# GeoArch

Report 2015/03

# Analyses of copper ingots from St Michael's Mount

Dr Tim Young
30th December 2015

# Analyses of copper ingots from St Michael's Mount

**Dr T.P. Young**

## Abstract

*This report describes the investigation of 25 fragments of copper and copper alloy (twenty four copper ingot fragments and one prilly lump of leaded tin bronze) recovered from a hoard of late Bronze Age (Ewart Park phase) date, found on St Michaels Mount in 2009. Two further pieces, one a casual surface find of a fragment of copper ingot from 2004, the other a fragment, possibly casting debris, of leaded tin bronze found in 1995, were also investigated.*

*Metalwork hoards of the Ewart Park phase are differentiated from the earlier parts of the Bronze Age by the relatively common occurrence of copper ingots. Previous analyses of a small numbers of ingots from elsewhere in Southern Britain have shown a wide variation in lead isotope composition, although most are characterised by low levels of impurities, with some variation in trace elements. These features have largely prohibited interpretation of the origin of the ingots, although various proposals have been made.*

*Following non-destructive investigation by portable XRF (pXRF) of all 27 pieces, polished blocks were prepared from 13 representative pieces (for pXRF and investigation under the SEM) and drilled samples were prepared from 7 for elemental analysis by ICP-MS (6 samples) and lead isotope analysis by MC-ICP-MS (6 samples).*

*The analysis of the ingots was complicated by their very coarse grainsize (with large sub-vertical dendrites). This introduced a heterogeneity (a 'nugget' effect) on a scale so coarse that it prevented meaningful elemental analysis using typical methodologies on drilled samples. Alternative approaches of large-area analyses were employed, using pXRF on all 13 cut sections, and scanning μXRF (within the SEM) on two of the polished blocks to attempt to gain suitably low detection limits for the trace-elements.*

*The dominant metal of the ingot fragments from the 2009 hoard was copper, with rather low trace element concentrations, but with appreciable levels of iron and zinc, together with lower levels of nickel, arsenic, lead, silver and antimony. The presence of even slightly elevated zinc contents (typically 0.13%) in such ingots is unusual, and may suggest an origin in a zinc-bearing copper mineralisation, such as that of the Llanymynech area on the Shropshire/Powys border.*

*The lead isotope ratios for the ingot fragments proved to be extremely diverse, with many peripheral to, or outside, the range of most southern British Bronze Age artefacts. The only apparently deliberately leaded alloy was the piece found in 1995 (for which the LI were not analysed); two other samples (one a bronze lump, the other an arsenical copper ingot fragment) had lead contents approaching 2% and these had LI ratios coinciding with those from galena from Shropshire. For those samples with very low lead contents (i.e. those for which the deliberate addition of lead was unlikely) there was a very side spread of isotopic ratios. Although there was not a precise overlap of fields, the range broadly corresponded to that observed in analyses of galena from Shropshire and galena and malachite from Llanymynech.*

*In summary, a model is proposed in which the copper ingots were derived from the Llanymynech/Shropshire area of the Welsh borders, although a more precise origin is not determinable. The only samples of bronze were not in the form of ingots, suggesting a potentially local origin, as casting waste following alloying with local tin. The 1995 piece also suggests that some deliberate alloying with lead was undertaken, although the lead content of Llanymynech copper may be strongly elevated.*

# Contents

Abstract ..... 1

1. Methods ..... 2

2. Results
2.a 2009 hoard materials ..... 3
2.a.1 Description ..... 3
2.a.1. i General ..... 3
2.a.1. ii Details ..... 3
2.a.2 Classification ..... 4
2.a.3 Detailed sample analysis ..... 5
2.a.4 Summary – elemental analysis ..... 6
2.a.5 Summary – lead isotope analysis ..... 6

2.b Historical finds ..... 6
2.b.1 Description ..... 6
2.b.1. i General ..... 6
2.b.1. ii Details ..... 6
2.b.2 Classification ..... 6
2.b.3 Detailed sample analysis ..... 7
2.b.4 Summary – elemental analysis ..... 7
2.b.5 Summary – lead isotope analysis ..... 7

3. Interpretation ..... 7
3.a Comparison with archaeological materials .. 7
3.b Comparison with geological materials ..... 8
3.c Summary ..... 10

4. Conclusion ..... 11

5. References ..... 13

Figure Cations ..... 14

Table 1. pXRF data, assessment phase ..... 15
Table 2. wt% by pXRF data, assessment phase 18
Table 3. Samples and final groups ..... 21
Table 4. pXRF data, analysis phase..... 22
Table 5. final calibrated pXRF data ..... 23
Table 6. elemental compositions by ICP-MS ..... 24
Table 7. elemental data compilation ..... 25
Table 8. lead isotope data ..... 26
Table 9. analyses of previously studied ingots .. 27
Table 10. analysis of ores, Four Crosses ..... 28
Table 11. analyses of copper, N Wales ..... 29

Figures ..... 30

Appendix ..... 35

# 1. Methods

***Material:*** The programme of analysis was focused on twenty five fragments of copper and copper alloy found in 2009 on St Michaels Mount. Fourteen of these formed the first batch of material investigated and were supplied in an 'as found' condition. A second batch of material comprised eleven ingot fragments that had received some degree of physical cleaning, plus two historic finds (from 1995 and 2004) from the area. Images of the pieces pre-sampling are supplied in the Appendix.

***Assessment Stage:*** An initial assessment (Young 2014) entailed giving each piece was a preliminary analysis by handheld portable XRF (pXRF). The specimens were analysed on a semi-quantitative basis using a Bruker Tracer III-SD portable X-Ray fluorescence spectrometer (instrument belonging to the Department of Archaeology, Cardiff University, and the National Museum Wales). The instrument was operated with the Bruker 'yellow' filter (300µm Al + 25µm Ti), at 40kV and 9.60 µA, with a filament current of 189 µA, for 100s.

The instrument was controlled by a PC running Bruker's S1PXRF with spectra stored as pdz files and csv files. The output was converted for measurement of net peak areas in Bruker's Spectra (Artax) software (Table1).

Calibration of the results was obtained through linear correlation with the net peak areas with those recorded by Nicholas & Manti (2014) on a series of copper alloy standards, using exactly the same instrument and settings. The raw net peak area values are provided in Table 1 and the calibrated analyses (using the above technique) are given in Table 2. These preliminary measurements were strongly influenced by the superficial corrosion of the ingots and were therefore not representative of the underlying metal. They provided, nonetheless, a broad classification of the materials into five preliminary groups on which to base the subsequent sampling. For ease of reference, the specimens (both those from the 2009 hoard and the two historical finds) were assigned codes in numerical order according to these groups (SMM1-SMM27; Table 3).

***Analysis Stage:*** The intention of the second stage of the project was to focus on using ICP-MS for detailed analysis. The initial findings of by ICP-MS, together with further observation of the ingot fragments, showed that the inhomogeneity within the ingot was on too coarse a scale for useful elemental analysis by drilled sample. Some mapping of the textures was undertaken on the scanning electron microscope and this too documented elemental heterogeneity (co-variability of iron and cobalt and particularly of zinc and nickel) on a coarse scale. Full statistical investigation of the observations was not possible with the scope of the project, but by expanding the analyses to the maximum scale possible within the limits of the polished mounts (to the order of 100mm$^2$) it seemed likely that a representative area was being sampled.

The only tools available to work on this scale were the portable XRF (pXRF; has a broad beam, but fairly low sensitivity and accuracy) and analytical tools with the scanning electron microscope. The scanning micro-XRF (µ-XRF) was chosen over the other built-in analytical tools of the electron microscope (wavelength and energy dispersive X-Ray spectroscopy), because of its good sensitivity and relative speed when undertaking large area, high resolution mapping. Even so, the collection of large µ-XRF maps required over-night data acquisition and considerable subsequent processing, so only two samples could be investigated this way.

***Sampling (blocks):*** Further investigation was then pursued on a subset of thirteen samples, including at least one representative example from each group (SMM1, 2, 3, 4, 5, 6, 7, 8, 9, 14, 15, 16, 17). The selected samples were cut on a water-cooled diamond saw to provide a cut section through the entire thickness of the ingot. The samples were then reduced to a smaller group of seven (SMM2, 4, 6, 7, 8, 15, 16; one example from Groups 1-3 and two from Group 4 and 5) for detailed analysis. The cut piece from each of these samples was mounted in a resin block and

polished (by the Department of Earth Science, the Open University), for examination under the scanning electron microscope.

***Portable XRF (pXRF):*** These cut surfaces of the sawn samples were then re-analysed using the pXRF on the cut metal faces, using the same instrument settings and calibration as previously.

Each piece was analysed twice, with each analysed area elliptical and approximately 10x8mm. These analyses are presented in Table 5. In this second set of analyses, because the samples were fresh cut surfaces, rather than irregular, external, corroded ones, the calibrated data are believed to be good estimates of metal composition.

***Scanning XRF (µXRF):*** Electron microscopy was undertaken on the Zeiss Sigma HD Analytical Field Emission Gun SEM (ASEM) in the School of Earth and Ocean Sciences, Cardiff University. The samples were examined using backscattered electron imagery. Analyses were undertaken using scanning micro-XRF (µXRF) over small areas. Following the identification of extreme heterogeneity within the small areas investigated, two samples (SMM3 and SMM6) were selected for detailed mapping with the µXRF over larger areas (approximately 100 $mm^2$) with a 50µm pixel size, 200 x 189 resolution and a 25 mSec point dwell time. Calibration of the µXRF was assisted by use of a block with certified copper alloy standards, kindly loaned by the Department of Archaeology and Conservation, Cardiff University. The assistance of Mr Matthew Loocke (School of Earth and Ocean Sciences, Cardiff University) with the operation of the microscope and subsequent data processing is gratefully acknowledged.

***Sampling (turnings):*** further sampling was then undertaken by drilling samples from the cut faces of the seven selected cut pieces. Each drill hole was 1mm in diameter and up to 4mm deep. Wherever possible, the drill holes were oriented perpendicular to the orientation of the dendrites, in order to try to obtain representative samples.

The drill turnings were divided into two, to provide samples for ICP-MS elemental analysis and for lead isotope analysis.

***Inductively-Coupled Plasma Mass Spectrometer (ICP-MS):*** the ICP-MS analyses were undertaken on solutions (taken from samples SMM2, 4, 6, 8, 15 and 16) using the ThermoElemental X-series Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) in the School of Earth and Ocean Sciences, Cardiff University. The ICP-MS elemental results are present in Table 6.

***Lead Isotope analysis (LI):*** lead isotope ratios were determined for six samples (from SMM 4, 6, 7, 8, 15 and 16). The lead isotope analyses were undertaken by ALS Scandinavia AB, of Luleå, Sweden, using a Thermo Scientific Neptune Plus high resolution multi-collector ICP-MS (MC-ICP-MS). The lead isotope results are presented in Table 8.

Samples were prepared by $HNO_3$ and ion exchange separation. The instrument employs internal standardisation and external calibration with bracketing isotope SRMs. The standard deviation was calculated from two independent consecutive measurements.

# 2. Results

## *2.a 2009 hoard materials*

### *2.a.1 Description*

2.a.11 i General

The ingot fragments from the hoard were mostly rather equant in plan, and ranged from 25g to 515g in weight. The largest piece (SMM3) was the only one that provided evidence for the original size of the ingots, for if symmetrical, the ingot of which this piece was a fragment would have had a minimum radius of 65mm, but might have been slightly larger. The maximum thickness of the ingots was approximately 30mm.

The ingot fragments showed a coarse internal structure where torn apart, with the fibrous structure presumably reflecting the nature of the primary dendrites. The fibres ranged up to approximately 3mm in width where coarsest (Plate 1).

The base of the ingots was typically very gently dimpled. Several ingots appeared to show a slight bevel 30-40mm from the margin, where they started to thin more rapidly. The dendritic fibres started close to the base of the ingots, but the upper layer of the ingots was formed by a chilled layer up to 3 or 4mm in thickness.

The ingots frequently contained large rounded cavities (oblate in the plane of the ingot). These occasionally occurred in the body of the dendritic zone, but were more commonly found close the top of the ingots. The areas near the margin of the ingots were commonly seen to be very porous.

As well as show some deformation around the torn margins of the fragments, several ingots showed modification including flattening of the upper cavities and possible flattening of the fibres on some torn surfaces. It is possible this deformation may have, at least in part, between subsequent to the breaking of the ingot, perhaps to make the fragments slightly more compact, or to reduce protruding sharp edges.

2.a.11 ii Details

***SMM2*** (SMM-09-BP-0007-23): overall 65mm x 40mm x 28mm deep (149g), forming the distal end of a lobate flow of copper alloy, extending over (and probably also below), what appear to be fuel moulds, Shows abrupt fractures at proximal end. Polished mount shows some small vesicles/voids near the margin and several internal ones forming the focus of corrosion.

***SMM3*** (SMM-09-AT-007-24): 70x75x28mm (515g), and if symmetrical would have had a 65mm minimum radius, but could be more. The fibres are well developed on the torn edges. The polished sample was taken from near the ingot margin.

***SMM4*** (SMM-09-AU-007): 50x48x28mm thick (325g). This is a piece from the margin of an ingot. One side shows a vertical tear with dendrites, the other shows a very irregular face, suggestive of breakage through

internal voids. The base is gently dimpled, the top markedly convex. The polished mount has long section through ingot, with the frayed edge to the left; the neat edge is to the right .

***SMM6*** (SMM-09-BI-007-39): 37x37x14mm (74g); thin fragment of probable ingot that is rather rich in internal voids. All 4 edges are probably fractures. Some margins show very pale weathering.

***SMM7*** (SMM-09-BQ-007): 50x22 x26mm (206g), a fragment from towards the margin of an ingot. The long edge on the polished mount is the upper surface. The dendrites start a few mm below the top, and are well-formed and inclined. Specimen appears to have been fractured from SMM12.

***SMM8*** (SMM-09-AW): 50x65x30mm (229g), a large piece from a well formed acute ingot margin, with well-developed dendrites. The mounted section is oblique to the dendrites and in the lower part of the ingot, with the longest edge being the base.

***SMM9*** (SMM-09-BL-007-42): 73x43x24mm thick ingot fragment (244g) with good oblique dendrites and fine top with large oblate rounded voids.

***SMM10*** (SMM-09-AZ-007-36): 47x24x12mm (53g), slightly concavo-convex edge from an ingot with a hint of dendrites on one fracture.

***SMM11*** (SMM-09-BD 007-34): 48x27x12mm (54g), thin fragment that is distorted, probably by hammering, twisted and cracked. The original dendritic internal structure has been reduced to a granular appearance.

***SMM12*** (SMM-09-BE 007-35): 40x32x28mm (145g), a good dendritic ingot fragment with all edges fractures. It has rounded cavities, particularly towards the top. Specimen appears to have been fractured from SMM7.

***SMM13*** (SMM-09-BN 007-44): 35x35x23mm (134g) fibrous ingot fragment. It is pale on top and at one end. It bears numerous large rounded cavities.

***SMM14*** (SMM-09-BP): 47x47x19mm (219g), thin ingot fragment, with voids near top and, some fibres (slightly masked by possible tubular vesicles), section shows ends of two top. The polished sections shows parallel voids in upper part.

***SMM15*** (SMM-09-AV): 57x57x26mm (299g), with oblique dendrites. The drilled sample was from the quenched top; the cut sample from the upper part of the section.

***SMM16*** (SMM-09-BO): 40x30x30mm (175g), dendritic ingot fragment. The section was cut obliquely through the dendrites in lower part.

***SMM17*** (SMM-09-BJ): 48x62x32mm (353g). It possesses poorly-developed dendrites, but large internal voids, with the ones on top near the edge partially flattened by hammering.

***SMM18*** (SMM-09-BG 007-37): 63x50x30mm (357g). This is a well-formed ingot fragment. The top bears a quenched layer with many small cavities, below which the fibres are well-developed and mostly vertical, but become oblique in a small area.

***SMM19*** (SMM-09-BM): a 36x35x23mm (115g) fibrous ingot fragment, with some horizontal cracking on the thin end and a large internal void in the centre of dendritic zone.

***SMM20*** (SMM-09-BA 007-31): 23x15x13mm (57g), was a thin, but fibrous ingot fragment.

***SMM21*** (SMM-09-AX-28): 20x19x14mm (25g), was a small ingot fragment.

***SMM22*** (SMM-09-BK): 32x40x17mm (106g), this was an ingot fragment with many rounded void and some fibres.

***SMM23*** (SMM-09-AY 007-29): 23x27x13mm (36g), a small rather porous ingot fragment.

***SMM24*** (SMM-09-AX 007-28 ): 20x20x20mm (24g), a tiny fragment with cavities, from near an ingot margin.

***SMM25*** (SMM-09-BH 007-38): 35x37x13mm (74g), this was a dense, fibrous, plate-like ingot fragment.

***SMM26*** (SMM-09-BF): 46x27x18mm (63g), small fragment from rather porous ingot margin, the section was through the complete profile with the voids near upper margin

***SMM27*** (SMM-09-BB 007-32): 46x36x 22mm (134g). Fragment from lip of ingot, fibres on one surface look as if they may have been closed up by hammering.

### *2.a.2 Classification*

The assessment identified five groups of specimens on the basis of non-destructive pXRF analysis of the material as supplied. To ease sample handling, the pieces were assigned numbers (SMM1-27; Table 3) according to these groups:

*Group 1: bronze*. Two pieces, one heavily leaded (SMM1, an ingot fragment from the 1995 excavations), the other moderate lead (SMM2, a prilly block of metal from the 2009 hoard, of different morphology to the ingot fragments).
*Group 2: Copper with high Ag, As, Sb* (2 from the hoard)
*Group 3: Copper with high Fe, Co, As, Ag, Sb, Pb* (1 from the hoard and 1 other)
*Group 4: Copper with high Fe, Co* (7 from the hoard)
*Group 5: Copper with low traces* (14 from the hoard)

It was noted in the assessment that '*these groupings are affected by both the state of alteration of the metal and the degree of cleaning, and actually hint at a rather low diversity of composition with the hoard. All of these materials might actually be rather similar metal, but with varying degrees and types of corrosion*'.

The analysis of the cut samples by pXRF during the analysis phase supported this assessment. These data are presented in Tables 4 and 5.

A first group was confirmed as comprising **leaded bronze** – with two members (sample SMM2 from the hoard and earlier find SMM1), both from Assessment Group 1.

A single piece from the hoard (SMM4) was of **leaded arsenical copper** (and had been one of two samples in Assessment Group 2).

The single ingot fragment found in 2004 was of **copper with raised cobalt and bismuth** (SMM5; one of the two samples that had been in Assessment Group 3).

The final group, **copper with low traces***,* included all the analysed material in Groups 4 and 5, together with one specimen from each of Assessment Groups 2 and 3 (SMM3, SMM6, SMM7, SMM8, SMM9, SMM14, SMM15, SMM16 and SMM17). The similarity in the results at the assessment stage allowed the confident allocation of the unanalysed remainder of Assessment Groups 4 and 5 to this category (SMM10, SMM11, SMM12, SMM13, SMM18, SMM19, SMM20, SMM21, SM22, SMM23, SMM24, SMM25, SMM26, SMM27).

### *2.a.3 Detailed sample analyses:*

***SMM2:*** this sample was investigated by pXRF alone. It was a lead-bearing bronze with 1.7% lead and 9.9% tin. The other impurities include 0.15% silver, 0.15% antimony, 0.11% zinc, but with very low levels (<0.05%) of nickel and iron.

