5 (destruction layer 3A/3B), Phase 3, end.	Tanged blade	Blade has a convex curve (at the top), and straight parallel sides, with a rounded tip. The tang is set mid line of the blade, rectangular in section. Complete tanged iron knife.	Blade: length 15.5cm, thickness 0.5-2.7cm, width 0.2cm. Tang: length 4.2cm, thickness 1.2cm, width 0.4cm.	Corroded
LB11b	A1980.669	Field no. 230.CU, Context 5 (destruction layer 3A/3B), Phase 3, end.	Tanged blade	Blade has a convex curve (at the top), and straight parallel sides, with a rounded tip. The tang is set mid line of the blade, rectangular in section. Complete tanged iron knife.	Blade: length 15.5cm, thickness 0.5-2.7cm, width 0.2cm. Tang: length 4.2cm, thickness 1.2cm, width 0.4cm.	Corroded
LB12	A1980.661	Field no. SF 604.DV, Context 4 (layer 3B), Phase 3, primary broch.	Spearhead	Roman iron socketed spearhead with broken tip, a narrow leaf shaped blade with an ovular(?) cross section; it has a circular socket, possibly nailed (Manning 1976: 18 and fig 12, no. 4)	Length 12.5cm, width of socket 1.5-2.9cm, thickness (blade) 1.1-2.8cm, thickness (socket) 1.5-2.0 cm.	F+P (Hv=154), P at the grains boundaries (0.15% C)
LB15	A1980.730	Field no. 270.CR, Context 6 (layer 3B), Phase 4, post broch.	Leaf-shaped tanged blade	Leaf-shaped blade, parallel sides, pointed at one end; possibly rivetted flat blade of iron knife.	Length 5.0cm, thickness 0.1-1.2cm, width 0.3cm.	Piled F+P+martensite, P (Hv=266), F+M (Hv=454)
LB21	A1980.697	Field no. 567.DL, Context 4 (layer 3B), Phase 3, primary broch.	Knife blade	Iron object with a triangular form, pointed at one end, with convex sides; point of iron knife blade.	Length 3.9cm, thickness 0.4-2.0cm, width 0.2cm.	F+P (Hv=209-220)
LB34a	A1980.650	Field no. 462.DP, Context 5 (destruction layer 3A/3B), Phase 3, end.	Knife blade	Point of a flat knife blade, the sides of which were probably parallel.	Length 6.2cm, max width 1.9cm, thickness 1-1.5mm.	F probably containing phosphorus as well
LB34b	A1980.650	Field no. 462.DP, Context 5 (destruction layer 3A/3B), Phase 3, end.	Knife blade	Point of a flat knife blade, the sides of which were probably parallel.	Length 6.2cm, max width 1.9cm, thickness 1-1.5mm.	F probably containing phosphorus as well
LB34c	A1980.650	Field no. 462.DP, Context 5 (destruction layer 3A/3B), Phase 3, end.	Knife blade	Point of a flat knife blade, the sides of which were probably parallel.	Length 6.2cm, max width 1.9cm, thickness 1-1.5mm.	F probably containing phosphorus as well
Slags						
LBB1	A1980.829	Field no 709.FD, Context ? (layer 3B, top), Phase 2/3, destruction of broch.	Bloomery slag	Large mass of spongy iron, perhaps a 'bloom', or slag, from a smelting furnace.	Missing	Table 3
LBB2	A1980.149 or .946	Field no. 897.GP, Context ? (layer ?).	Bloomery slag		Missing	Table 4

TABLE 1 (3)

LBB1	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO	Total
spec 1- fayalite	1.05	0.78	3.24	30.25	0.16	1.30	1.69	3.12	0.15	0.40	57.87	100.00
spec 2- glass	0.75	0.41	2.74	40.32	0.17	1.85	5.24	13.57	0.44	0.54	34.00	100.00
spec 3- wustite	0.00	0.00	0.31	5.27	0.35	2.15	0.08	2.55	0.35	1.83	87.11	100.00
LBB2	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**SO_3**	**P_2O_5**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**FeO**	**Total**
area analysis	*1.03*	*0.56*	*3.27*	*65.8*	*0.21*	*0.81*	*3.52*	*3.53*	*0.25*	*0.25*	*20.87*	*100*
spot analysis on glass phase	*0.35*	*0.45*	*6.05*	*52.74*	*0*	*2.2*	*4.41*	*4.52*	*0.53*	*0.24*	*28.52*	*100*
metallic inclusion	0.52	0	0.78	3.03	0	0	0.54	0.24	0	0.73	94.17	100
alumino-silicate inclusion	0	0	14.94	69.35	0	0	15.16	0.1	0.1	0	0.36	100

TABLE 2 SEM-EDAX ANALYSIS OF SLAG SAMPLES LBB1 AND LBB2. COMPOSITIONS ARE NORMALISED TO 100%.

