

# The Relationship between Iron Age Hill Forts, Roman Settlements and Metallurgy on the Atlantic Fringe

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## Abstract

This thesis presents geochemical records of metalliferous enrichment of soils and isotope analysis of metal finds at Iron Age and Romano-British period settlements in North Ceredigion, Mid Wales, UK. The research sets out to explore whether North Ceredigion's Iron Age sites had similar metal-production functions to other sites along the Atlantic fringe. Six sites were surveyed using portable x-ray fluorescence (pXRF), a previously unused method in the archaeology of Mid Wales. Also tested was the pXRF (Niton XLT700 pXRF) with regard to how environmentally driven matrix effects may alter its *in situ* analyses results. Portable x-ray fluorescence was further used to analyse testing a range of certified reference materials (CRM) and site samples to assess target elements (Pb, Cu, Zn and Fe) for comparative accuracy and precision against Atomic absorption spectroscopy (AAS) and Inductively coupled plasma mass spectrometry (ICP-MS) for both *in situ* and laboratory sampling. At Castell Grogwynion, one of the Iron Age sites surveyed recorded > 20 times Pb enrichment compared to background values of 110 ppm. Further geophysical surveys confirmed that high dipolar signals correlated to the pXRF Pb hotspots were similar to other known Iron Age and Roman period smelting sites, but the subsequent excavation only unearthed broken pottery and other waste midden development. Broken pottery remains were dated to no earlier than the medieval period suggesting a re-occupation, possibly for Pb prospection. It was established that Pb and metal rich soils within the villa footprint have similar isotope signatures to local ores found ca. 4km east, suggesting local ores were used in its construction, possibly with some evidence of *in situ* metal working.

Key words; pXRF, Iron Age, Roman period, Ceredigion, Pb

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## Glossary

AD	Anno Domini (after Christ)
AAS	Atomic Absorption Spectrometry
BA	Bronze Age
BC	Before Christ
BIA	British Iron Age
BP	Before present
CAD	Computer aided drawing
CRM	Certified reference material
DEM	Digital Elevation Models
DGPS	Differential global positioning system
DSM	Digital Surface Model
DTM	Digital terrain Model
EBA	Early Bronze Age
GPS	Global positioning system
GRIP	Greenland Ice Core Project
IA	Iron Age
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IGPET	Igneous Petrology software
Ka yr	Thousand years
LBA	Late Bronze Age
LiDAR	Light detection and radar
Ma yr	Million Years
MI	Micro Litres
MVT	Mississippi Valley Type
NDT	Niton data transfer program
NHSS	National Heritage Science Strategy

Ppm	parts per million
ppb	parts per billion
pXRF	Portable x-ray fluorescence
RCAHMW	Royal Commission for Ancient and Historic buildings Wales
RPD	Relative percentage difference
Rsd	Relative standard deviation
$\mu\text{g/ml-1}$	Micro gram per milli litre
$\mu\text{g/g-1}$	Micro grams per gram
XRF	x-ray florescence

# Chapter 1

## Introduction

There is evidence to suggest that metal exploitation by both mining and smelting metal rich ores has been operating in Wales from the Early Bronze Age until the late Roman period *ca.* 4800 – 1574 yrs. BP (Cunliffe, 1978, 2004; Timberlake, 1987, 1988, 1994, 1995, 2003, 2004, 2011, 2013; Musson *et al.*, 1991; Mighall and Chambers, 1995, 1997; Mighall *et al.*, 2002, 2009; Crew, 2002; Craddock, 2003; Pickin and Timberlake 1988; James, 2006; Jenkins *et al.*, 2001). However, there is an anomalous gap in the history of metallurgy in Ceredigion between 2800 - 1950 yrs. BP, which is referred to as the Iron Age. This is a mystery, as North Ceredigion is rich in metal ores and numerous Iron Age settlements located near these ore lodes (Timberlake, 2003; Driver, 2005). This thesis will investigate this gap in our knowledge.

The aim of this thesis is to investigate hill forts and Romano-British settlements for metalliferous deposits concomitant with this period of use. If evidence of metallurgical practice is found it may further explain the gap in our knowledge of the Iron Age relationship with metal and whether metal exploitation in North Ceredigion continues through the period, as it does at other sites North Ceredigion and is contemporaneous with other sites on the Atlantic fringe.

Wide archaeological research has utilised site artefact typology, field geophysics and laboratory based geochemical techniques to identify geochemical archives and settlements where metals have been produced across Europe and the Near East. This study uses portable x-ray spectrometry (pXRF) to assess *in situ* soils for enriched metalliferous content, which may suggest past metal exploitation. Use of this type of portable analytic method has seen only limited application in the field of archaeo-metallurgy on many of the metal rich soil and sediment archives, which attest to prehistoric and classical periods of metallurgy on the North Atlantic fringe. This includes Wales, south west Britain, Ireland, and northern Spain.