The lead isotope ratios were almost identical to the very low lead copper ingot fragment SMM8.

Given the high lead content, this sample would be classifiable as similar to IMP-LI 22b.

In terms of its trace element impurities there is considerable similarity between SMM2 and SMM4. Both show just under 2% lead, and SMM2 shows approximately the dilution of al impurities concomitant with its 9.9% tin. Given that SMM2 is in the form of a prilly mass quite different in morphology from the ingot fragments, it is tempting to see the bronze as having been produced by alloying ingot material with tin.

The similarity of the LI between SMM2 and SMM8 will be discussed further below.

***SMM3***: This sample was investigated sing both pXRF and µ-XRF. The agreement between the analyses is rather poor. The pXRF analysis suggests a metal rich in silver, but with the other impurities at low levels. In contrast the µ-XRF suggested a composition in which arsenic and lead were both moderately elevated.

It is uncertain to what extent these analytical differences are due to technique and to what extent to the sample heterogeneity. Sample heterogeneity was certainly observed under the SEM (as it was in SMM6). The µ-XRF did not show enhanced arsenic and lead in sample SMM6, so a systematic difference between the tools seems unlikely. Arsenic and lead are known to be preferentially concentrated in the weathering products, so it is possible that the µ-XRF analysis has preferentially detected weathering products, perhaps even below the exposed surface of the mount. Interestingly, a somewhat similar raised level of arsenic and lead was detected by the ICP-MS in several samples, and again a sample bias towards altered materials might possibly be the reason.

***SMM4:*** this sample had an unusual composition amongst the assemblage. Its composition was marked by pXRF indicating high concentrations of arsenic (1.13%), lead (2.0%) and silver (0.24%), as well as 0.13% zinc. The ICP-MS sample supported this composition, with 1.3% arsenic, 0.4% lead and 1.4% silver, as well as 0.11% zinc. Both sets of data supported a composition with very low levels of iron, cobalt and nickel.

The LI ratios plot within the right hand end of the EWLIO envelope, approximately in the centre of the array of analyses of galena from the West Shropshire orefield. This is the general region designated as IMP-LI 20 by Rohl & Needham (1998). This group is rather heterogeneous and may not indicate a single source (Rohl & Needham 1998, 107).

***SMM6:*** this sample was initially placed into group 4 (Cu with high Fe, Co, As, Ag, Sb, Pb) during the assessment. Refinement of the pXRF groups has involved placing the sample into final Group 3, on the basis of its high iron content and slightly elevated arsenic content.

Two replicates were analysed by ICP-MS, with the results emphasising the heterogeneity with respect to nickel, silver, antimony, and tin. As with some of the other samples, the lower values of impurities indicated by the techniques with a broader sample are believed to be closer to the bulk compositional values.

This sample was also examined by µ-XRF, which suggested a composition with almost 0.2% zinc, 0.2% antimony but just 0.08% arsenic, 0.01% tin and 0.05% lead. This estimate is broadly in agreement with the pXRF data, but markedly higher levels of silver and antimony. The coarse compositional variation is illustrated in Plate 2.

The LI ratios plot well outside the EWLIO; however, there are two analyses of galena from the West Shropshire Orefield, which plot only just inside the EWLIO envelope in this area and two items of IMP-LI 19 also plot in this general area (#331 a copper prill from Petters and #397 a copper ingot fragment from Wickham Park).

***SMM7***: this item was analysed by both pXRF and ICP-MS. The low-volume drilled sample examined by ICP-MS differs from the broad area pXRF in showing higher lead and tin (and to lesser extent higher arsenic and lower silver).

***SMM8:*** this sample was of a low lead copper ingot, with low impurity levels. It was analysed by both pXRF and ICP-MS. The two techniques are broadly in line, but with the ICP-MS determining lower iron, cobalt and silver, but higher arsenic, lead and nickel. All of these elements are involved in the heterogeneity observed in sample SMM6.

The LI analysis of this sample plot close to the centre of the main IMP-LI 21 array.

***SMM9***: this sample was analysed by pXRF only, and this showed low concentrations of all impurities except zinc (at a comparable level with most other samples) and nickel (at its highest level in any of the samples).

***SMM14***: this sample was analysed by pXRF only. Impurities were all at a low level, apart from silver and zinc, which were at levels within the range exhibited by other samples/

***SMM15***: is a sample of low-impurity copper ingot; in particular it shows silver and antimony below detection of the pXRF. Antimony was also below detection for the ICP-MS, but silver was measured at 0. 03%. Nickel (at 0.09%, ICP-MS; 0.06% pXRF), arsenic (at 0.1%, ICP-MS; 0.08% pXRF) and zinc (at 0.06%, ICP-MS; 0.14% pXRF) were significant impurities.

The LI ratios were markedly different to those of the other samples, lying below the trend of the EWLIO in terms of $^{208}Pb/^{206}Pb$. The only reported by Rohl & Needham (1998) that plotted in this area were galena from Navan, the southern Grampians and the Donegal and Connemara Dalradian,

***SMM16:*** this sample was placed into Group 5 (copper with low levels of traces) in the initial pXRF analysis. Subsequent refinement of the pXRF data has generally confirmed that observation. The drilled sample for ICP-MS appears to have encountered a relatively lead-rich zone (Pb = 0.4wt%; compared with 0.05wt% estimated from the pXRF). pXRF estimated the zinc content as 0.13%. The iron, cobalt and nickel contents are all very low, as are silver and antimony. Arsenic was extremely low at approximately 0.01wt%

The LI values place this sample at left side of the discriminant diagrams employed by Rohl & Needham (1998).

These characteristics place SMM16 in Rohl & Needham's (1998) group IMP-LI 19. They commented that this group may not have had a single source, but suggested a possible 'Middle Rhine' origin. Subsequent LI analyses of malachite from Llanymynech plot in precisely this area (*Oxalid* database).

***SMM17***: this sample was analysed by pXRF only. All impurities were at low levels, coincident with concentrations in other samples.

### *2.a.4 Summary - Elemental analysis:*

The dominant group of ingot materials comprised copper with very low levels of trace elements. These included all of the specimens subjected to detailed analysis that had been allocated to provisional Groups 4 and 5 (SMM7-9 and SMM14-17 respectively), with the difference probably being largely the amount of adhering corrosion products (such that Group 4 contained more of the 'as found' ingot fragments and Group 5 more of the fragments that had been cleaned). In addition, one of the samples placed in Group 2 (SMM3) proved to have a similar composition. Most of the analyses in this group have very low arsenic (<0.013%), but two show slightly elevated levels. Specimen SMM6 was broadly similar, but was slightly arsenical (0.15%) SMM15 (0.088%) and SMM7 (0.10%). This group therefore contains 9 of 11 of the specimens from the 2009 hoard that were examined in detail, which probably indicates that 22 out of the 27 pieces if ingot in the hoard may be placed here. In addition, it was noted that specimen SMM7 joined specimen SMM12 (both in preliminary Group 4), divided by one of the original hot fractures.

One of the samples was a leaded tin bronze (SMM2). Not only was this specimen of a distinctive composition, but it was also a distinct morphology, comprising multiple individual lobate flows into a fuel bed – and was therefore not a fragment from a 'bun-shaped' ingot. In detail, this specimen also showed moderately high silver (0.15%) and antimony (0.15%) as well as 1.7% lead and 9.9% tin. Arsenic is present at levels close to those in the large group described above (0.06%).

Specimen SMM4 was also leaded (2.0%) and had an elevated silver content (0.24%), but did not have a particularly high antimony content (0.06%), but was markedly arsenical (1.13%). It had extremely low cobalt and nickel.

For the main group of copper ingot fragments (SMM3, 6, 7, 8, 9, 14, 15, 16 and17), the impurity metals are present at very low levels. For all the analyses ingot fragments (i.e. the main group plus SMM4) the levels were:

Fe: average 0.17%, maximum 1.0%
Co: average 0.02%, maximum 0.08%
Ni: average 0.04%, maximum 0.15%
Zn: average 0.13%, maximum 0.14%
As: average 0.15%, maximum 1.1%
Pb: average 0.2%, maximum 2.0%
Sn: average 0.03%, maximum 0.07%
Sb: average 0.03%, maximum 0.06%
Ag: average 0.09%, maximum 0.24%
Bi: below detection

If the exceptional high-lead, high-arsenic, high-silver piece (SMM4) is excluded, then the figures are:

Fe: average 0.19%, maximum 1.0%
Co: average 0.06%, maximum 0.5%
Ni: average 0.04%, maximum 0.15%
Zn: average 0.13%, maximum 0.14%
As: average 0.04%, maximum 0.15%
Pb: average 0.05%, maximum 0.09%
Sn: average 0.02%, maximum 0.07%
Sb: average 0.03%, maximum 0.06%
Ag: average 0.08%, maximum 0.15%
Bi: below detection

In summary, the hoard contained ingots or lumps of three compositions: leaded bronze (lump SMM2), arsenical leaded copper (ingot fragment SMM4) and copper with low impurity levels (SMM3, 6, 7, 8, 9, 14, 15, 16 and17)

### *2.a.5 Summary - lead isotope analysis*

The results of the lead isotope analysis are presented in Table 5. The data show a wide spread of values (Figures 1-3) which bear little relationship to the concentration of lead in the metal (Figure 4); if the lead was added from a single, different source, then the samples with high concentrations of lead would be expected to show the lead isotope value of the lead source, whereas the low-lead metals would show the lead isotope values of the copper sources.

Sample SMM15 shows anomalous LI ratios. Sample SMM4 (the arsenical leaded copper) plots with examples of IMP-LI 20, the leaded bronze (SMM2) and copper (SMM8) plot with previous determinations assigned to IMP-LI 22 and IMP-LI 21 (respectively), and copper SMM16 plots with examples of IMP-LI 19 (and copper SMM6 is arguably on a similar trend).

## *2.b Historical finds*

### *2.b.1 Description*

2.b.1 i General

The two historical finds differed in morphology from the pieces in the hoard. The piece from the 1995 excavation was a small, approximately plano-convex piece, up to 47mm across. It did not have the morphology of an ingot fragment, and may have been

casting waste or similar. The casual find from 2004 was a large fragment from a large ingot, with a distinctly more bluish colour to its green weathering products than those of the hoard.

2.b.1 ii Details

***SMM1*** (SMM95-AA-c235): 40x47x15mm (96g). Small plano-convex piece, with fractures on two edges, but the base has convexity in two senses, suggesting this is not from the lip of a regular ingot. Although original (Herring 2000) described as an ingot, it might rather be casting waste or a flow lobe somewhat similar to SMM2 (although has rounded not flat tops to the flow lobes). The colour of the metal shows zonation, with pale outer parts on the polished mount.

***SMM5*** (SMM-04-CA ): 158x78x47mm thick (1237g), was a large piece of large ingot; if symmetrical the ingot would have had a radius if at least 130mm, and the ingot would have weighed at least 7kg. The top was chilled, with inclined dendrites below. The polished mount has its long axis parallel to the fibres on fracture. The straight edge of the mounted sample is the base; the rounded end isc.22mm above base (i.e. close to mid-thickness of ingot). The weathering products are slightly blueish. The top is quenched, with cavities, and overlies a body which is fibrous, but also with occasional rounded voids. The thin end of the piece shows very pale weathering, and the cut sample was prepared from near the near ingot margin.

### *2.b.2 Classification*

SMM1, as a leaded bronze, was placed in Group 1 during the assessment. Some analytical details of this piece were given by Herring (2000), but the analytical approach allowed little detail beyond recognition of a heavily leaded composition. The new determination of the bulk composition of the lobe as sectioned, as a leaded bronze with 19% lead and 6.1% tin.

SMM5 was placed in Group 3 in the assessment (Copper with high Fe, Co, As, Ag, Sb, Pb). The determination of the importance of these impurities in the non-destructive analysis was largely borne-out by the re-analysis of the cut section by pXRF. The composition is slightly different from all the other materials analysed here, raised cobalt and bismuth being the key differentiation.

### *2.b.3 Detailed sample analyses:*

***SMM1***: this sample was analysed by pXRF only. The lead content is very high, and the value of 19% is an estimate of the bulk concentration across the whole of the cut section; it is likely that it is strongly relatively enriched in the external parts of the material. The other key characteristics of the material are a high content of arsenic and of antimony.

***SMM5:*** this sample was analysed by pXRF only. The composition was broadly similar to the analysed copper ingots from hoard, sharing with them moderately elevated contents of zinc (determined as 1276ppm), arsenic (4323ppm) and lead (5382ppm). The raised levels of cobalt (5195ppm) and bismuth (760ppm) differentiate this ingot from those of the hoard.

### *2.b.4 Summary - Elemental analysis:*

The fragment of probable casting debris found in 1995 (SMM1) was a highly leaded (19.2%) tin bronze (tin 6.1%). Modelling of the composition on a lead and tin free basis, suggests that the copper component was slightly arsenical (0.48%) and, like the leaded tin bronze flow from the hoard (SMM2), contained moderate antimony (0.19%). This raises the possibility that the antimony had entered the metal with the alloying elements – either the lead or tin. Alternatively, the high arsenic and moderately high antimony of these items might argue for an association with elements of IMP-LI 20 (although they lack the high nickel content of many of those items).

The ingot fragment recovered in 2004 (SMM5) was a slightly arsenical (arsenic 0.43%) and leaded (lead 0.54%) copper. The metal differs from all the other analyses in possessing elevated cobalt (0.52%) and was the only material to show detectable bismuth (0.08%).

### *2.b.5..Summary - Lead Isotope analysis*

The lead isotope ratios of the historical finds were not investigated.

# 3. Interpretation

*3.a Comparison with archaeological materials*

Plano-convex (bun-shaped) copper ingots are a significant feature of Late Bronze Age (Ewart Park Phase) hoards across much of Britain (Northover 1988, 138). An interpretation of the origin of metals, on the basis of trace element contents and lead isotope ratios is complicated by the very small proportion of these finds that have been analysed and published (Table 9).

The analyses of both the chemical composition and LI ratios of the materials from St Michael's Mount show a high degree of variability. In particular the LI ratios plot in a wide variety of locations with respect to the EWLIO field of Rohl & Needham (1998; Figures 1 – 4). Four of the six detailed analyses are peripheral to the field or outside it; the other two lie in the central cluster of Ewart Park material.

This would permit an interpretation between two quite different extremes possibilities – either to suggest that the hoard was formed of ingot fragments of disparate origin, or alternatively that material reflects a small number, or even just one source, but one with variable composition.

Both strands of evidence, elemental composition and lead isotope ratios, need to be considered in any attempt to discriminate between these possibilities. Of these two strands of evidence, the arguments based on elemental data were developed first, particularly by Northover (1980, 1982, 1998).

Northover (1980) used the term 'T' metal for the general Late Bronze Age casting metal of mixed origin (much may be recycled earlier material).

Northover (1982) identified two metal types in the preceding Wilburton Phase: 'S' metal and 'H' metal. The Wilburton phase also saw the reintroduction of alloying with lead (Northover 1980, 1982); both 'S' and

'H' metals commonly occur in a strongly leaded composition. Northover (1982, 92) suggested that lead entered the system in the Guilsford area (i.e. the Powys/Shropshire boundary near to Llanymynech), although he suggested that other lead sources may have been employed in the subsequent Ewart Park phase.

'S' metal has arsenic, antimony, nickel and silver as principal impurities with arsenic and antimony typical greater than 0.3% with antimony more abundant than nickel. Nickel and silver are typically present in the range of 0.1-0.5%, and cobalt in the range 0.01-0.1%

'H' metal has arsenic as principal impurity, and with antimony, nickel and silver all less than 0.10% and often with cobalt more abundant than nickel. 'H' metal is found in the plate scrap metal common in this phase and Northover (1982, 85) suggested it might have had a British origin.

He argued that 'S' metal had a European origin and more specifically an eastern origin. He commented that although the Llanymynech area (the only area where Wilburton metalwork occurs in a British copper-producing area) could not have produced 'S' metal, the Llanymynech area could have produced the lead employed for the leaded bronzes. Northover (1998) also discussed the origin of the lead in Wilburton metalwork; he suggested that '*a single British source was involved*' and that *'archaeological evidence would suggest that the most likely source area was the upper Severn Basin'*.

Northover (1988, 137) commented that the impurities in typical Ewart Park bronzes were similar to those of the preceding Wilburton period, but at lower levels such that arsenic and antimony were both usually below 0.4% and nickel below 0.2%. 'H'-type metals, with an elevated lead content, occur in a number of items within the Ewart Park phase Stogursey (Somerset) hoard.

Northover (1998) suggested that there were two possible origins: continental (associated with the origin of Carp's Tongue metalworking) and British (suggested by the occurrence of ingots in the West Country). Any fresh British metal would, he suggested, would be a low lead bronze with 8-12% tin and with arsenic the only impurity above 0.1%. He commented that whilst a British origin for some of the low impurity ingots (particularly those from the West Country) might be reasonable it would be 'almost impossible to prove' on compositional grounds.

In terms of Northover's general definition, the present material shows more affinity with 'H' metal, but only shows high cobalt contents in a few analyses.

The zinc content of 'H' metal was not discussed in previous work, but a compilation of available analyses of Ewart Park Phase ingots is presented in Table 9.

Later, the lead isotope ratio evidence was developed by Rohl and Needham (1998). They suggested that the tight clustering of the lead isotope data for many pieces of Ewart Park phase bronze metalwork, despite the variable nature of the trace element composition, included both low- and high- lead contents, might suggest that either there was a dominant lead source for the phase that had a lead isotope ratio similar to that of the raw copper, or that the low-lead metals had been leaded and then de-leaded, possibly to remove other impurities.

The scattered distribution of the LI ratios for the present material (Figure 1) might suggest metal of a variety of origins might be present. It must be remembered, however, that primary, freshly-smelted, copper may reflect the diversity of LI ratios in the source material more closely than remelted and mixed metal which may tend towards a more 'average' composition.

When compared with the plot of the LI ratios of other Ewart Park ingots (Figure 2), there is a broad similarity in the distribution, with the exception of the outlier to the present data, sample SMM15. The location of the analyses for SMM6 and SMM16 towards the upper range of $^{208}Pb/^{206}Pb$ is paralleled by analyses of a copper ingot fragment from Wickham Park (Rohl & Needham 1998 #397), one of the ingot fragments from Stoke Hoo (Rohl & Needham 1998 #383) and one of the copper prills from Pettters Field (Rohl & Needham 1998 #331); SMM16 closely parallels two of the ingot fragments from Stoke Hoo (Rohl & Needham 1998 #378, #382); SMM4 resembles an ingot fragment from Runnymede (Rohl & Needham 1998 #362). The other ingots from Stoke Hoo and those from Stogursey plot with a linear array in the centre of the EWLIO field of Rohl & Needham (1998), along with analyses of SMM2 and SMM8 of the present project.

Rohl & Needham (1998) divided the Ewart Park material mostly between groups IMP-LI 19, 20, 21 and 22. They commented that *'the isotope measurements are extremely widespread, such that it is virtually impossible to reconcile them with a single source region, either in Britain or the neighbouring parts of Europe*'.

IMP-LI 19 are analyses at the low $^{207}Pb/^{206}Pb$ of the EWLIO field. Rohl & Needham (1998, 107) suggest that the impurity pattern contains As, Sb <.14% and Ag, Ni <0.08%. The analyses of SMM16 show a similar composition

The IMP-LI 20 of Rohl & Needham (1998, 107) was a small group with slightly more abundant impurities, with silver and nickel up to 0.43% and antimony and silver between 0.014% and 0.14%. This group only included a single ingot fragment (#362) – and the pattern is not expressed in the present material. The Stoke Hoo ingot #383 is also towards the same region of the plots, and has a high arsenic content (as SMM4), but unlike SMM4 also has a high antimony content.