5.5 Appendix 3: EDXRF Analysis of Copper Alloy Samples from Leckie Broch by David Dungworth

5.5.1 Introduction

Thirty-one copper alloy samples from Leckie broch were selected for EDXRF analysis. This follows a previous study of copper alloy samples from the nearby broch at Fairy Knowe, Buchlyvie and builds on a larger program of analysis of Iron Age and Roman copper alloys from northern Britain (Dungworth 1995; 1996; 1997).

5.5.2 Analytical Method

Thirty-one copper alloy samples were obtained for analysis to provide a representative range of alloys for the site. Unfortunately no samples were available for phase 1 or 2. Most of the samples came from phase 3 deposits with some from phase 4, one from phase 5 and the remainder unstratified. The samples were obtained either as small pieces of metal (typically a few millimetres across) or as swarf from drilling (typically 50 mg obtained using a 1 mm diameter drill bit).

All of the samples were analysed using EDXRF (20 kV and 100μA). The elements sought were: Cu, Zn, Sn, Pb, Fe, Ni, Mn, As and Sb. The results were calibrated using a series of mutli-element standards. The results (including minimum detectable levels and error estimates) are presented in the appendix. Further details of sample preparation and the analytical method can be found in Dungworth (1995).

5.5.3 Results

The analysed copper alloy artefacts from Leckie broch are broadly similar to those from southern Scotland and northern England from the Roman period. The alloys contain varying proportions of copper, zinc, tin and lead. They also contain minor and trace levels of a range of other metallic elements. The alloys have been assigned to groups depending on the proportions of zinc, tin and lead (figure 1). Copper is used to describe alloys with a combined zinc and tin composition of less than 5%. Brass covers alloys with more than 15% zinc. Bronze refers to alloys with at least 5% tin and less than 5% zinc. Gunmetal is used to describe the remaining alloys (containing appreciable amounts of zinc and tin). Alloys containing more than 1% lead are further described as leaded.

A few of the artefacts analysed belong to categories that have been analysed elsewhere (e.g. Dungworth 1995). For example, the alloy used for the mirror (A.1980.37) from Leckie is a high tin bronze (speculum) and is entirely typical of those used for Roman mirrors (Dungworth 1997: figure 1). Similarly, the rim of a cast bowl (A.1980.41) is made from a leaded bronze typical for such vessels in the Roman world. Low lead levels are found in most of the scraps of wrought metal (sheet, rivet, chain, etc) which would ensure that the metal was ductile (cf. Dungworth 1997: 902).

It was hoped that the typical range of metals used could be determined by taking samples from 'everyday' objects.

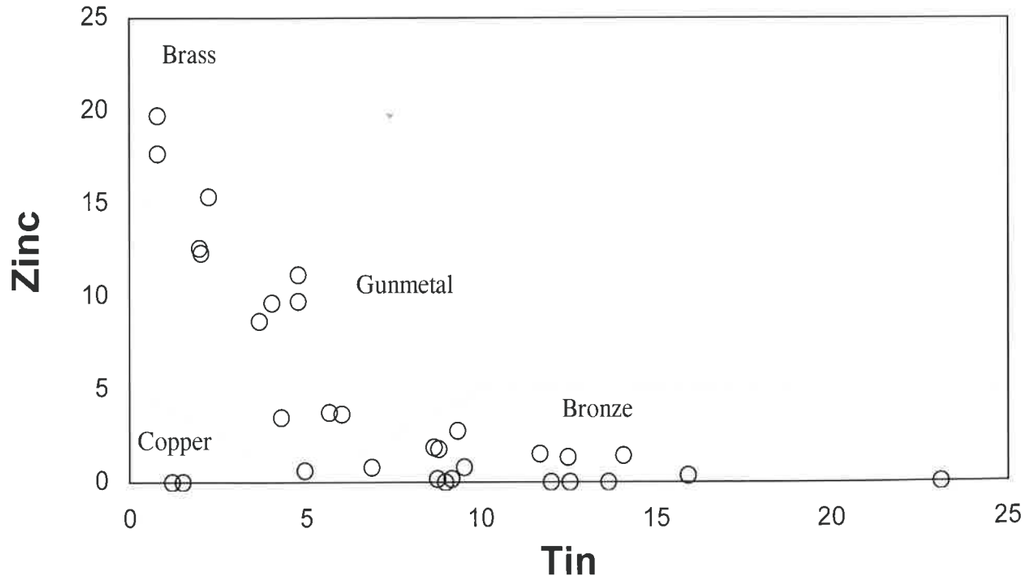

FIGURE 1. PLOT OF ZINC AND TIN FOR LECKIE COPPER ALLOYS (THE ALLOY TYPES AND THEIR BOUNDARIES ARE SUPERIMPOSED)