Rohl & Needham (1998,107) divided the central cluster on the LI ratio plots into IMP-LI 21 for ingots with very low lead levels (Stogursey, Petters, Stoke Hoo and Heathery Burn), distinguishing them from IMP-LI 22 for leaded objects with similar LI ratios. They suggested a possible Alderley Edge origin for this almost impurity-free group.

IMP-LI 22 was a group formed of materials plotting in the same area, but leaded. The impurities are (Rohl & Needham 1998, 108):

Arsenic 0.043-0.75%
Antimony 0.024 - 0.75%
Silver 0.014 – 0.43%
Nickel 0.014-0.24%

They commented that this group is essentially Northover's (1980) 'T' metal, but further subdivided the group into IMP-LI 22a (for high concentrations of impurities), IMP-LI 22b (for intermediate

concentrations) and IMP-LI 22c (for low concentrations).

Northover (1988) described Ewart Park metal as typically low-lead, with all traces except arsenic below 0.1%.

In summary, the new material from Saint Michael's Mount shows a pattern of lead isotope ratios equivalent to the total range exhibited by all analysed ingots of the period. The trace elements are also rather variable, with low impurity contents being typical, but with constant moderately elevated zinc, commonly elevated lead and occasional examples of elevated arsenic. This variability could be seen as a reflection of the variability of ingots of the period in general, as illustrated by Rohl & Needham's (1998) use of IMP-LI 19, 20, 21 and 22, with no clear identification of source(s).

### *3.b Comparison with geological materials*

The above discussion has noted the linkage made by Northover (1982) between the Ewart Park metals and the Welsh borders area and also the tentative link with Alderley Edge, made by Rohl & Needham (1998) for the low-impurity IMP- LI 21.

The understanding of the relationship between ores and metal has been challenged by Williams (2014), who has demonstrated that ores at the Great Orme mine, rich in goethite and malachite, could produce smelted metal with much higher levels of impurities than previously believed (e.g. Ixer and Davies 1996, Ixer and Budd 1998 and Ixer 2001). The Great Orme mine would thus appear to be the likely source of a considerable amount of Middle Bronze Age copper.

The Great Orme metal would be incompatible with the present material in many ways (it has silver and zinc contents that are too low, and the LI ratios are not appropriate being strongly radiogenic). However, a rather similar set of observations has also been made (Young 2010) on the ores from Llanymynech – the area proposed as a likely source of the lead by Northover (1982). The Llanymynech ore has been little studied *in situ*, but materials from a Middle Iron Age smelting site at Four Crosses, in the valley below the mine, have been examined (Young 2010). Analysis showed copper prills with variable, but locally high contents of nickel (rarely up to 2%), zinc (up to 0.9%), arsenic (up to 4.3%), silver (up to 0.44%) and lead (up to 14%). Similar data were produced from a "bowl-furnace", also of middle Iron Age date, found behind the rampart of the Llanymynech Hillfort (Musson & Northover 1989) and from Llwyn Bryn-dinas (Musson *et al.* 1991; Northover 1992; Table 7).

Ore fragments in the furnaces at Four Crosses showed a mineralogy of goethite (bearing cobalt, lead and silver), rosasite (a copper-zinc carbonate), azurite (copper carbonate) containing intergrowths of mimetite (lead chloro-arsenate) and malachite (a copper carbonate bearing considerable amounts of zinc, nickel and arsenic), in addition to minor relicts of chalcopyrite and possible anglesite.

The analyses of the copper prills at Four Crosses reflect the composition of the smelting products of very small ore volumes, whereas the bulk composition of any ingot produced at Four Crosses would have had a more modest content of these impurities. Nonetheless, Iron Age artefacts from Wales have shown elevated zinc contents, at levels well above those of the Ewart Park copper.

Although smelting of the ores exploited in the Iron Age in the Llanymynech area would have produced metal with higher impurity levels (particularly of zinc) than observed in the St Michael's Mount ingots, the general pattern of impurities shows great similarity. The ore from which the current ingots was smelted would merely have needed a lower proportion of rosasite and zincian malachite; such an ore might well occur in the same area, or even within the same mine. Thus Northover's (1982) statement that the Llanymynech area could not have produced 'S' metal, with its high arsenic and antimony contents, must be challenged (since many of the arguments presented by Williams 2014 are equally applicable to Llanymynech). Further work is needed to determine what composition of copper was produced in that area, but certainly strongly elevated arsenic and moderately elevated antimony could be obtained on occasion (Table 11).

The LI ratios of the Welsh borders ores also show a close relationship to those of the ingots (Figure 3). In particular, the galena and one of the malachite samples on the OXALID database from Llanymynech lies very close to sample SMM16 (i.e. IMP-LI 19) . Samples SMM2, SMM4 and SMM8 (with SMM2 and SMM4 being samples with high, c. 2%, lead contents) plot within the array of data from galena from Shropshire, just 20km S of Llanymynech, which broadly corresponds to the LI ratios of IMP-LI 20 and 21). Sample SMM6 also plots close to Shropshire galena analyses, even if slightly off the main array. The LI ratios of the samples with higher lead (SMM2, SMM4) are compatible (according to the data presented by Rohl & Needham 1998) with the Welsh borders or NE Wales, but not with the Mendips or Alderley Edge, two of the commonly suggested lead sources (Rohl & Needham 1998; Rohl 1996; OXALID database; Fletcher *et al.* 1993; Haggerty *et al.* 1996). However, at just 2%, the lead in these samples may be from smelting, not from subsequent alloying.

Only the LI ratios for SMM15 lie outside the range of values recorded for minerals from the Welsh borders. The LI ratios for this sample correspond to some ores from the Dalradian (both in Ireland and Scotland) and possibly with some materials from Brittany, according to the data presented by Rohl & Needham. The elemental data for SMM15 do not appear markedly different from those of other ingot fragments from the group, and the LI ratios of the specimens are not compatible with such an origin, so it may be that these LI data are anomalous for some reason.

Thus the Shropshire/Powys border has produced evidence for ores capable of producing metals with a wide range of both LI ratios and trace impurities – broadly matching the range observed within the Saint Michael's mount ingots. The area was already known to have been capable of producing lead with a suitable LI ratios to have been that used for alloying with bronze (e.g. in IMP-LI 21) – although other sources would have equal claim.

Proving conclusively that region was the source of the copper ingots would be very difficult – data with a wide spread are much more difficult to correlate and discriminate, than data with just a narrow range of variation. The compositions of the St Michael's Mount copper ingots are certainly compatible with an origin in that region. All have lead contents within the range of observed primary lead from smelting, and do not require lead alloying to have been undertaken.

The historical materials are slightly different to the 2009 hoard. Because they did not form part of the 2009 hoard, they have not been investigated as fully as other materials, and have no measurements of lead isotopes.

The piece from 2004 (SMM5; SMM-04-CA), a substantial (1.2kg) fragment from a very large copper ingot, is rich in cobalt (0.5%) and contains detectable bismuth (0.08%). The piece continues to thicken across its length, so if symmetrical, the original ingot would have been at least 250mm in diameter and at least 7.5kg in weight.

The small fragment of 'ingot' from the 1995 excavations (SMM1; SMM95-AA-c235) is a highly leaded bronze (19% Pb; 6% Sn). It has a thin, almost discoidal form, and may be a piece of casting waste rather than an ingot. This piece might well, like prilly mass SMM2, have been produced by alloying the copper from ingots of the composition of those in this collection.

### *3.c Summary*

Lead was a significant (>0.5%) impurity in none of the main suite of low-impurity ingots from the hoard, according to the pXRF data, although µXRF suggested a lead content only just below 0.5% in one sample of copper. ICP-MS suggested a level of 0.9% in one and just below 0.5% in two ingot fragments, but these may be the result of localised inhomogeneity affecting analyses of the small samples.

Lead was more elevated in the other four samples, reaching 19% in the possible casting waste (SMM1, from the 1995 excavations), almost 2% in the leaded bronze prilly mass from the hoard (SMM2) and from the leaded arsenical copper ingot fragment from the hoard (SMM4) and 0.5% in the isolated Co-, Bi- rich ingot found in 2004 (SMM5).

Arsenic is a persistent but very variable impurity, being below 0.02% in six of the hoard ingot fragments, just below 0.1% in one and over 0.1% in two others. The hoard also contained an arsenic-rich ingot fragment (SMM4; 1.1%). The bronze prilly lump from the hoard contains a modest 0.06% arsenic. The two historic metal finds possessed around 0.4% arsenic.
The amount of zinc in the materials was measured at approximately 0.1% in almost all the specimens and by multiple techniques. Since the identification of an elevated zinc content is an important piece of provenancing evidence, the concurrence of the data from the various independent techniques is crucial in increasing confidence in the robustness of the observation. Because of the problems with measuring zinc in copper alloys by X-Ray spectroscopy, the element is frequently omitted from those analysed in previous work (e.g. Table 6), but where determined, the zinc content was extremely low (only two samples on Table 6 have a content above 0.01%, and none was above 0. 05%.

Antimony was variable, but was at its highest levels in the two bronze samples, perhaps indicating with that the antimony was in part introduced with the tin.

Provenancing the copper ingots from the hoard is not straightforward. In terms of variability of their lead isotope ratios, the analysed specimens show similar variability to the total exhibited by those previously analysed from Britain. The elemental composition does not, however, resemble that of previously analysed ingots. Northover (1988) discussed the potential origin of the previously-known copper ingots and raised the possibility of multiple sources. He mentioned an origin in the West Country for some of the copper, citing the occurrence of hoards such as Stogursey in the SW. however, there appears to be no clear association of hoards bearing ingots with geographical regions, except that they are probably actually more common in the east of England. Interpretation is hampered by the east British origin of all the ingots (Table 6) for which elemental analyses are available.

Review of the available data has shown that the LI ratios of analysed ingots, both previously and in this study, show a broad correlation with the LI ratios of mineralisation on the England-Wales border. This phenomenon has been mentioned before, with Northover (1988) suggesting that the region might have supplied the lead used in alloying (particularly during the Wilburton Phase). For this to be relevant to the low-impurity materials, then, as postulated by Rohl & Needham (1998) lead from a British source (they favoured the Mendips) might have been used in alloying and subsequently removed. The pattern of lead distribution in the present material, however, suggests that the lead may be an accidental incorporation at the smelting stage. The observed lead contents are all (apart from the highly leaded bronze sample SMM1 from the 2004 excavations) within the range observed in freshly-melted copper from the Llanymynech area (Table 8).

Of the previously-analysed ingots, only three show moderately elevated lead (one ingot and a lump from Runnymede Bridge and an ingot fragment from Stoke Hoo) and one has high lead (8.9%; Beeston Regis 1, #28, Lawson undated). Of these, only one (the ingot fragment from Stoke Hoo; Rohl & Needham 1998 #383) has associated lead isotope data, and this has a high $^{208}Pb/^{206}Pb$ ratio (see above)., so does not support a Mendip origin for the lead.

The lead isotope ratios, the high (but variable) lead content and the moderately elevated nickel, zinc and silver contents are all features that suggest a link to the Llanymynech area. Unlike the interpretation of Northover (1982) for the preceding Wilburton Phase, where lead from the region may have been added to copper from other sources, it seems likely that it was a lead-bearing copper ore that was smelted. This ore would appear to have been less zinc-rich than those subsequently smelted in the area in the Iron Age.

The most lead-rich material (the casting waste from the 1995 excavations; SMM1) is likely to have been deliberately alloyed with lead, but the other samples, even those compositionally defined as 'leaded', are likely to be smelting products, rather than having had a deliberate addition of lead.

SMM4, the leaded arsenical copper piece, shows elevated arsenic, lead and silver. The trace element suite otherwise resembles that of the other ingot fragments

If the tentative identification of the Welsh borders as the source of the ingots is correct, then it has considerable implication for the nature of metal supply in the late Bronze Age. The issue of sourcing is, however, fraught with ambiguity due to the great similarity of LI ratios for the various potential sources, both of copper and of lead, and to the potential generation of low-impurity copper from multiple sources. Much more work is required demonstrate the

attribution to that area, in terms of refining the analyses of the ingots, in improving understanding of the potential resources and in locating evidence on the ground for Late Bronze Age exploitation.

In addition to the copper ingots, the hoard contained a single piece of prilly bronze. This piece (SMM2) has a broadly similar suite of impurities to the copper ingots, albeit relatively rich in antimony and poor in arsenic compared with the average.

The previous find of leaded bronze (SMM1), shows some similarity to SMM2, sharing with it the elevated antimony level (0.19%), but having an elevated arsenic level too (0.48%), when recalculated to exclude the lead and tin.

The large historic ingot find (SMM5) is statistically different from the average copper ingot for cobalt, arsenic, lead and bismuth. The high levels of cobalt and bismuth are particularly prominent.

# 4. Conclusion

Obtaining good quality bulk chemical composition of the ingots proved an unexpectedly tricky task. The scale of the inhomogeneity was unanticipated. There is no indication that previous authors sought to determine inhomogeneity on such a coarse scale in ingots and there are no method statements in the published literature that sampling practice has differed between standard artefacts and ingots.

Within this study, the elemental analysis of drilled samples proved inadequate to characterise the bulk ingot composition. Previously-published work has mostly employed area or grid analyses of the flattened and mounted drill turnings on a microprobe, but that technique should be even less effective than dissolution and analysis by ICP-MS. There is good reason, therefore, to be distrustful of all previous elemental analyses of ingots, particularly for those elements (iron, cobalt, zinc and nickel) demonstrated to be strongly zoned within the ingots.

It is likely that not only does growth of the very large dendrites allow for primary zonation and differentiation within the solidifying ingot, but the coarse microstructure allows for alteration and weathering to penetrate the ingot along compositionally-, and texturally-, defined zones.

ICP-MS would have been a useful technique to have employed, had the initial samples been larger. If drilled samples were taken across the grain of the dendrites, then it is possible that the turnings from drill holes 10mm deep might have provided a more representative sample. Drill samplings should never be taken parallel to the dendrites (i.e. from either the upper or lower surface of the ingot). Repeating the ICP-MS investigation with larger sample sizes was not possible within the financial constraints of the project.

Analysis of bulk chemical composition in this project rests on pXRF and µXRF. The pXRF data are derived from a beam which impacts the sample over an elliptical area of approximately 10mm by 8mm. This is sufficiently large that it should provide a good bulk estimate (on present understanding of the nature of the inhomogeneity in the ingots). The analysis of cut surfaces provided a good planar target that can be positioned close to the instrument window, improving the reliability of the data recorded. The biggest problem with the pXRF is the calibration of the spectrum. The calibration employed for the data presented here is a simple linear calibration employing data from the same instrument, operated under the same conditions, under carefully controlled conditions, using samples of certified composition (Nicholas & Manti 2014). Visual inspection of the calibration data shows a variable confidence in this calibration between different elements, although much more work would be require to derive numerical estimates of variance.

The µXRF is a new tool and as such must be regarded as somewhat experimental. It was calibrated using a mounted set of certified alloys held by the Conservation Section of the Cardiff University Archaeology Department. One advantage of the µXRF was the generation of elemental mapping alongside the estimate of bulk composition. The requirement for analysis of a very large area meant that special editing of the data was required to remove all areas of epoxy resin from consideration in the data processing. There are differences between the µXRF and pXRF analyses of the same sample, but it is unclear if this is analytical error or an indication of sample inhomogeneity. Re-analysis by pXRF of the polished mounts, rather than the cut blocks, would be desirable to investigate this.

In summary, the bulk elemental analysis of the ingots was a significant exercise in attempting to produce an estimate of a bulk composition from materials with coarse inhomogeneity. The difficulties experienced here illuminate the care that must be taken in using and interpreting published data. Although acceptable estimates have been produced in this study, they could, no doubt, be improved by both further work on the samples and by further improvement of the calibration techniques.

Notwithstanding the analytical challenges, the assemblage includes a range of composition that can mostly be interpreted as the ingots being of freshly-smelted metal.

For the majority of ingot fragments from the 2009 hoard (nine analysed in detail, extrapolated to twenty two pieces on the basis of the non-destructive analysis undertaken during the assessment), the impurities of the copper are low, but variable and they have a moderately elevated zinc content. An origin for these in the Welsh borders area is suggested, on the basis of the variability of the impurities, the zinc content and the LI ratios of SMM16 and possibly of SMM6.

Since the zinc content is central to this interpretation, the potential error in determining zinc from X-Ray spectroscopic techniques (because of the overlap with copper) might create a degree of uncertainty. The elemental data derived by ICP-MS provide, however, entirely independent evidence to support zinc contents of approximately 0.13%. This figure is an order of magnitude higher than that previously reported from Ewart Park Phase metalwork. Zinc will be lost from copper alloy during each remelting, so what is crucial here is that the zinc contents are elevated with respect to the previous ingot analyses (Table 9), rather than just the artefact analyses (e.g. as compiled by Rohl & Needham 1998).

One ingot fragment (SMM4) has strongly elevated arsenic and lead, features which would be compatible with an origin in the same area. The LI ratios fall in the field of measured examples of galena from nearby Shropshire. One of the main group of ingot fragments (SMM6) showed slightly elevated traces and may have

been somewhat intermediate with composition of SMM4.

The historical copper ingot fragment found in 2004 (SMM5) has moderately elevated arsenic and lead, high cobalt (apparently higher than in any metal in the Rohl & Needham 1998 database) and detectable bismuth. This is a composition that is not precisely matched by previous analyses. The cobalt value is so high as to be suspicious. In the assessment analyses the superficial cobalt levels were higher in SMM9, a sample with low bulk cobalt on analysis of the cut section. If the cobalt value is ignored, the other impurities contrast much less strongly with those of the main group of ingots from the 2009 hoard.

The historical find of casting waste (from 1995; SMM1) was a very heavily leaded metal (the analysis gave 19% lead and 6.1% tin, but the metal was highly variable). On a lead- and tin- free basis (Table 7) the metal shows high nickel (0.09%), arsenic (0.48%) antimony (0.19%) and silver (0.13%). This composition includes a higher level of impurities than most of the copper ingot fragments, but is moderately similar to piece SMM6 (except for an elevated arsenic content).

The leaded bronze lump from the 2009 hoard is very similar its tin- and lead-free composition to the casting waste (SMM1), except for a lower arsenic content. Thus it too, is similar to ingot fragment SMM6. Overall it seems likely that all pieces except for the 2004 ingot (SMM5) and the leaded arsenical copper fragment (SMM4) share sufficient characteristics to reasonably certainly suggest a common copper source, notwithstanding the closest similarity of the bronzes to the copper ingot fragment SMM6 which is possibly a slight outlier to the main group. It is even possible that the ingot fragment SMM4 derives from the same geological area, given the potential variability of the ore. Even ingot fragment SMM5 shares the moderately elevated zinc content with the main group. It is possible therefore that all the materials derive from this single area.

This conclusion illustrates some of the potential problems with provenancing copper in small ingots that may be far less thoroughly mixed than ingots formed from larger smelting operations – and which may, therefore, exhibit more of the inhomogeneity present in the geological source materials.

## 5. References


FLETCHER, C.J.N., SWAINBANK, G. & COLMAN, T.B. 1993. Metallogenic evolution in Wales: constraints from lead isotope modelling. *Journal of the Geological Society*, **150**, 77-82.

HAGGERTY, R., BUDD, P., ROHL, B. & GALE, N.H> 1996. Pb-isotope evidence for the role of Mesozoic basins in the genesis of Mississippi Valley-type mineralization in Somerset, UK. *Journal of the Geological Society*, **153**, 673-676.

HERRING, P. 2000. *St Michael's Mount Archaeological Works, 1995-8*. Truro: Cornwall Archaeological Unit:
- *Fragment of plano-convex copper ingot*, P. Herring 46-47 with Figs 17,18 on p66
- *Appendix 5 Analysis of a small copper ingot*, 196-198

IXER R.A. 2001, An assessment of the Great Orme Mine, Llandudno, North Wales, *Proceedings of the Yorkshire Geological Society,* **53**, 213-219.

IXER R A & BUDD P 1998. The mineralogy of Bronze Age copper ores from the British Isles: implications for the composition of early metalwork. *Oxford Journal of Archaeology,* **17**, 15-41.

IXER, R.A. & DAVIES, J. 1996. Mineralisation at the Great Orme copper mines, Llandudno, North Wales, *UK Journal of Mines and Minerals,* **17**, 7-14.

LAWSON, A.J. undated, Three Late Bronze Age Hoards from North East Norfolk (with a contribution on metal composition by Paul Craddock, Duncan Hook and Caitlin Buck). http://hbsmrgateway2.esdm.co.uk/norfolk/DataFiles/Docs/AssocDoc38554.pdf (Accessed 20/12/15)

MUSSON, C.R., BRITNELL, W.J., NORTHOVER, J.P. & SALTER, C.J. 1992. Excavations and metal-working at Llwyn Bryn-dinas Hillfort, Llangedwyn, Clwyd. *Proceedings of the Prehistoric Society*, **58**, 265-283.

MUSSON, C.R. & NORTHOVER, J.P. 1989. Llanymynech Hillfort, Powys and Shropshire: observations on construction work, 1981. *Montgomeryshire Collections*, **77**, 15-26.

NICHOLAS, M & MANTI, P. 2014. Testing the applicability of hand held portable XRF to the characterisation of archaeological copper alloys. *In* J. Bridgland (ed) *ICOM-CC 17th Triennial Conference Preprints, Melbourne, 15–19 September 2014.* Paris: International Council of Museums.

NORTHOVER, J P 1980. The analysis of Welsh Bronze Age metalwork, in H Savory (ed), *Guide catalogue of the Bronze Age collections* (Cardiff), 229-243.

NORTHOVER, J.P. 1982. The metallurgy of the Wilburton hoards. *Oxford Journal of Archaeology*, **1**, 69–109,

NORTHOVER, J.P. 1988. The analysis and metallurgy of British Bronze Age swords. *In* I. Colquhoun and C. Burgess, *The swords of Britain*. Prähistorische Bronzefunde IV, 5, 130–148.München.

NORTHOVER, J.P. 1991. Microfiche Appendix 13.4: Further comments on the composition of the Breiddin bronzes. *In:* C.R. Musson, *The Breiddin Hillfort: a later Prehistoric Settlement in the Welsh Marches*, London, Council for British Archaeology.

ROHL, B. 1996. Lead isotope data from the isotrace laboratory, Oxford: *Archaeometry* database 2, galena from Britain and Ireland. *Archaeometry*, **38**, 1, 165-180.

ROHL, B and NEEDHAM, S 1998. *The Circulation of Metal in the British Bronze Age: The Application of Lead Isotope Analysis*, London, British Museum Occasional Paper 102.

WILLIAMS, A. 2014. Linking Bronze Age copper smelting slags from Pentrwyn on the Great Orme to ore and metal. *Historical Metallurgy 47(1), 93–110*

YOUNG, T.P. 2010. Archaeometallurgical residues from Domgay Lane, Four Crosses, Powys. *GeoArch Report 2010/23*, 51 pp.

YOUNG, T.P. 2014. Assessment of ingots from Saint Michaels Mount, Cornwall. *GeoArch Report 2014-33.* 9pp.

## Figure Captions

*Figure 1. LI ratios of samples from the 2009 hoard from St Michael's Mount, displayed against the field 'EWLIO' (England and Wales Lead Isotope Outline, Rohl & Needham 1998, 19).*

*Figure 2. LI ratios of samples from the 2009 hoard from St Michael's Mount, plotted with EWLIO and samples from Ewart Park Phase copper samples (after Rohl & Needham 1998). The dashed areas indicate the approximate distribution of the groups IMP-LI19, 20 and 21 (sensu Rohl & Needham 1998).*

*Figure 3. LI ratios of samples from the 2009 hoard from St Michael's Mount, plotted with EWLIO and samples of minerals from West Shropshire and Llanymynech (after Rohl & Needham 1998; Rohl 1996; OXALID database).*

*Figure 4. LI ratios of samples from the 2009 hoard from St Michael's Mount, displayed against the field 'EWLIO' (England and Wales Lead Isotope Outline, Rohl & Needham 1998, 19).The radius of the circles is proportional to the lead content, with the larger two circles indicating 2.0%.*

*Plate 1. Ingot fragments, showing the coarse fibrous nature of the fractured dendritic metal.*

*Plate 2. Element maps derived from µXRF mapping of sample SMM6. Each pixel is 50µm (200 x 189 resolution). Overall area 10mm wide.*

*Table 1: net peak areas for the pXRF analyses during non-destructive assessment phase analysis.*

| | Element | Cr | Mn | Fe | Co | Ni | Cu | Zn | As | Rh | Rh | Ag | Ag | Cd | Cd | Sn | Sn | Sb | Sb | Pb | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Line | K12 | K12 | K12 | K12 | K12 | K12 | K12 | K12 | K12 | L1 | K12 | L1 | K12 | L1 | K12 | L1 | K12 | L1 | L1 | M1 |
| **1. Bronze** | | | | | | | | | | | | | | | | | | | | | |
| smm95-sewer-235-aa-1 | clean | 449 | 718 | 148292 | 4926 | 220 | 311711 | 2365 | 94207 | 22369 | 111 | 1376 | 432 | 2135 | 0 | 92578 | 929 | 0 | 1210 | 1236088 | 635 |
| smm95-sewer-235-aa-2 | clean | 242 | 513 | 65092 | 1692 | 352 | 251013 | 867 | 129709 | 21652 | 120 | 1244 | 447 | 5370 | 0 | 77534 | 1104 | 164 | 816 | 2047938 | 1807 |
| smm95-sewer-235-aa-3 | clean | 417 | 145 | 22020 | 1187 | 2081 | 2021367 | 6294 | 32345 | 14786 | 193 | 1334 | 470 | 758 | 0 | 90076 | 2052 | 468 | 1149 | 629535 | 994 |
| smm95-sewer-235-aa-4 | clean | 262 | 210 | 951 | 8011 | 269 | 409310 | 1244 | 6687 | 31665 | 149 | 7990 | 570 | 381 | 0 | 19968 | 285 | 122 | 338 | 123124 | 285 |
| smm95-sewer-235-aa-5 | clean | 422 | 112 | 6872 | 7507 | 284 | 61068 | 340 | 14702 | 31913 | 174 | 7597 | 500 | 740 | 0 | 87382 | 1835 | 837 | 1016 | 248700 | 552 |
| item23 pt1 | batch 1 | 165 | 111 | 10607 | 829 | 1362 | 3046077 | 9790 | 13555 | 16543 | 173 | 2417 | 599 | 411 | 0 | 205602 | 1788 | 1651 | 652 | 214379 | 407 |
| item23 pt2 | batch 1 | 65 | 154 | 21223 | 1420 | 309 | 2209134 | 8455 | 24673 | 16420 | 179 | 1727 | 715 | 590 | 0 | 134493 | 72 | 1195 | 752 | 452111 | 522 |
| item23 pt3 | batch 1 | 328 | 315 | 16155 | 724 | 426 | 1270339 | 5149 | 20857 | 12589 | 151 | 1505 | 464 | 535 | 0 | 82511 | 766 | 644 | 583 | 349224 | 463 |
| **2. Cu with high Ag, As, Sb** | | | | | | | | | | | | | | | | | | | | | |
| smm09-007-au-1 | batch 2 | 292 | 149 | 15407 | 929 | 1 | 5012716 | 16584 | 380900 | 14819 | 343 | 11211 | 1005 | 142 | 1 | 1849 | 0 | 11263 | 754 | 216158 | 192 |
| smm09-007-au-2 | batch 2 | 324 | 805 | 21864 | 1502 | 1 | 4970432 | 17817 | 255850 | 14723 | 477 | 12051 | 906 | 174 | 0 | 2051 | 0 | 12217 | 947 | 178086 | 286 |
| item24 pt1 | batch 1 | 340 | 179 | 20062 | 1356 | 304 | 5313589 | 20899 | 5042 | 13121 | 384 | 6137 | 982 | 49 | 1 | 521 | 0 | 6604 | 972 | 5888 | 269 |
| item24 pt2 | batch 1 | 171 | 623 | 37825 | 2351 | 1 | 4323446 | 18728 | 14061 | 13388 | 485 | 3976 | 800 | 174 | 0 | 516 | 0 | 3703 | 1086 | 38925 | 243 |
| item24 pt3 | batch 1 | 39 | 504 | 102417 | 6553 | 469 | 5024869 | 22471 | 17064 | 14739 | 458 | 5275 | 860 | 135 | 0 | 739 | 0 | 6248 | 914 | 60271 | 281 |
| **3. Cu with high Fe, Co, As, Ag, Sb, Pb** | | | | | | | | | | | | | | | | | | | | | |
| smm04-ca-footpath-1 | batch 2 | 140 | 698 | 460248 | 57085 | 2946 | 1955182 | 11090 | 456111 | 16960 | 200 | 8577 | 843 | 140 | 48 | 1432 | 0 | 2661 | 1192 | 229450 | 252 |
| smm04-ca-footpath-2 | batch 2 | 230 | 111 | 242235 | 11950 | 1 | 2883953 | 11589 | 393954 | 15423 | 291 | 12639 | 639 | 125 | 0 | 1370 | 0 | 2053 | 694 | 280696 | 269 |
| item39 pt1 | batch 1 | 225 | 239 | 367543 | 13057 | 68 | 2264934 | 10216 | 321964 | 17777 | 367 | 45063 | 578 | 31 | 1 | 2613 | 0 | 52431 | 1851 | 78751 | 453 |
| item39 pt2 | batch 1 | 159 | 78 | 191013 | 7591 | 1 | 4414684 | 16922 | 39373 | 15468 | 396 | 3668 | 669 | 63 | 1 | 625 | 0 | 6220 | 943 | 69382 | 311 |
| smm-007-bi-39-cx958 | batch 2 | 1 | 356 | 186133 | 7210 | 1 | 5135214 | 19059 | 35600 | 15351 | 426 | 3535 | 908 | 32 | 0 | 560 | 0 | 6474 | 1012 | 77269 | 169 |
| **4. Cu with high Fe, Co** | | | | | | | | | | | | | | | | | | | | | |
| item42 pt1 | batch 1 | 84 | 323 | 393156 | 72796 | 1825 | 3301592 | 11789 | 32839 | 13776 | 386 | 2738 | 692 | 152 | 0 | 1077 | 0 | 678 | 748 | 68787 | 230 |
| item42 pt2 | batch 1 | 108 | 111 | 369904 | 73590 | 3043 | 4114193 | 19493 | 118338 | 13659 | 387 | 3948 | 819 | 172 | 0 | 1498 | 0 | 1249 | 799 | 47230 | 238 |
| item44 pt1 | batch 1 | 219 | 415 | 45853 | 2475 | 1 | 4333712 | 17035 | 19619 | 14711 | 554 | 1471 | 785 | 228 | 0 | 2195 | 0 | 38 | 824 | 31551 | 306 |
| item44 pt2 | batch 1 | 410 | 700 | 356569 | 13524 | 1 | 3532211 | 21364 | 21624 | 14822 | 361 | 1183 | 891 | 206 | 0 | 713 | 0 | 285 | 896 | 25593 | 177 |
| smm09-007-130-2 | batch 2 | 183 | 860 | 137731 | 8288 | 1 | 4103275 | 20188 | 56265 | 15413 | 299 | 5461 | 789 | 103 | 98 | 821 | 0 | 458 | 913 | 29423 | 228 |

| | Element | Cr | Mn | Fe | Co | Ni | Cu | Zn | As | Rh | Rh | Ag | Ag | Cd | Cd | Sn | Sn | Sb | Sb | Pb | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Line | K12 | K12 | K12 | K12 | K12 | K12 | K12 | K12 | K12 | L1 | K12 | L1 | K12 | L1 | K12 | L1 | K12 | L1 | L1 | M1 |
| smm09-007-aw-1 | batch 2 | 519 | 1415 | 333862 | 12538 | 337 | 3837292 | 17888 | 6060 | 13158 | 356 | 1771 | 847 | 135 | 0 | 801 | 0 | 150 | 768 | 10322 | 168 |
| smm09-007-aw-2 | batch 2 | 153 | 1048 | 50706 | 3259 | 48 | 5122094 | 28507 | 10367 | 13951 | 363 | 1224 | 1017 | 166 | 0 | 688 | 0 | 202 | 1031 | 32227 | 222 |
| item34 pt1 | batch 1 | 267 | 536 | 100972 | 30631 | 785 | 4414476 | 21028 | 28958 | 12898 | 413 | 2216 | 846 | 169 | 0 | 666 | 0 | 621 | 806 | 16900 | 200 |
| item34 pt2 | batch 1 | 267 | 536 | 100972 | 30631 | 785 | 4414476 | 21028 | 28958 | 12898 | 413 | 2216 | 846 | 169 | 0 | 666 | 0 | 621 | 806 | 16900 | 200 |
| item34 pt3 | batch 1 | 276 | 161 | 276036 | 31141 | 658 | 2815456 | 14152 | 151420 | 12792 | 281 | 2474 | 579 | 169 | 0 | 608 | 0 | 1417 | 729 | 89589 | 162 |
| item35 pt1 | batch 1 | 221 | 1466 | 320550 | 19670 | 583 | 3674545 | 19184 | 16510 | 15218 | 290 | 4326 | 744 | 302 | 0 | 754 | 0 | 185 | 834 | 13537 | 254 |
| item35 pt2 | batch 1 | 186 | 166 | 53814 | 2799 | 1 | 3319930 | 14463 | 12578 | 13056 | 386 | 4115 | 686 | 100 | 0 | 1223 | 0 | 148 | 776 | 10369 | 160 |
| item36 pt1 | batch 1 | 114 | 772 | 106823 | 38601 | 1262 | 4259849 | 21142 | 27035 | 14793 | 291 | 3768 | 928 | 205 | 0 | 1091 | 0 | 784 | 977 | 162791 | 171 |
| item36 pt2 | batch 1 | 357 | 451 | 209380 | 37943 | 1129 | 2850324 | 13649 | 54413 | 15498 | 236 | 4976 | 537 | 277 | 0 | 1691 | 0 | 484 | 625 | 174900 | 78 |
| **5. Cu with low traces** | | | | | | | | | | | | | | | | | | | | | |
| smm09-007-av-1 | batch 2 | 16 | 899 | 19681 | 1322 | 690 | 6521237 | 20396 | 6447 | 14136 | 398 | 2863 | 1027 | 191 | 0 | 607 | 43 | 341 | 573 | 20627 | 77 |
| smm09-007-av-2 | batch 2 | 128 | 511 | 34054 | 2133 | 194 | 5527298 | 21338 | 18841 | 14745 | 370 | 2017 | 788 | 228 | 0 | 655 | 27 | 243 | 1508 | 122002 | 213 |
| smm09-007-ax-1 | batch 2 | 380 | 599 | 22150 | 2145 | 422 | 5734240 | 22587 | 5741 | 12649 | 397 | 3918 | 1163 | 50 | 0 | 428 | -1 | 358 | 562 | 8627 | 257 |
| smm09-007-ax-2 | batch 2 | 243 | 36 | 28681 | 2255 | 1 | 4985064 | 21651 | 23415 | 12980 | 418 | 6457 | 970 | 307 | 0 | 415 | 0 | 438 | 691 | 27661 | 175 |
| smm09-007-bf-1 | batch 2 | 244 | 305 | 12793 | 1066 | 9 | 4975681 | 24243 | 16942 | 12170 | 355 | 807 | 909 | 208 | 0 | 1080 | 0 | 101 | 364 | 17527 | 248 |
| smm09-007-bf-2 | batch 2 | 279 | 275 | 12687 | 945 | 1 | 6090656 | 18148 | 25033 | 13568 | 520 | 1260 | 1294 | 247 | 1 | 2221 | 0 | 99 | 539 | 28985 | 232 |
| smm09-007-bj-1 | batch 2 | 130 | 425 | 31687 | 1726 | 1865 | 5959421 | 23114 | 26818 | 15184 | 506 | 1191 | 1044 | 195 | 0 | 549 | 0 | 179 | 721 | 57122 | 181 |
| smm09-007-bj-2 | batch 2 | 247 | 1 | 10415 | 1264 | 14283 | 5578220 | 15567 | 72979 | 15296 | 1012 | 1430 | 699 | 159 | 1 | 684 | 0 | 99 | 403 | 17233 | 308 |
| smm09-007-bk-1 | batch 2 | 66 | 366 | 30538 | 1886 | 568 | 5783392 | 26514 | 5865 | 13256 | 467 | 1107 | 984 | 233 | 1 | 487 | 0 | 75 | 654 | 11719 | 387 |
| smm09-007-bk-2 | batch 2 | 186 | 834 | 73582 | 4510 | 325 | 4887945 | 24272 | 10964 | 14253 | 313 | 1437 | 951 | 145 | 0 | 556 | 0 | 89 | 752 | 32089 | 129 |
| smm09-007-bm-1 | batch 2 | 76 | 262 | 64281 | 2964 | 1 | 5327761 | 22058 | 11204 | 13538 | 484 | 2608 | 926 | 188 | 0 | 467 | 0 | 51 | 773 | 20523 | 353 |
| smm09-007-bm-2 | batch 2 | 102 | 310 | 37539 | 2039 | 246 | 5113442 | 26955 | 8752 | 12697 | 530 | 2805 | 774 | 162 | 1 | 545 | 0 | 52 | 473 | 7078 | 371 |
| smm09-007-bo-1 | batch 2 | 108 | 484 | 79110 | 4557 | 1 | 5228446 | 28574 | 13852 | 14427 | 453 | 1625 | 892 | 356 | 0 | 2092 | 4 | 149 | 669 | 5298 | 115 |
| smm09-007-bo-2 | batch 2 | 416 | 1134 | 31895 | 2235 | 1 | 6285955 | 28288 | 6284 | 13696 | 449 | 1567 | 854 | 285 | 0 | 1402 | 0 | 184 | 687 | 3801 | 228 |

| | Element | Cr | Mn | Fe | Co | Ni | Cu | Zn | As | Rh | Rh | Ag | Ag | Cd | Cd | Sn | Sn | Sb | Sb | Pb | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Line | K12 | K12 | K12 | K12 | K12 | K12 | K12 | K12 | K12 | L1 | K12 | L1 | K12 | L1 | K12 | L1 | K12 | L1 | L1 | M1 |
| smm09-007-bp-1 | batch 2 | 227 | 461 | 33017 | 2362 | 412 | 5765953 | 19576 | 6860 | 13404 | 522 | 3342 | 882 | 110 | 0 | 597 | 0 | 364 | 890 | 7651 | 68 |
| smm09-007-bp-2 | batch 2 | 172 | 422 | 155731 | 6174 | 461 | 4883860 | 11344 | 17707 | 15463 | 546 | 10306 | 620 | 394 | 0 | 1093 | 0 | 364 | 884 | 27425 | 240 |
| item28 pt1 | batch 1 | 1 | 484 | 26744 | 1550 | 1 | 5070885 | 21534 | 17002 | 13136 | 322 | 1438 | 918 | 80 | 0 | 2045 | 24 | 504 | 751 | 17998 | 215 |
| item28 pt2 | batch 1 | 80 | 413 | 105260 | 4556 | 1 | 2751619 | 14213 | 116256 | 13603 | 265 | 4547 | 735 | 292 | 0 | 20673 | 328 | 4755 | 1089 | 83112 | 76 |
| item29 pt1 | batch 1 | 395 | 766 | 45369 | 3399 | 1 | 4748284 | 23761 | 23285 | 13807 | 401 | 1989 | 938 | 83 | 0 | 1897 | 5 | 234 | 873 | 19840 | 55 |
| item29 pt2 | batch 1 | 413 | 627 | 36237 | 2402 | 1 | 4285620 | 22589 | 15820 | 13988 | 374 | 1507 | 872 | 326 | 1 | 1360 | 17 | 130 | 559 | 16248 | 213 |
| item31 pt1 | batch 1 | 121 | 524 | 26233 | 1923 | 428 | 5724276 | 22351 | 5580 | 13768 | 455 | 2004 | 975 | 189 | 0 | 554 | 0 | 197 | 750 | 12691 | 225 |
| item31 pt2 | batch 1 | 226 | 313 | 43039 | 2678 | 1 | 3397542 | 13982 | 13809 | 12636 | 422 | 5943 | 776 | 142 | 1 | 813 | -1 | 385 | 616 | 46916 | 129 |
| item32 pt1 | batch 1 | 203 | 920 | 50961 | 4563 | 1 | 5616223 | 20450 | 7012 | 14434 | 591 | 2137 | 738 | 230 | 0 | 794 | 0 | 140 | 891 | 14890 | 263 |
| item32 pt2 | batch 1 | 266 | 204 | 21476 | 2346 | 1 | 4716564 | 15716 | 11669 | 13344 | 434 | 2367 | 783 | 213 | 1 | 541 | -1 | 34 | 628 | 11536 | 149 |
| item32 pt3 | batch 1 | 212 | 1 | 16630 | 1198 | 1 | 5823020 | 19198 | 3637 | 14059 | 583 | 1596 | 940 | 327 | 0 | 624 | -1 | 19 | 717 | 3346 | 276 |
| item37 pt1 | batch 1 | 1 | 167 | 18596 | 1491 | 1 | 4223023 | 14719 | 14268 | 13244 | 431 | 1874 | 786 | 200 | 0 | 451 | 0 | 232 | 707 | 9057 | 116 |
| item37 pt2 | batch 1 | 464 | 309 | 40457 | 2409 | 1 | 4234272 | 15816 | 20997 | 13654 | 355 | 1720 | 798 | 73 | 0 | 527 | 0 | 167 | 794 | 8061 | 109 |
| item38 pt1 | batch 1 | 588 | 451 | 42808 | 2804 | 1801 | 5193872 | 25120 | 13145 | 14518 | 392 | 2306 | 813 | 154 | 1 | 472 | 0 | 474 | 811 | 32114 | 172 |
| item38 pt2 | batch 1 | 457 | 1156 | 49359 | 2599 | 1393 | 4782839 | 18583 | 20917 | 14540 | 326 | 2179 | 948 | 198 | 0 | 702 | 0 | 275 | 989 | 30947 | 165 |

*Table 2: Calibrated pXRF results in elemental wt% for non-destructive assessment phase analysis. These analyses are dominated by corrosion products.*

| | Element | Mn | Fe | Ni | Cu | Zn | As | Pb | Sn | Sb | Ag |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1. Bronze** | | | | | | | | | | | |
| smm95-sewer-235-aa-1 | clean | 0.04 | 3.81 | 0.01 | 7.94 | 0.04 | 2.77 | 76.12 | 9.27 | 0.00 | |
| smm95-sewer-235-aa-2 | clean | 0.02 | 1.15 | 0.01 | 4.39 | 0.01 | 2.61 | 86.48 | 5.33 | 0.02 | |
| smm95-sewer-235-aa-3 | clean | 0.01 | 0.56 | 0.05 | 50.98 | 0.11 | 0.94 | 38.36 | 8.93 | 0.06 | |
| smm95-sewer-235-aa-4 | clean | 0.05 | 0.12 | 0.03 | 51.41 | 0.11 | 0.97 | 37.37 | 9.86 | 0.08 | |
| smm95-sewer-235-aa-5 | clean | 0.02 | 0.67 | 0.03 | 5.90 | 0.02 | 1.64 | 58.08 | 33.20 | 0.44 | |
| item23 pt1 | batch 1 | 0.00 | 0.24 | 0.03 | 68.98 | 0.16 | 0.35 | 11.73 | 18.30 | 0.20 | |
| item23 pt2 | batch 1 | 0.01 | 0.55 | 0.01 | 56.75 | 0.15 | 0.73 | 28.06 | 13.58 | 0.17 | |
| item23 pt3 | batch 1 | 0.02 | 0.65 | 0.02 | 51.08 | 0.14 | 0.97 | 33.93 | 13.04 | 0.14 | |
| **2. Cu with high Ag, As, Sb** | | | | | | | | | | | |
| smm09-007-au-1 | batch 2 | 0.00 | 0.25 | 0.00 | 82.24 | 0.19 | 7.20 | 8.57 | 0.12 | 1.00 | 0.42 |
| smm09-007-au-2 | batch 2 | 0.03 | 0.38 | 0.00 | 85.21 | 0.21 | 5.05 | 7.38 | 0.14 | 1.14 | 0.47 |
| item24 pt1 | batch 1 | 0.01 | 0.37 | 0.01 | 98.02 | 0.27 | 0.11 | 0.26 | 0.04 | 0.66 | 0.26 |
| item24 pt2 | batch 1 | 0.03 | 0.84 | 0.00 | 95.71 | 0.29 | 0.36 | 2.08 | 0.04 | 0.44 | 0.20 |
| item24 pt3 | batch 1 | 0.02 | 1.93 | 0.01 | 93.76 | 0.29 | 0.37 | 2.72 | 0.05 | 0.63 | 0.22 |
| **3. Cu with high Fe, Co, As, Ag, Sb, Pb** | | | | | | | | | | | |
| smm04-ca-footpath-1 | batch 2 | 0.04 | 13.07 | 0.08 | 55.06 | 0.22 | 14.80 | 15.61 | 0.16 | 0.41 | 0.55 |
| smm04-ca-footpath-2 | batch 2 | 0.00 | 5.66 | 0.00 | 66.85 | 0.19 | 10.52 | 15.72 | 0.12 | 0.26 | 0.67 |
| item39 pt1 | batch 1 | 0.01 | 10.29 | 0.00 | 62.89 | 0.20 | 10.30 | 5.28 | 0.29 | 7.90 | 2.85 |
| item39 pt2 | batch 1 | 0.00 | 3.95 | 0.00 | 90.52 | 0.24 | 0.93 | 3.44 | 0.05 | 0.69 | 0.17 |
| smm-007-bi-39-cx958 | batch 2 | 0.01 | 3.34 | 0.00 | 91.54 | 0.24 | 0.73 | 3.33 | 0.04 | 0.63 | 0.14 |
| **4. Cu with high Fe, Co** | | | | | | | | | | | |
| item42 pt1 | batch 1 | 0.02 | 10.09 | 0.05 | 84.08 | 0.21 | 0.96 | 4.23 | 0.11 | 0.09 | 0.16 |
| item42 pt2 | batch 1 | 0.00 | 7.81 | 0.06 | 86.14 | 0.29 | 2.86 | 2.39 | 0.12 | 0.14 | 0.19 |

| | Element Line | Mn | Fe | Ni | Cu | Zn | As | Pb | Sn | Sb | Ag |
|---|---|---|---|---|---|---|---|---|---|---|---|
| item44 pt1 | batch 1 | 0.02 | 1.03 | 0.00 | 96.23 | 0.26 | 0.50 | 1.69 | 0.19 | 0.00 | 0.07 |
| item44 pt2 | batch 1 | 0.03 | 8.98 | 0.00 | 88.27 | 0.37 | 0.62 | 1.55 | 0.07 | 0.04 | 0.07 |
| smm09-007-130-2 | batch 2 | 0.04 | 3.15 | 0.00 | 93.00 | 0.32 | 1.47 | 1.61 | 0.07 | 0.06 | 0.28 |
| smm09-007-aw-1 | batch 2 | 0.06 | 7.96 | 0.01 | 90.73 | 0.30 | 0.17 | 0.59 | 0.07 | 0.02 | 0.10 |
| smm09-007-aw-2 | batch 2 | 0.04 | 0.97 | 0.00 | 96.80 | 0.38 | 0.23 | 1.47 | 0.05 | 0.02 | 0.05 |
| item34 pt1 | batch 1 | 0.02 | 2.20 | 0.02 | 95.59 | 0.32 | 0.72 | 0.88 | 0.06 | 0.07 | 0.11 |
| item34 pt2 | batch 1 | 0.02 | 2.20 | 0.02 | 95.59 | 0.32 | 0.72 | 0.88 | 0.06 | 0.07 | 0.11 |
| item34 pt3 | batch 1 | 0.01 | 7.92 | 0.02 | 80.18 | 0.28 | 4.97 | 6.16 | 0.07 | 0.22 | 0.16 |
| item35 pt1 | batch 1 | 0.07 | 7.92 | 0.01 | 90.06 | 0.33 | 0.47 | 0.80 | 0.07 | 0.02 | 0.24 |
| item35 pt2 | batch 1 | 0.01 | 1.58 | 0.00 | 96.53 | 0.29 | 0.42 | 0.73 | 0.14 | 0.02 | 0.27 |
| item36 pt1 | batch 1 | 0.03 | 2.23 | 0.03 | 88.26 | 0.31 | 0.65 | 8.15 | 0.09 | 0.09 | 0.18 |
| item36 pt2 | batch 1 | 0.02 | 5.90 | 0.03 | 79.64 | 0.27 | 1.75 | 11.81 | 0.19 | 0.07 | 0.32 |
| **5. Cu with low traces** | | | | | | | | | | | |
| smm09-007-av-1 | batch 2 | 0.03 | 0.30 | 0.01 | 98.42 | 0.22 | 0.11 | 0.75 | 0.04 | 0.03 | 0.10 |
| smm09-007-av-2 | batch 2 | 0.02 | 0.58 | 0.00 | 93.64 | 0.25 | 0.37 | 4.99 | 0.04 | 0.02 | 0.08 |
| smm09-007-ax-1 | batch 2 | 0.02 | 0.38 | 0.01 | 98.63 | 0.27 | 0.11 | 0.36 | 0.03 | 0.03 | 0.15 |
| smm09-007-ax-2 | batch 2 | 0.00 | 0.56 | 0.00 | 96.95 | 0.29 | 0.52 | 1.30 | 0.03 | 0.05 | 0.29 |
| smm09-007-bf-1 | batch 2 | 0.01 | 0.25 | 0.00 | 98.05 | 0.33 | 0.38 | 0.83 | 0.08 | 0.01 | 0.04 |
| smm09-007-bf-2 | batch 2 | 0.01 | 0.21 | 0.00 | 97.80 | 0.20 | 0.46 | 1.12 | 0.14 | 0.01 | 0.05 |
| smm09-007-bj-1 | batch 2 | 0.01 | 0.52 | 0.03 | 96.35 | 0.26 | 0.50 | 2.23 | 0.03 | 0.02 | 0.04 |
| smm09-007-bj-2 | batch 2 | 0.00 | 0.18 | 0.25 | 97.07 | 0.19 | 1.46 | 0.72 | 0.05 | 0.01 | 0.06 |
| smm09-007-bk-1 | batch 2 | 0.01 | 0.52 | 0.01 | 98.46 | 0.32 | 0.12 | 0.48 | 0.03 | 0.01 | 0.04 |
| smm09-007-bk-2 | batch 2 | 0.03 | 1.46 | 0.01 | 96.27 | 0.33 | 0.25 | 1.53 | 0.04 | 0.01 | 0.06 |

| | Element Line | Mn | Fe | Ni | Cu | Zn | As | Pb | Sn | Sb | Ag |
|---|---|---|---|---|---|---|---|---|---|---|---|
| smm09-007-bm-1 | batch 2 | 0.01 | 1.18 | 0.00 | 97.24 | 0.28 | 0.24 | 0.91 | 0.03 | 0.01 | 0.11 |
| smm09-007-bm-2 | batch 2 | 0.01 | 0.73 | 0.00 | 98.20 | 0.36 | 0.19 | 0.33 | 0.04 | 0.01 | 0.12 |
| smm09-007-bo-1 | batch 2 | 0.02 | 1.48 | 0.00 | 97.35 | 0.37 | 0.30 | 0.24 | 0.15 | 0.02 | 0.07 |
| smm09-007-bo-2 | batch 2 | 0.03 | 0.50 | 0.00 | 98.73 | 0.31 | 0.11 | 0.14 | 0.09 | 0.02 | 0.06 |
| smm09-007-bp-1 | batch 2 | 0.02 | 0.57 | 0.01 | 98.52 | 0.23 | 0.14 | 0.32 | 0.04 | 0.03 | 0.13 |
| smm09-007-bp-2 | batch 2 | 0.02 | 3.04 | 0.01 | 94.53 | 0.15 | 0.39 | 1.28 | 0.08 | 0.04 | 0.45 |
| item28 pt1 | batch 1 | 0.02 | 0.52 | 0.00 | 97.69 | 0.29 | 0.38 | 0.84 | 0.15 | 0.05 | 0.06 |
| item28 pt2 | batch 1 | 0.02 | 3.20 | 0.00 | 82.86 | 0.30 | 4.03 | 6.05 | 2.45 | 0.78 | 0.31 |
| item29 pt1 | batch 1 | 0.03 | 0.93 | 0.00 | 96.90 | 0.34 | 0.55 | 0.98 | 0.15 | 0.03 | 0.09 |
| item29 pt2 | batch 1 | 0.03 | 0.83 | 0.00 | 97.27 | 0.36 | 0.41 | 0.89 | 0.12 | 0.02 | 0.08 |
| item31 pt1 | batch 1 | 0.02 | 0.45 | 0.01 | 98.48 | 0.27 | 0.11 | 0.53 | 0.04 | 0.02 | 0.08 |
| item31 pt2 | batch 1 | 0.02 | 1.21 | 0.00 | 94.39 | 0.27 | 0.44 | 3.15 | 0.09 | 0.06 | 0.38 |
| item32 pt1 | batch 1 | 0.03 | 0.90 | 0.00 | 97.90 | 0.25 | 0.14 | 0.63 | 0.05 | 0.01 | 0.08 |
| item32 pt2 | batch 1 | 0.01 | 0.45 | 0.00 | 98.29 | 0.23 | 0.28 | 0.58 | 0.04 | 0.00 | 0.11 |
| item32 pt3 | batch 1 | 0.00 | 0.29 | 0.00 | 99.17 | 0.23 | 0.07 | 0.14 | 0.04 | 0.00 | 0.06 |
| item37 pt1 | batch 1 | 0.01 | 0.44 | 0.00 | 98.26 | 0.24 | 0.38 | 0.51 | 0.04 | 0.03 | 0.10 |
| item37 pt2 | batch 1 | 0.01 | 0.94 | 0.00 | 97.63 | 0.26 | 0.56 | 0.45 | 0.05 | 0.02 | 0.09 |
| item38 pt1 | batch 1 | 0.02 | 0.81 | 0.03 | 96.91 | 0.33 | 0.28 | 1.45 | 0.03 | 0.05 | 0.10 |
| item38 pt2 | batch 1 | 0.04 | 1.00 | 0.03 | 96.48 | 0.26 | 0.49 | 1.51 | 0.06 | 0.03 | 0.10 |

*Table 3: Sample codes, specimens and final chemical groups. The shaded rows are the historic finds.*

| Specimen | Specimen Weight | Sample code | Sample | Assessment Group | Assessment Batch | Analysis Block | Analysis Turnings | Analysis ICP | Analysis LI |
|---|---|---|---|---|---|---|---|---|---|
| ***Leaded bronze*** | | | | | | | | | |
| SMM95-AA-c235 | 96 | SMM1 | Casting waste? | 1 | 2 (historic) | y | | | |
| SMM-09-BP-0007-23 | 149 | SMM2 | Prilly lump | 1 | 1 | y | y | | y |
| ***Leaded arsenical copper*** | | | | | | | | | |
| SMM-09-AU-007 | 325 | SMM4 | Ingot fragment | 2 | 2 | y | y | y | y |
| ***Copper with raised Co, Bi*** | | | | | | | | | |
| SMM-04-CA | 1237 | SMM5 | Ingot fragment | 3 | 2 (historic) | y | | | |
| ***Copper with low traces*** | | | | | | | | | |
| SMM-09-AT-007-24 | 515 | SMM3 | Ingot fragment | 2 | 1 | y | | | |
| SMM-09-BI-007-39 | 74 | SMM6 | Ingot fragment | 3 | 1 | y | y | y | y |
| SMM-09-BQ-007 | 206 | SMM7 | Ingot fragment | 4 | 2 | y | y | y | |
| SMM-09-AW | 229 | SMM8 | Ingot fragment | 4 | 2 | y | y | y | y |
| SMM-09-BL-007-42 | 244 | SMM9 | Ingot fragment | 4 | 1 | y | | | |
| SMM-09-AZ-007-36 | 53 | SMM10 | Ingot fragment | 4 | 1 | | | | |
| SMM-09-BD 007-34 | 54 | SMM11 | Ingot fragment | 4 | 2 | | | | |
| SMM-09-BE 007-35 | 145 | SMM12 | Ingot fragment | 4 | 1 | | | | |
| SMM-09-BN 007-44 | 134 | SMM13 | Ingot fragment | 4 | 1 | | | | |
| SMM-09-BP | 219 | SMM14 | Ingot fragment | 5 | 2 | y | | | |
| SMM-09-AV | 299 | SMM15 | Ingot fragment | 5 | 2 | y | y | y | y |
| SMM-09-BO | 175 | SMM16 | Ingot fragment | 5 | 2 | y | y | y | y |
| SMM-09-BJ | 353 | SMM17 | Ingot fragment | 5 | 2 | y | | | |
| SMM-09-BG 007-37 | 357 | SMM18 | Ingot fragment | 5 | 1 | | | | |
| SMM-09-BM | 115 | SMM19 | Ingot fragment | 5 | 2 | | | | |
| SMM-09-BA 007-31 | 57 | SMM20 | Ingot fragment | 5 | 1 | | | | |
| SMM-09-AX - 28 | 25 | SMM21 | Ingot fragment | 5 | 2 | | | | |
| SMM-09-BK | 106 | SMM22 | Ingot fragment | 5 | 2 | | | | |
| SMM-09-AY 007-29 | 36 | SMM23 | Ingot fragment | 5 | 1 | | | | |
| SMM-09-AX 007-28 | 24 | SMM24 | Ingot fragment | 5 | 1 | | | | |
| SMM-09-BH 007-38 | 74 | SMM25 | Ingot fragment | 5 | 1 | | | | |
| SMM-09-BF | 63 | SMM26 | Ingot fragment | 5 | 2 | | | | |
| SMM-09-BB 007-32 | 134 | SMM27 | Ingot fragment | 5 | 1 | | | | |

*Table 4: raw pXRF peak areas extracted by Artax, for analyses taken on freshly-cut faces of the specimens. The shaded rows are the historic finds.*

| Sample | Element Line | Mn K12 | Fe K12 | Co K12 | Ni K12 | Cu K12 | Zn K12 | As K12 | Se K12 | Ag K12 | Ag L1 | Sn K12 | Sn L1 | Sb K12 | Sb L1 | Pb L1 | Pb M1 | Bi L1 | Bi M1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SMM1-a | | | 645 | 180 | 2134 | 2194141 | 3302 | 10057 | | 1287 | 807 | 43902 | 1329 | 236 | 728 | 253386 | 1434 | | |
| SMM1-b | | | 1060 | 280 | 1902 | 2208631 | 3364 | 8305 | | 1194 | 799 | 48550 | 1256 | 390 | 790 | 219954 | 1417 | | |
| SMM2-a | | | 906 | 116 | 1661 | 2645932 | 4849 | 1414 | | 1731 | 1105 | 79296 | 2345 | 590 | 821 | 22888 | 210 | | |
| SMM2-b | | | 609 | 331 | 1046 | 2310482 | 4305 | 1630 | | 1849 | 960 | 62948 | 1907 | 414 | 748 | 17837 | 132 | | |
| SMM3-a | | 49 | 1179 | 694 | 1054 | 3266822 | 5934 | 47 | | 2273 | 1197 | 114 | 0 | 1934 | 256 | 251 | 105 | | |
| SMM3-b | | | 457 | 164 | 1098 | 3384728 | 6673 | 156 | | 2263 | 1296 | 135 | 0 | 2241 | 262 | | | | |
| SMM4-a | | | 878 | 203 | 1 | 3223178 | 6081 | 32912 | | 3511 | 1232 | 508 | 0 | 3120 | 353 | 27448 | 108 | | |
| SMM4-b | | | 954 | 118 | 1 | 3221453 | 6143 | 32696 | | 3461 | 1258 | 418 | 0 | 2940 | 360 | 27536 | 128 | | |
| SMM5-a | | | 18277 | 17451 | 1803 | 3269356 | 6157 | 13740 | | 1710 | 1118 | 180 | 0 | 161 | 240 | 5846 | 160 | 2109 | 36 |
| SMM5-b | | | 17506 | 17010 | 1811 | 3252182 | 6037 | 11348 | | 1657 | 1316 | 182 | 0 | 115 | 153 | 9037 | 79 | | |
| SMM6-a | | | 15903 | 2474 | 2183 | 3310060 | 6509 | 4104 | | 1790 | 1233 | 185 | 0 | 3504 | 318 | 1405 | 81 | | |
| SMM6-b | | | 16143 | 2538 | 2453 | 3212043 | 6213 | 4338 | | 1480 | 1187 | 163 | 0 | 3535 | 374 | 978 | 171 | | |
| SMM7-a | | | 963 | 307 | 1 | 3411059 | 6471 | 2939 | 527 | 1688 | 1219 | 189 | -1 | 152 | 202 | 1192 | 89 | | |
| SMM7-b | | | 863 | 34 | 251 | 3406526 | 6448 | 3032 | 566 | 1539 | 1263 | 287 | 0 | 315 | 228 | 1065 | 164 | | |
| SMM8-a | | | 1077 | 439 | 1 | 3417497 | 6435 | | | 970 | 1330 | 62 | 59 | 47 | 231 | | | | |
| SMM8-b | | | 65477 | 1975 | 1 | 3225669 | 6412 | | | 1076 | 1326 | 187 | 0 | 64 | 440 | | | | |
| SMM9-a | | 57 | 1384 | 789 | 4473 | 3255310 | 5711 | 146 | | 185 | 10 | 235 | 95 | | | 1018 | 180 | | |
| SMM9-b | | | 1548 | 230 | 4861 | 3262158 | 6182 | 383 | | 1350 | 1113 | 77 | 0 | 139 | 228 | 1281 | 116 | | |
| SMM14-a | | | 1115 | 312 | 638 | 3389828 | 6464 | 277 | | 1603 | 1234 | 166 | 0 | 137 | 102 | 387 | 190 | | |
| SMM14-b | | | 946 | 467 | 684 | 3390947 | 6546 | 192 | | 1744 | 1268 | 193 | 116 | | | 491 | -22 | | |
| SMM15-a | | | 798 | | 2270 | 3395671 | 6833 | 2308 | 249 | | | 369 | 14 | | | 1046 | 171 | | |
| SMM15-b | | | 1066 | 363 | 1479 | 3418777 | 6859 | 2373 | 276 | | | | | | | 1165 | 105 | | |
| SMM16-a | | | 907 | 269 | 1 | 3412963 | 6674 | 463 | | | | 484 | -22 | 87 | 69 | 610 | 107 | | |
| SMM16-b | | | 850 | 252 | 1 | 3406135 | 6319 | 318 | | | | 722 | 2 | 149 | 184 | 715 | 52 | | |
| SMM17-a | | | 1109 | 160 | 603 | 3201078 | 6016 | 1 | 24 | 729 | 1318 | | | | | 217 | 162 | | |
| SMM17-b | | | 927 | 263 | 735 | 3270463 | 6060 | 47 | | 988 | 1210 | | | | | 273 | 45 | | |

*Table 5. Calibrated pXRF data, for analyses from freshly-cut surfaces, using the calibration approach described in the text. The numbers here are the average of the two analyses for each sample given Table 2. All values in ppm, except Cu in wt%.The shaded rows are the historic finds.*

| sample | specimen | Mn | Fe | Co | Ni | Cu | Zn | As | Se | Pb | Sn | Sb | Ag | Bi |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SMM1 | SMM95-AA-c235 | < | 289 | 78 | 689 | 73.93 | 783 | 3550 | < | 191924 | 61045 | 1383 | 947 | < |
| SMM2 | SMM-09-BP-0007-23 | < | 268 | 83 | 482 | 87.83 | 1136 | 628 | < | 17365 | 98737 | 1511 | 1453 | < |
| SMM3 | SMM-09-AT-007-24 | 14 | 249 | 131 | 328 | 99.57 | 1320 | 35 | < | 92 | 146 | 421 | 1545 | < |
| SMM4 | SMM-09-AU-007 | < | 276 | 48 | < | 96.37 | 1279 | 11306 | < | 19866 | 544 | 578 | 2371 | < |
| SMM5 | SMM-04-CA | < | 5394 | 5195 | 550 | 97.54 | 1276 | 4323 | < | 5382 | 213 | 319 | 1145 | 760 |
| SMM6 | SMM-09-BI-007-39 | < | 4895 | 766 | 715 | 98.80 | 1349 | 1475 | < | 870 | 207 | 570 | 1125 | < |
| SMM7 | SMM-09-BQ-007 | < | 269 | 50 | 37 | 99.47 | 1319 | 1004 | 184 | 796 | 273 | 340 | 1071 | < |
| SMM8 | SMM-09-AW | < | 10147 | 366 | < | 98.68 | 1336 | < | < | < | 147 | 544 | 692 | < |
| SMM9 | SMM-09-BL-007-42 | 17 | 451 | 157 | 1449 | 99.48 | 1270 | 93 | < | 848 | 187 | 188 | 532 | < |
| SMM14 | SMM-09-BP | < | 305 | 115 | 198 | 99.62 | 1338 | 79 | < | 312 | 207 | 81 | 1118 | < |
| SMM15 | SMM-09-AV | < | 274 | 53 | 558 | 99.58 | 1400 | 788 | 88 | 781 | 213 | < | < | < |
| SMM16 | SMM-09-BO | < | 259 | 77 | < | 99.68 | 1329 | 132 | < | 468 | 693 | 201 | < | < |
| SMM17 | SMM-09-BJ | < | 317 | 66 | 210 | 99.73 | 1302 | < | < | 182 | < | < | 601 | < |

*Table 6: elemental compositions determined by ICP-MS. All values in ppm, except for Cu (in wt%).*

| Run | | P | Fe | Co | Ni | Cu | Zn | As | Se | Ag | Sn | Sb | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2649 | 245.7 | n.d. | 2.3 | 94.71 | 1133 | 13170 | 26.85 | 4327 | 84.69 | 854.4 | 14060 |
| | 2 | 2689 | 266.2 | n.d. | 4.7 | 93.72 | 1139 | 13610 | 47.43 | 4192 | 99.54 | 858.2 | 14310 |
| | 3 | 2731 | 265.4 | n.d. | 12.1 | 94.51 | 1151 | 13680 | 68.05 | 4657 | 73.48 | 935.9 | 14600 |
| **SMM4** | | **2690** | **259** | **n.d.** | **6** | **94.3** | **1141.0** | **13487** | **47.4** | **4392** | **86** | **882.8** | **14323.3** |
| s | | 41.0 | 11.6 | n.d. | 5.1 | 0.5 | 9.2 | 276.5 | 20.6 | 239.2 | 13.1 | 46.0 | 270.2 |
| %RSD | | 1.52 | 4.48 | n.d. | 80.23 | 0.56 | 0.80 | 2.05 | 43.42 | 5.45 | 15.22 | 5.21 | 1.89 |
| | 1 | 3476 | 4664 | 363.3 | 1277 | 98.3 | 907.6 | 1311 | 70.65 | 1721 | 6044 | 836.3 | 398 |
| | 2 | 3673 | 4784 | 364.2 | 1321 | 99.5 | 924.6 | 1344 | 148 | 1559 | 5980 | 861.7 | 398.4 |
| | 3 | 3752 | 4687 | 368.4 | 1307 | 100.3 | 949.5 | 1387 | 177.9 | 1595 | 6213 | 869.9 | 406.8 |
| **SMM6** | | **3634** | **4712** | **365.3** | **1302** | **99.4** | **927.2** | **1347** | **132.2** | **1625** | **6079** | **856.0** | **401.1** |
| s | | 142.1 | 63.7 | 2.7 | 22.5 | 1.0 | 21.1 | 38.1 | 55.3 | 85.1 | 120.4 | 17.5 | 5.0 |
| %RSD | | 3.91 | 1.35 | 0.75 | 1.73 | 1.01 | 2.27 | 2.83 | 41.87 | 5.23 | 1.98 | 2.05 | 1.24 |
| | 1 | 6057 | 4583 | 310.6 | 1188 | 97.39 | 1795 | 1696 | 42.38 | 8699 | 6234 | 2780 | 413.2 |
| | 2 | 5928 | 4752 | 307.2 | 1223 | 99.97 | 1866 | 1707 | 132.7 | 9837 | 6376 | 2896 | 420.1 |
| | 3 | 5978 | 4609 | 328.9 | 1247 | 100.6 | 1863 | 1743 | 145 | 9586 | 6536 | 2884 | 424.6 |
| **SMM6B** | | **5988** | **4648** | **315.6** | **1219** | **99.3** | **1841.3** | **1715** | **106.7** | **9374** | **6382** | **2853.3** | **419.3** |
| s | | 65.0 | 91.0 | 11.7 | 29.7 | 1.7 | 40.2 | 24.6 | 56.0 | 597.9 | 151.1 | 63.8 | 5.7 |
| %RSD | | 1.09 | 1.96 | 3.70 | 2.43 | 1.71 | 2.18 | 1.43 | 52.52 | 6.38 | 2.37 | 2.24 | 1.37 |
| | 1 | 3709 | 1031 | n.d. | 220.6 | 97.48 | 1230 | 1503 | 204.2 | 8379 | 1428 | 119.5 | 336.4 |
| | 2 | 3827 | 1111 | n.d. | 228.2 | 96.16 | 1323 | 1579 | 201.8 | 9121 | 1520 | 124.9 | 341 |
| | 3 | 3874 | 1080 | n.d. | 239 | 95.97 | 1312 | 1565 | 196.8 | 9333 | 1387 | 139.4 | 344.4 |
| **SMM7** | | **3803** | **1074** | **n.d.** | **229** | **96.5** | **1288.3** | **1549** | **200.9** | **8944** | **1445** | **127.9** | **340.6** |
| s | | 85.0 | 40.3 | n.d. | 9.2 | 0.8 | 50.8 | 40.4 | 3.8 | 500.9 | 68.1 | 10.3 | 4.0 |
| %RSD | | 2.24 | 3.76 | n.d. | 4.03 | 0.85 | 3.94 | 2.61 | 1.88 | 5.60 | 4.71 | 8.04 | 1.18 |
| | 1 | 2496 | 113.2 | n.d. | 185.5 | 100.3 | 1055 | 95.24 | 11.76 | 4535 | 185.5 | 175.2 | 51.95 |
| | 2 | 2638 | 127.3 | n.d. | 198 | 100.1 | 1090 | 113.1 | 13.62 | 5111 | 339.2 | 186.2 | 51.92 |
| | 3 | 2640 | 129 | n.d. | 193.7 | 99.24 | 1110 | 94.19 | 30.36 | 4970 | 439.9 | 173.8 | 52.77 |
| **SMM8** | | **2591** | **123** | **n.d.** | **192** | **99.9** | **1085.0** | **101** | **18.6** | **4872** | **322** | **178.4** | **52.2** |
| s | | 82.6 | 8.7 | n.d. | 6.4 | 0.6 | 27.8 | 10.6 | 10.2 | 300.2 | 128.1 | 6.8 | 0.5 |
| %RSD | | 3.19 | 7.04 | n.d. | 3.30 | 0.56 | 2.57 | 10.54 | 55.13 | 6.16 | 39.85 | 3.81 | 0.92 |
| | 1 | 2689 | 183.7 | n.d. | 838.1 | 97.81 | 629.9 | 1059 | 105.5 | 340.4 | 1126 | -32.06 | 314.7 |
| | 2 | 2736 | 212.7 | n.d. | 858.8 | 99.34 | 656.5 | 1090 | 152.2 | 319.4 | 1208 | -31.57 | 327.3 |
| | 3 | 2796 | 184.7 | n.d. | 880.1 | 100.8 | 659 | 1087 | 125 | 494.3 | 1445 | -30.22 | 329.8 |
| **SMM15** | | **2740** | **194** | **n.d.** | **859** | **99.3** | **648.5** | **1079** | **127.6** | **385** | **1260** | **-31.3** | **323.9** |
| s | | 53.6 | 16.5 | n.d. | 21.0 | 1.5 | 16.1 | 17.1 | 23.5 | 95.5 | 165.7 | 1.0 | 8.1 |
| %RSD | | 1.96 | 8.50 | n.d. | 2.44 | 1.51 | 2.49 | 1.59 | 18.39 | 24.82 | 13.15 | -3.05 | 2.50 |
| | 1 | 4049 | 650.3 | n.d. | 74.15 | 98.18 | 651.9 | 372.6 | 28.03 | 3606 | 2835 | 67.2 | 148.7 |
| | 2 | 4131 | 663.7 | n.d. | 79.97 | 98.55 | 693 | 385.6 | 70.13 | 4141 | 3029 | 68.21 | 154.6 |
| | 3 | 4215 | 623.4 | n.d. | 83.54 | 99.19 | 669 | 405.9 | 67.65 | 3419 | 2723 | 71.8 | 158.6 |
| **SMM16** | | **4132** | **646** | **n.d.** | **79** | **98.6** | **671.3** | **388** | **55.3** | **3722** | **2862** | **69.1** | **154.0** |
| s | | 83.0 | 20.5 | n.d. | 4.7 | 0.5 | 20.6 | 16.8 | 23.6 | 374.7 | 154.8 | 2.4 | 5.0 |
| %RSD | | 2.01 | 3.18 | n.d. | 5.98 | 0.52 | 3.08 | 4.33 | 42.74 | 10.07 | 5.41 | 3.50 | 3.23 |
| | 1 | 4135 | 687.1 | n.d. | 74.54 | 101.9 | 862 | 407.8 | 62.51 | 4168 | 3101 | 57.53 | 165.1 |
| | 2 | 4091 | 695.8 | n.d. | 82.53 | 100.6 | 903.1 | 432.7 | 110 | 4928 | 3237 | 62.02 | 172 |
| | 3 | 4268 | 665.4 | n.d. | 79.86 | 101.7 | 888.2 | 415 | 64.89 | 4373 | 3619 | 67.14 | 176.9 |
| **SMM16B** | | **4165** | **683** | **n.d.** | **79** | **101.4** | **884.4** | **419** | **79.1** | **4490** | **3319** | **62.2** | **171.3** |
| s | | 92.2 | 15.7 | n.d. | 4.1 | 0.7 | 20.8 | 12.8 | 26.8 | 393.2 | 268.6 | 4.8 | 5.9 |
| %RSD | | 2.21 | 2.29 | n.d. | 5.15 | 0.69 | 2.35 | 3.06 | 33.81 | 8.76 | 8.09 | 7.73 | 3.46 |

*Table 7. Compilation of elemental analytical data. The shaded rows are the historic finds.*

| | | | | Fe | Co | Ni | Cu | Zn | As | Se | Pb | Sn | Sb | Ag | Bi |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SMM1 | pXRF | Gp. 1 | Leaded bronze | 289 | 78 | 689 | 74 | 783 | 3550 | 0 | 191924 | 61045 | 1383 | 947 | 0 |
| | | | recalculated Sn- and Pb-free | ***387*** | ***104*** | ***922*** | ***99*** | ***1049*** | ***4752*** | ***0*** | - | - | ***1852*** | ***1268*** | |
| SMM2 | pXRF | Gp. 1 | Leaded bronze * | 268 | 83 | 482 | 88 | 1136 | 628 | 0 | 17365 | 98737 | 1511 | 1453 | 0 |
| | | | recalculated Sn- and Pb-free | ***303*** | ***94*** | ***546*** | ***99*** | ***1285*** | ***710*** | ***0*** | - | - | ***1709*** | ***1644*** | ***0*** |
| SMM3 | pXRF | Gp 2 | Copper | 249 | 131 | 328 | 100 | 1320 | 35 | 0 | 92 | 146 | 421 | 1545 | 0 |
| SMM3 | micro-XRF | Gp 2 | | 1138 | 34 | 306 | 99 | 1052 | 1246 | 18 | 4607 | 9 | 1401 | 183 | nd |
| SMM4 | pXRF | Gp 2 | Leaded arsenical copper * | 276 | 48 | 0 | 96 | 1279 | 11306 | 0 | 19866 | 544 | 578 | 2371 | 0 |
| SMM4 | ICP-MS | Gp 2 | | 259 | nd | 6 | 94 | 1141 | 13487 | 47 | 4392 | 86 | 883 | 14323 | 0 |
| SMM5 | pXRF | Gp 3 | Copper with raised Co, Bi | 5394 | 5195 | 550 | 98 | 1276 | 4323 | 0 | 5382 | 213 | 319 | 1145 | 760 |
| SMM6 | pXRF | Gp 3 | Copper | 4895 | 766 | 715 | 99 | 1349 | 1475 | 0 | 870 | 207 | 570 | 1125 | 0 |
| SMM6 | micro-XRF | Gp 3 | | 2418 | 285 | 295 | 99 | 1832 | 823 | 10 | 574 | 95 | 1987 | 441 | nd |
| SMM6 | ICP-MS | Gp 3 | | 4712 | 365 | 1302 | 99 | 927 | 1347 | 132 | 401 | 6079 | 856 | 1625 | nd |
| SMM6b | ICP-MS | Gp 3 | | 4648 | 316 | 1219 | 99 | 1841 | 1715 | 107 | 419 | 6382 | 2853 | 9374 | nd |
| SMM7 | pXRF | Gp4 | Copper | 269 | 50 | 37 | 99 | 1319 | 1004 | 184 | 796 | 273 | 340 | 1071 | 0 |
| SMM7 | ICP-MS | Gp4 | | 1074 | nd | 229 | 97 | 1288 | 1549 | 201 | 8944 | 1445 | 128 | 341 | nd |
| SMM8 | pXRF | Gp4 | Copper | 10147 | 366 | 0 | 99 | 1336 | 0 | 0 | 0 | 147 | 544 | 692 | 0 |
| SMM8 | ICP-MS | Gp4 | | 123 | nd | 192 | 100 | 1085 | 101 | 19 | 4872 | 322 | 178 | 52 | nd |
| SMM9 | pXRF | Gp4 | Copper | 451 | 157 | 1449 | 99 | 1270 | 93 | 0 | 848 | 187 | 188 | 532 | 0 |
| SMM14 | pXRF | Gp 5 | Copper | 305 | 115 | 198 | 100 | 1338 | 79 | 0 | 312 | 207 | 81 | 1118 | 0 |
| SMM15 | pXRF | Gp 5 | Copper | 274 | 53 | 558 | 100 | 1400 | 788 | 88 | 781 | 213 | 0 | 0 | 0 |
| SMM15 | ICP-MS | Gp 5 | | 194 | nd | 859 | 99 | 648 | 1079 | 128 | 385 | 1260 | bd | 324 | nd |
| SMM16 | pXRF | Gp 5 | Copper | 259 | 77 | 0 | 100 | 1329 | 132 | 0 | 468 | 693 | 201 | 0 | 0 |
| SMM16 | ICP-MS | Gp 5 | | 664 | nd | 79 | 100 | 778 | 403 | 67 | 4106 | 3091 | 66 | 163 | nd |
| SMM17 | pXRF | Gp 5 | Copper | 317 | 66 | 210 | 100 | 1302 | 8 | 4 | 182 | 0 | 0 | 601 | 0 |

*Table 8. Lead isotope analyses. Analysis undertaken by ALS Scandinavia AB, Luleå, Sweden.*

| Sample ID | Lab ID | | | | | | | | | Surplus data | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $^{208}Pb/^{207}Pb$ | | $^{207}Pb/^{206}Pb$ | | $^{206}Pb/^{204}Pb$ | | $^{208}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{87}Sr/^{86}Sr$ | |
| | | | 2 SD | | 2 SD | | 2 SD | | | | *2 SD* |
| SMM2 | U11051824 | 2.4568 | *0.0002* | 0.84923 | *0.00014* | 18.415 | *0.006* | 38.421 | 15.639 | 0.7099 | *0.0024* |
| SMM4 | U11051825 | 2.4451 | *0.0002* | 0.85893 | *0.00011* | 18.170 | *0.006* | 38.160 | 15.607 | 0.7098 | *0.0022* |
| SMM6 | U11051826 | 2.4764 | *0.0001* | 0.84494 | *0.00009* | 18.540 | *0.004* | 38.794 | 15.665 | 0.7057 | *0.0017* |
| SMM8 | U11051827 | 2.4575 | *0.0003* | 0.84925 | *0.00016* | 18.434 | *0.009* | 38.472 | 15.655 | 0.7075 | *0.0018* |
| SMM15 | U11051828 | 2.4156 | *0.0003* | 0.86781 | *0.00024* | 17.952 | *0.010* | 37.632 | 15.579 | 0.7196 | *0.0097* |
| SMM16 | U11051829 | 2.4768 | *0.0002* | 0.83555 | *0.00021* | 18.717 | *0.005* | 38.735 | 15.639 | 0.7103 | *0.0020* |
| SMM16, repl. | U11051829 | 2.4766 | *0.0003* | 0.83572 | *0.00024* | 18.713 | *0.007* | 38.731 | 15.639 | 0.7099 | *0.0023* |

*Table 9: compilation of available analytical data from Ewart Park Phase ingots and related materials. Sources: Rohl & Needham (1998), OXALID database, Lawson undated.*

| Locality | Material | Rohl & Nededham | | Pb isotope ratios | | | Elemental composition | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | # | IMP-LI | $^{208}Pb/^{206}Pb$ | $^{207}Pb/^{206}Pb$ | $^{206}Pb/^{204}Pb$ | Cu | Sn | Pb | Ag | Fe | As | Sb | Zn | Au | Ni | Co | Bi |
| Stogursey | Bronze ingot | 370 | | 2.07927 | 0.84534 | 18.498 | | | | | | | | | | | | |
| Stogursey | Copper ingot | 371 | | 2.07966 | 0.84590 | 18.492 | | | | | | | | | | | | |
| Wickham Park | Copper Ingot | 397 | 19 | 2.08382 | 0.84079 | 18.589 | 99 | nd | 0.06 | 0.05 | 0.02 | 0.11 | 0.08 | nd | | 0.06 | nd | nd |
| Petters Sports Field | Prill | 331 | 19 | 2.08268 | 0.84274 | 18.592 | 97 | 0.1 | 0.1 | nd | 0.02 | 0.1 | 0.05 | | | 0.01 | nd | |
| Petters Sports Field | Prill | 333 | 21 | 2.08579 | 0.84894 | 18.420 | 97 | nd | 0.1 | 0.03 | 0.03 | 0.1 | 0.05 | | | 0.01 | nd | |
| Heathery Burn Cave | Copper ingot frag. | 316 | 21 | 2.08907 | 0.85022 | 18.391 | 98 | 0.3 | 0.002 | 0.08 | nd | 0.04 | 0.05 | nd | | nd | nd | |
| Stoke Hoo | Copper ingot frag. | 377 | | 2.08759 | 0.85036 | 18.354 | | | | | | | | | | | | |
| Stoke Hoo | Copper ingot frag. | 378 | 19 | 2.05404 | 0.83586 | 18.720 | 99.04 | 0.01 | 0.03 | 0.056 | 0.015 | 0.04 | 0.007 | 0 | 0 | 0.029 | 0.007 | 0 |
| Stoke Hoo | Copper ingot frag. | 379 | 21 | 2.08058 | 0.84612 | 18.470 | 98.5 | nd | 0.01 | 0.001 | 0.3 | 0.015 | 0.015 | nd | | 0.03 | nd | 0.003 |
| Stoke Hoo | Copper ingot frag. | 380 | 21 | 2.08226 | 0.84696 | 18.464 | 98.5 | 0.03 | 0.07 | 0.031 | 0.092 | 0.37 | 0.031 | 0.01 | 0.847 | 0.018 | 0 | 0 |
| Stoke Hoo | Copper ingot frag. | 381 | | 2.08380 | 0.84717 | 18.454 | | | | | | | | | | | | |
| Stoke Hoo | Copper ingot frag. | 382 | 19 | 2.06609 | 0.83654 | 18.709 | 98.32 | 0.07 | 0.01 | 0.01 | 0.22 | 0.09 | 0.005 | 0 | 1.266 | 0.01 | 0 | 0 |
| Stoke Hoo | Copper ingot frag. | 383 | 0 | 2.10034 | 0.85150 | 18.384 | 95.31 | 0.07 | 0.75 | 0.075 | 0.547 | 1.73 | 0.995 | 0.02 | 0.358 | 0.036 | 0.036 | 0.009 |
| Runnymede Bridge | Copper ingot frag. | | | | | | 98.8 | <0.10 | 0.05 | 0.032 | 0.02 | <0.03 | <0.01 | <0.006 | <0.003 | 0.141 | 0.003 | <0.01 |
| Runnymede Bridge | Lump | | | | | | 97.7 | <0.15 | 0.01 | 0.003 | 0.09 | <0.05 | <0.03 | <0.007 | <0.004 | 0.028 | <0.003 | <0.03 |
| Runnymede Bridge | Copper ingot frag. | | | | | | 97.5 | <0.10 | 0.03 | 0.006 | 0.04 | <0.03 | <0.01 | <0.006 | <0.003 | 0.156 | <0.002 | <0.01 |
| Runnymede Bridge | Lump | | | | | | 96.2 | <0.13 | 0.27 | 0.008 | 0.03 | <0.04 | <0.01 | <0.008 | <0.004 | 0.013 | <0.003 | <0.01 |
| Runnymede Bridge | Copper ingot frag. | | | | | | 96.2 | <0.17 | 0.1 | 0.005 | 0.17 | <0.06 | 0.03 | 0.048 | <0.005 | 0.003 | <0.003 | <0.03 |
| Runnymede Bridge | Lump | | | | | | 96.1 | <0.17 | 0.1 | 0.02 | 0.12 | 0.49 | 0.05 | <0.009 | <0.005 | 0.031 | <0.003 | <0.03 |
| Runnymede Bridge | Lump | | | | | | 95.5 | <0.14 | 0.02 | 0.048 | 0.07 | <0.05 | 0.03 | <0.007 | <0.004 | 0.141 | 0.003 | <0.03 |
| Runnymede Bridge | Copper ingot frag. | | | | | | 95.4 | <0.15 | 0.11 | 0.015 | 0.18 | 0.4 | 0.04 | 0.01 | <0.004 | 0.012 | <0.003 | <0.03 |
| Runnymede Bridge | Copper ingot frag. | | | | | | 95.3 | <0.13 | 0.07 | 0.046 | 0.06 | 0.49 | 0.03 | <0.008 | <0.004 | 0.019 | <0.003 | <0.01 |
| Runnymede Bridge | Copper ingot frag. | | | | | | 95.1 | <0.11 | 0.69 | 0.03 | 0.06 | <0.03 | <0.01 | <0.006 | <0.003 | 0.072 | 0.012 | <0.01 |
| Runnymede Bridge | Copper ingot frag. | 362 | 20 | 2.1037 | 0.85927 | 18.21 | 94.1 | <0.11 | 0.02 | 0.09 | 0.1 | <0.03 | 0.06 | <0.006 | <0.003 | 0.024 | <0.002 | <0.01 |
| Beeston Regis 1 #21 | Copper ingot frag. | | | | | | 98.5 | | 0.03 | 0.01 | | 0.05 | 0.03 | | | 0.03 | | |
| Beeston Regis 1 #28 | Copper ingot frag. | | | | | | 90 | | 8.9 | 0.02 | | 0.1 | 0.03 | | | 0.02 | 0.003 | |
| Beeston Regis 2 LA/10 | Copper ingot frag. | | | | | | 100 | 0.07 | 0.03 | 0.035 | 0.02 | 0.07 | 0.01 | | | 0.08 | 0.012 | |
| Beeston Regis 2 LB/11 | Copper ingot frag. | | | | | | 100 | 0.05 | 0.035 | 0.06 | 0.002 | 0.08 | 0.03 | | | 0.085 | 0.005 | |

*Table 10: Chemical analyses of ore samples from Four Crosses, selected elements only. Samples from the primary fill of furnace [2219] (after Young 2010 tables 5 and 6)*

| sample | note | context | $SO_3$ XRF Wt% | BaO XRF Wt% | NiO XRF Wt% | CuO XRF Wt% | ZnO XRF Wt% | MnO ICP-MS Wt% | $Fe_2O_3$ ICP-MS Wt% | $P_2O_5$ ICP-MS Wt% | Co ICP-MS ppm | Ni ICP-MS ppm | Sn ICP-MS ppm | U ICP-MS ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DFC14 | Fe-rich "sinter" | 2243 | 0.42 | 2.24 | 0.06 | 24.20 | 0.19 | 0.09 | 37.81 | 0.10 | 67.52 | 651.7 | 3.03 | 77.48 |
| DFC15 | Fe-rich malachite ore | 2229 | nd | nd | nd | nd | nd | 0.04 | 40.88 | 0.01 | 33.79 | 1162.8 | 1.54 | 45.44 |
| DFC17 | azurite | 2220 | nd | nd | nd | nd | nd | 0.01 | 1.48 | 0.00 | 50.74 | 2505.1 | 2.33 | 1.59 |

*Table 11: Comparison of copper composition with published microanalyses of impurities in raw copper from the Iron Age of N Wales, and interpreted to be from the Llanymynech area. Data adapted from Northover (1991, Table 2). < = below detection. Four Crosses data are the mean and range of the data in Young 2010, Table 8. (After Young 2010 Table 9)*

| sample | # | Fe | Ni | Zn | As | Ag | Sb | Pb |
|---|---|---|---|---|---|---|---|---|
| LBD1: Llwyn Bryn-dinas | 1 | 0.80 | 0.09 | 3.76 | 0.40 | 0.16 | 0.14 | 0.23 |
| | 2 | 0.79 | 0.11 | 3.37 | 0.38 | 0.11 | 0.07 | 0.06 |
| L1: Llanymynech hillfort | 1 | 0.04 | 0.11 | 1.02 | < | 0.42 | 0.06 | 0.25 |
| | 2 | 0.05 | 0.08 | 1.41 | 0.88 | 0.97 | 0.09 | 1.04 |
| | 3 | 0.05 | 0.06 | 1.03 | 0.11 | 0.22 | tr | 1.00 |
| | 4 | < | 0.07 | 0.11 | 0.64 | 0.43 | 0.03 | 0.41 |
| Four Crosses (Young 2010) | | | | | | | | |
| Mean value | | 1.23 | 0.34 | 0.21 | 1.17 | 0.10 | < | 2.28 |
| Maximum value | | 3.38 | 2.02 | 0.90 | 4.29 | 0.44 | < | 14.37 |

Figure 1

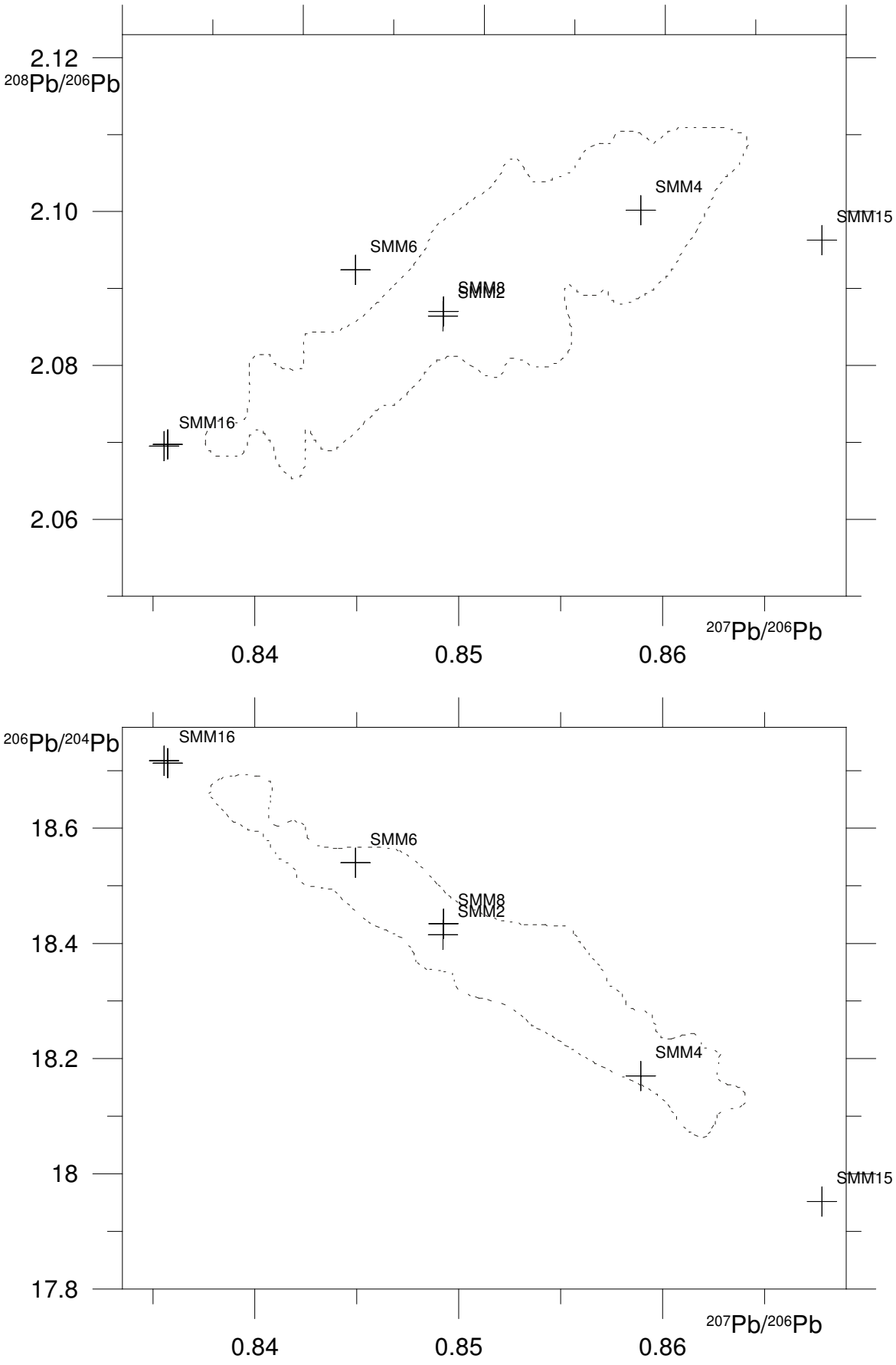

2.12
208Pb/206Pb
2.10
2.08
2.06
SMM4
SMM15
SMM6
SMM8
SMM2
SMM16
0.84
0.85
0.86
207Pb/206Pb
206Pb/204Pb
SMM16
18.6
SMM6
SMM8
SMM2
18.4
18.2
SMM4
18
SMM15
17.8
0.84
0.85
0.86
207Pb/206Pb

Figure 2

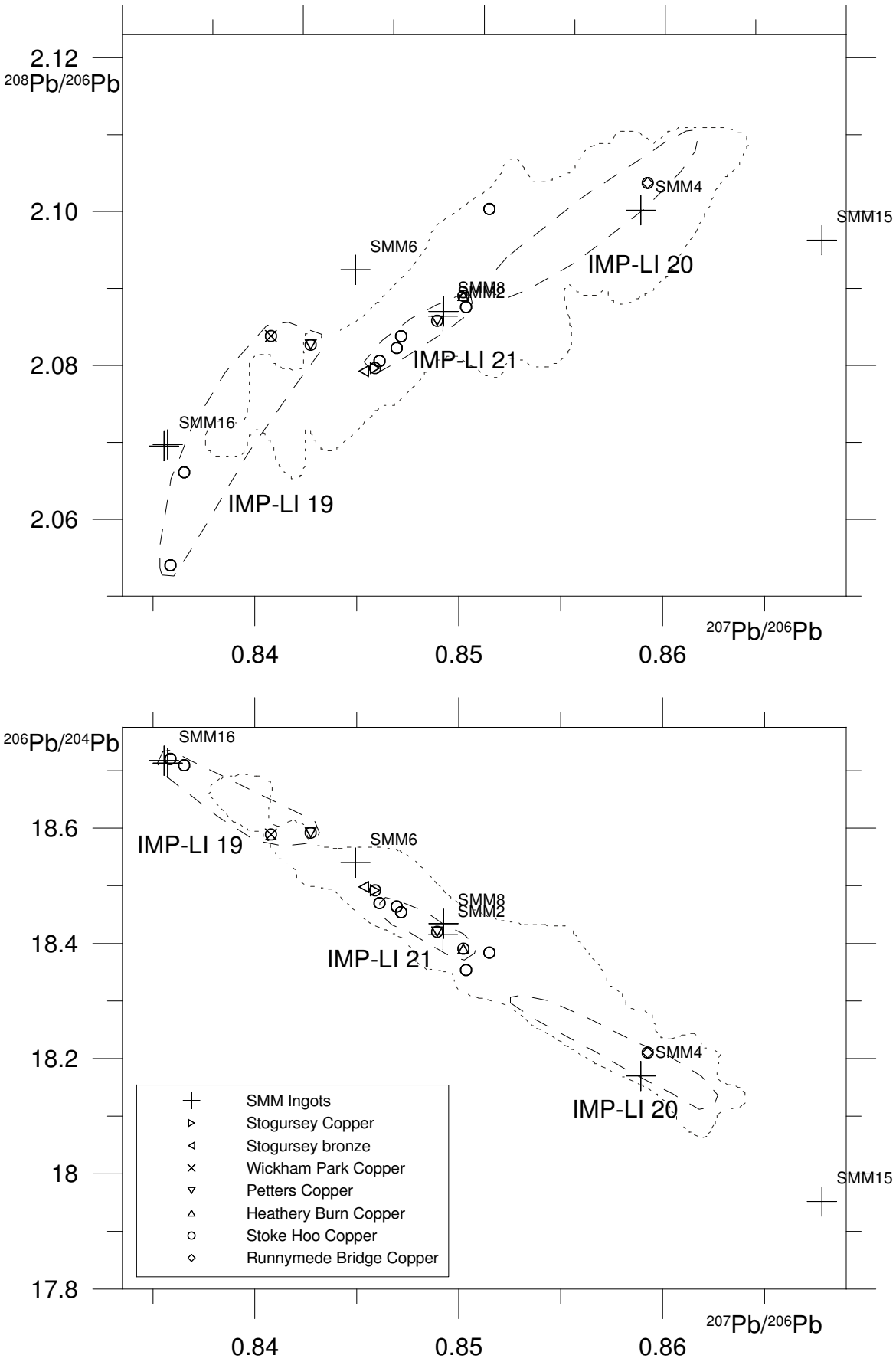

2.12
208Pb/206Pb
2.10
2.08
2.06
SMM4
SMM15
SMM6
IMP-LI 20
SMM8
SMM2
IMP-LI 21
SMM16
IMP-LI 19
0.84
0.85
0.86
207Pb/206Pb
206Pb/204Pb
18.6
18.4
18.2
18
17.8
SMM16
IMP-LI 19
SMM6
SMM8
SMM2
IMP-LI 21
SMM4
IMP-LI 20
SMM15
SMM Ingots
Stogursey Copper
Stogursey bronze
Wickham Park Copper
Petters Copper
Heathery Burn Copper
Stoke Hoo Copper
Runnymede Bridge Copper
0.84
0.85
0.86
207Pb/206Pb

Figure 3

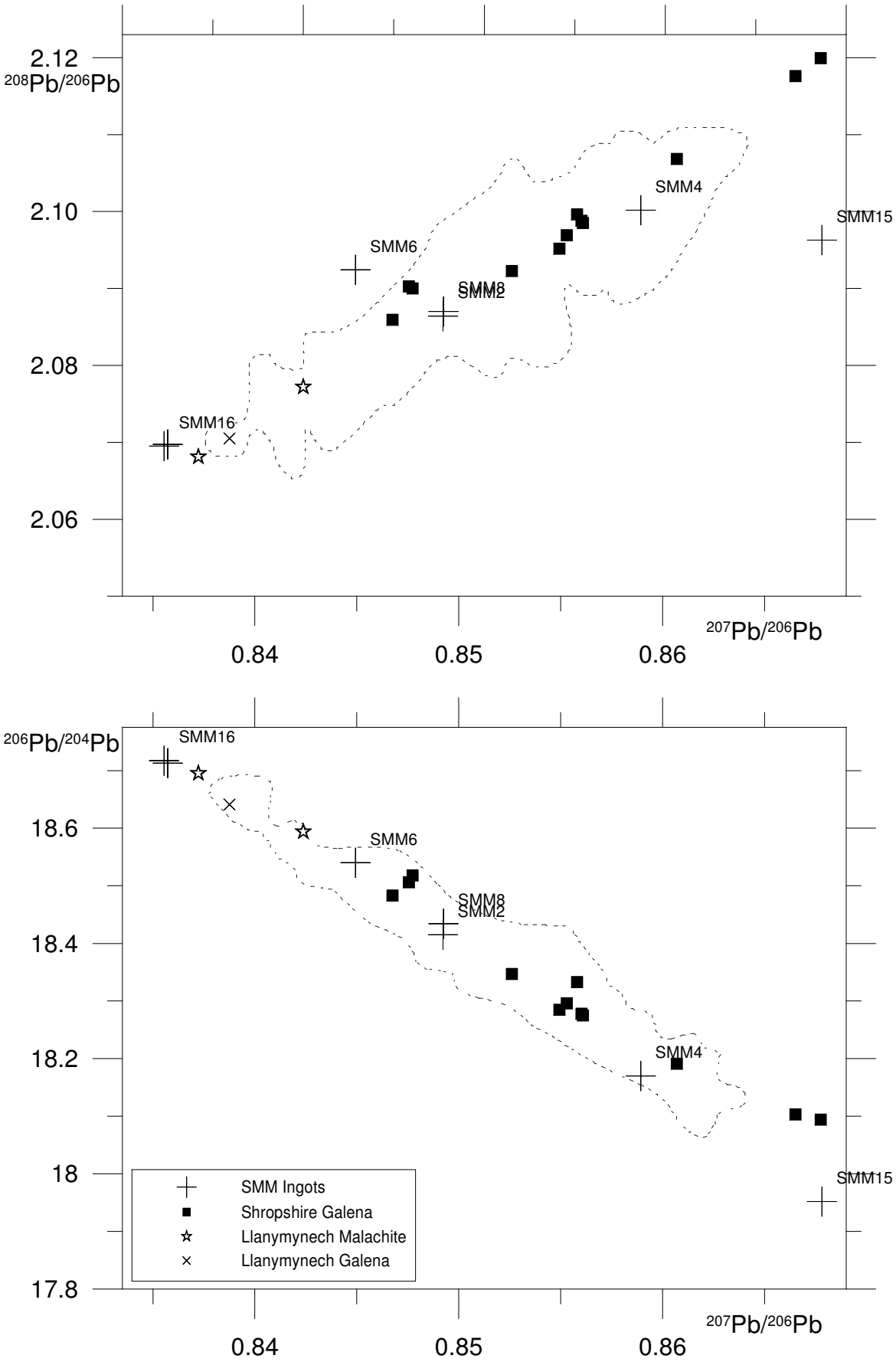
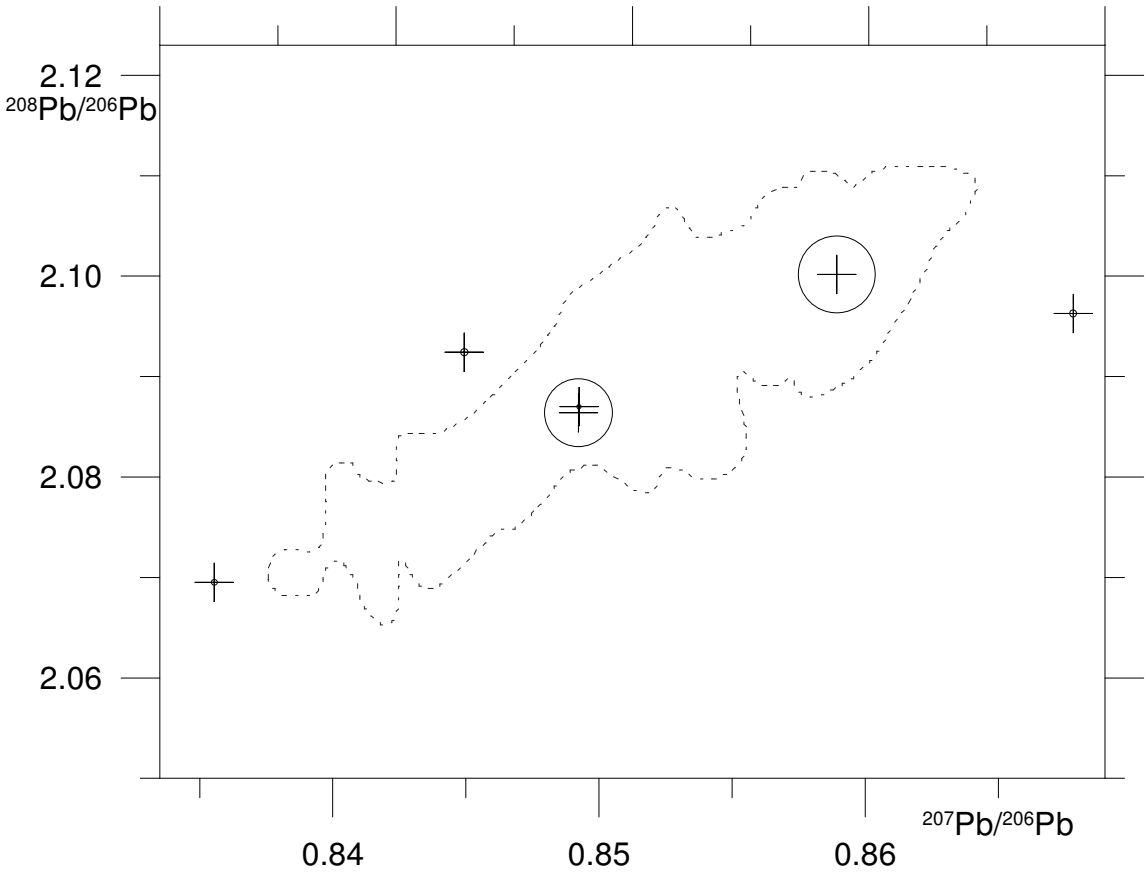
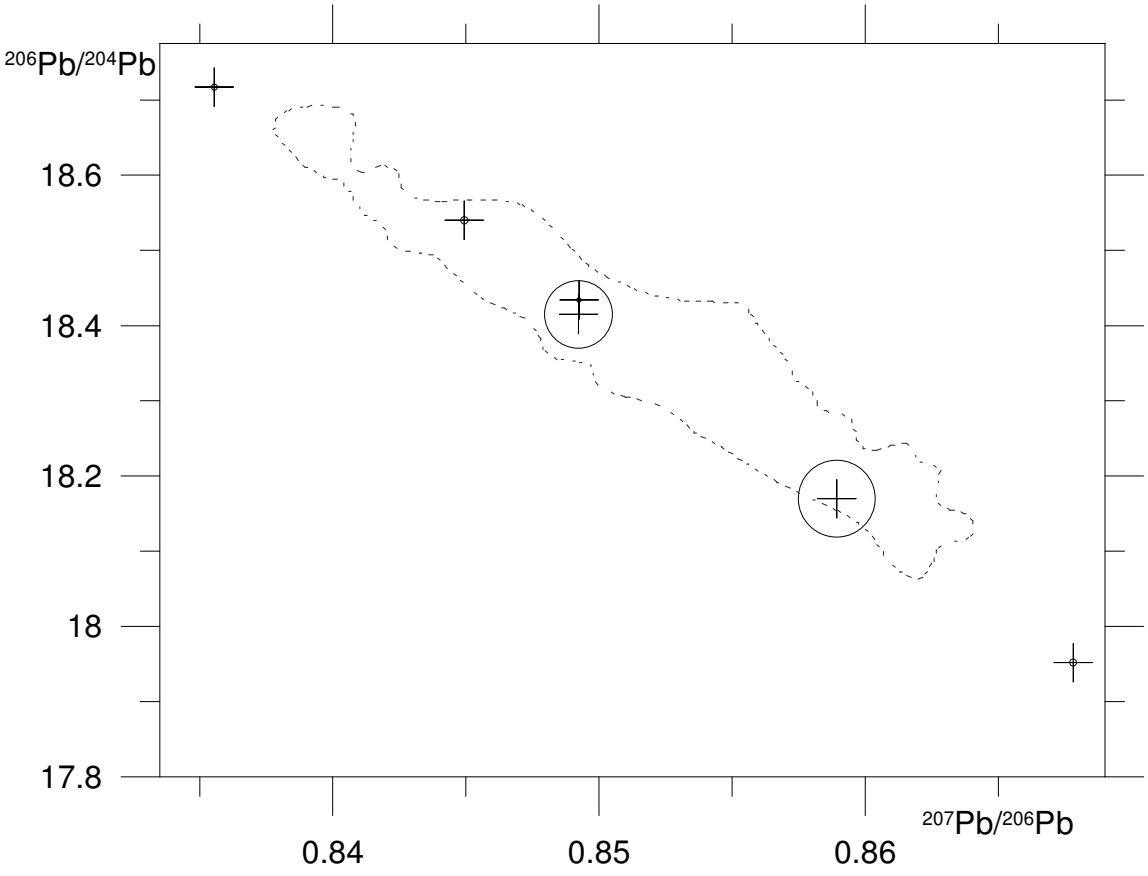

2.12
208Pb/206Pb
2.10
2.08
2.06
SMM4
SMM15
SMM6
SMM8
SMM2
SMM16
0.84
0.85
0.86
207Pb/206Pb
206Pb/204Pb
18.6
18.4
18.2
18
17.8
SMM Ingots
Shropshire Galena
Llanymynech Malachite
Llanymynech Galena

Figure 4

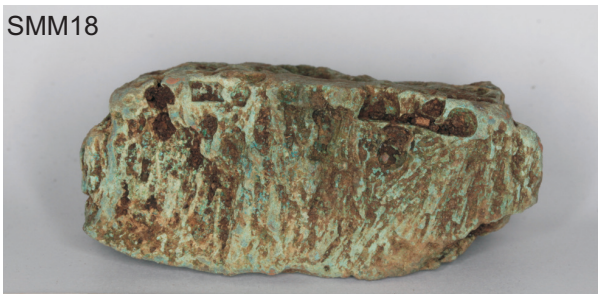

2.12
208Pb/206Pb
2.10
2.08
2.06
0.84
0.85
0.86
207Pb/206Pb


206Pb/204Pb
18.6
18.4
18.2
18
17.8
0.84
0.85
0.86
207Pb/206Pb

SMM3

SMM15

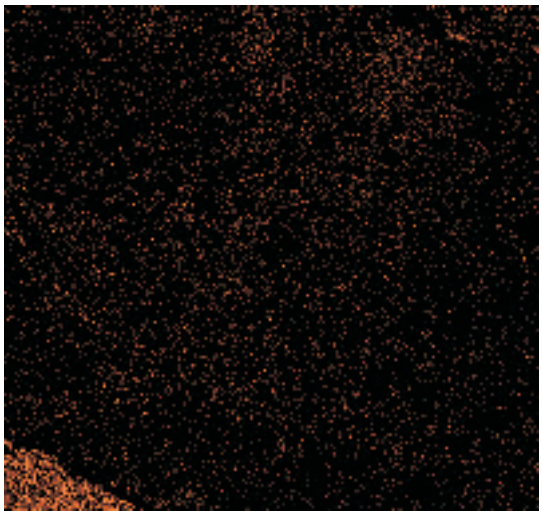
SMM18



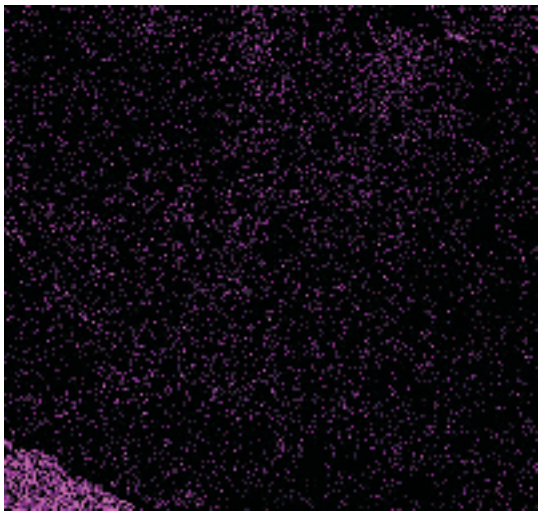
50mm

Cu

As

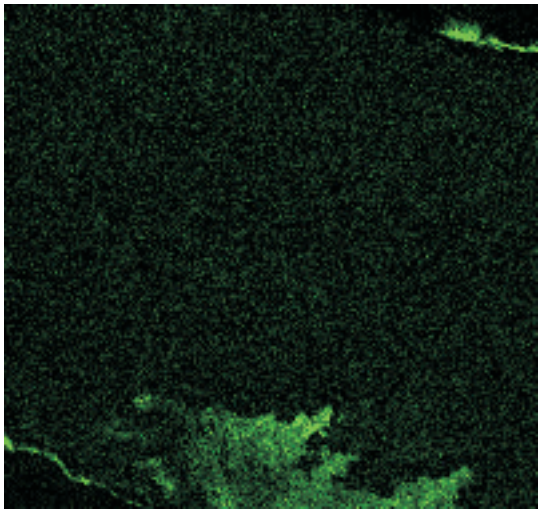


Pb

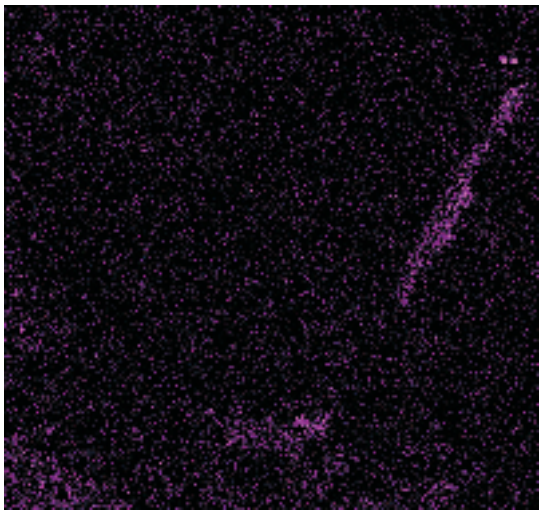


Co

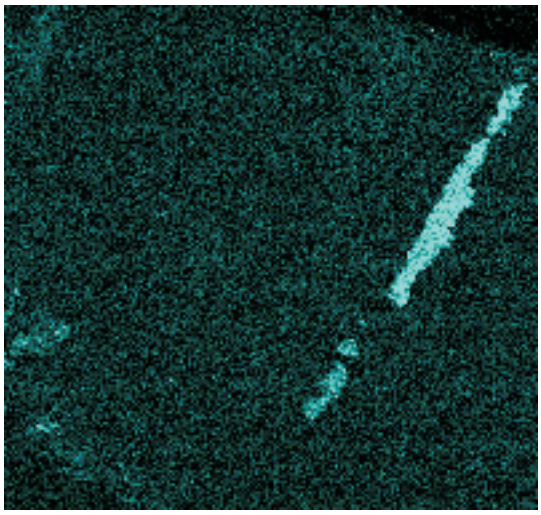
Fe



Ni



Zn



GeoArch

*geoarchaeological, archaeometallurgical & geophysical investigations*


Unit 6,
Western Industrial Estate,
Caerphilly,
CF83 1BQ

| | |
|---|---|
| *Office:* | 029 20881431 |
| *Mobile:* | 07802 413704 |
| *Fax:* | 08700 547366 |
| *E-Mail:* | Tim.Young@GeoArch.co.uk |
| *Web:* | www.GeoArch.co.uk |