Driver's (2005, 2013) research on the '*Architecture and Regional Identity and Power in the Iron Age landscape of Mid Wales*' raised questions about whether there is a

relationship between settlements and metallurgy in the hinterland and uplands of North Ceredigion during the Iron Age. Previous work using pXRF has been successful in identifying heavy metal deposition, from seven millennia of smelting processes in the ore rich Southern Faynan region of Jordan. Here it has been left *in situ*, undisturbed for millennia. Ceredigion also has a rich history of metal exploitation over the last five millennia but there has had been limited use of pXRF, which has mainly been concentrated on the re-deposition of mining waste deposited through overbank flooding and re-mobilised by river bank accretion since its initial deposition (Foulds *et al.*, 2014). The interest is whether or not pXRF could be applied to assess hill forts for any metalliferous evidence indicating past metallurgical processes. This thesis assesses this by analysing soil and artefacts to test three hypotheses:

1. There is a direct spatial relationship of Iron Age and Roman metallurgy at settlements in North Ceredigion.
2. The late Romano-British villa at Abermagwr used local ore to produce the metal in its construction.
3. Portable x-ray spectrometry (pXRF) is affected by environmental bias due to high water content.

This study surveyed six of a larger set of sites included in Driver's (2005) thesis and work by Davies and Driver (2011) on the Romano-British Abermagwr villa. These included three upland sites at Pen Dinas (Elerch), Banc-y-Darren, Castell Grogwynion (Castle of the White Stones), one lowland enclosure, Odyn Fach (Small or Little Kiln), two Roman sites Llys Arthur (Arthur's Place), and the Romano-British villa at Abermagwr.

### **1.1 Rationale for site selection**

Although there are numerous sites to choose from in North Ceredigion, this study selected sites for one or more of the following reasons;

- They provide a representative section of upland and lowland sites from both Iron Age and Roman periods and cover the Bronze to Iron Age transition period where it is suggested development started.

- Two of the Iron Age sites at the Northern fringe of Ceredigion are in close proximity to each other's lodes and may have some relationship with other nearby sites.
- Previous finds of metal rich artefacts at two of the Northern sites have not been re-examined since these finds.
- None of the sites have previously undergone a rigorous survey of the geochemistry of the soils.

As many sites are located close to ore lodes or mining that shows evidence of prehistoric exploitation, it was therefore, concluded that these sites may have soil archives that could be effectively analysed for any metal concentrations above background levels for mid Wales.

## **1.2 Thesis structure**

Chapter Two outlines the geological development of the Cambrian Ore Fields, with a detail description of the lodes and specific mineralisation and wealth of ore assemblages in North Wales and Ceredigion. Geochemical archives can record evidence of metalliferous activity in sediment deposited by both atmospheric and terrestrial pathways. These may be concentrated within or nearby the hill forts and settlements selected for this thesis. These kinds of deposits are often found in lacustrine cores, peat deposits, over bank river deposition and *in situ* contamination from past quasi industrial activities. The study will also consider changing land use and hill fort development and whether these have had any effect on the geochemical makeup of the soils. Additionally, how soil chemistry may affect the solubility of heavy metals and contamination pathways are explored. The study highlights other work that has been carried out on pre-historic and classical period metal production and the geochemical archives it has left within Britain, Ireland, Spain and the Near East, and what this research has added to the narrative of metal exploitation since its early

origins. It discusses the methods that have identified sites containing evidence of Bronze Age, Iron Age and Roman period metallurgical activity.

Chapter Three gives an overview of Iron Age hill fort development and chronology from the late Bronze Age until the Roman period. This is followed by a detailed description of the geographical and geological context of the study sites, with a description of previous research on or near the selected sites being outlined.

Chapter Four details the analytic methods used and how preliminary site visits developed sampling strategies for the initial site pXRF surveys at each location, and methods used to evaluate artefacts that have been found there. Descriptions of the laboratory techniques used for both analysing samples and finds made during site surveys are also provided as they are for the different software packages which were used, including Sigma plot, CAD and Arcmap and Arcscene, which were used in the presentation of contamination distribution. It further outlines how portable x-ray fluorescence was used for *in situ* sampling and how testing and comparative work was carried out, further outlining the advantages and dis-advantages of *in situ* analysis. It compares and contrasts the accuracy and precision of the pXRF with Atomic Adsorption Spectrometry (AAS) and Inductive Coupled Plasma- Mass spectrometry (ICP-MS). It critically evaluates other work carried out over the last two decades on pXRF analysis and compares some of this work to the findings of this study. A synthesis of all these findings builds a strong case for its application to *in situ* analysis, which is key for this study.

Chapter Five collates and describes all of the data and finds collected for this study, which includes the site surveys, geophysical field surveys and site excavations. It discusses each site's survey giving a spatial context by using maps and photographic evidence to support key findings. These include hot spots of enrichment which may be associated with pyro-metallurgy at the selected sites. It details the interpretation of hotspots and applies other methods to test the hypotheses formulated during the pXRF survey. It analyses unexpected finds, and how these could be further explored in a new avenue of enquiry into post- Roman use of hill forts and settlements.

Chapter Six draws together all of the points made in the results and interpretation section with an overall discussion highlighting how this study compares with similar work on pXRF. Moreover, how it has led to the outcomes and articles expected from this study and the reports and papers already published. It outlines the strengths of *in situ* analysis and how continued application by this method can add a new approach to archaeology and geochemical analyses, but also highlights the limitations of pXRF for certain elements. Finally, it discusses how the outcomes of this thesis could be further developed by exploring a larger set of Iron Age and Roman period settlements to understand how these have been used since the end of the Roman Period. This may add a further layer to the rich and diverse narrative of the metallurgical importance of Ceredigion's pre-historical and Classical periods.

Chapter Seven returns to the initial hypothesis testing set out in Chapter one and gives a final assessment of the outcomes.

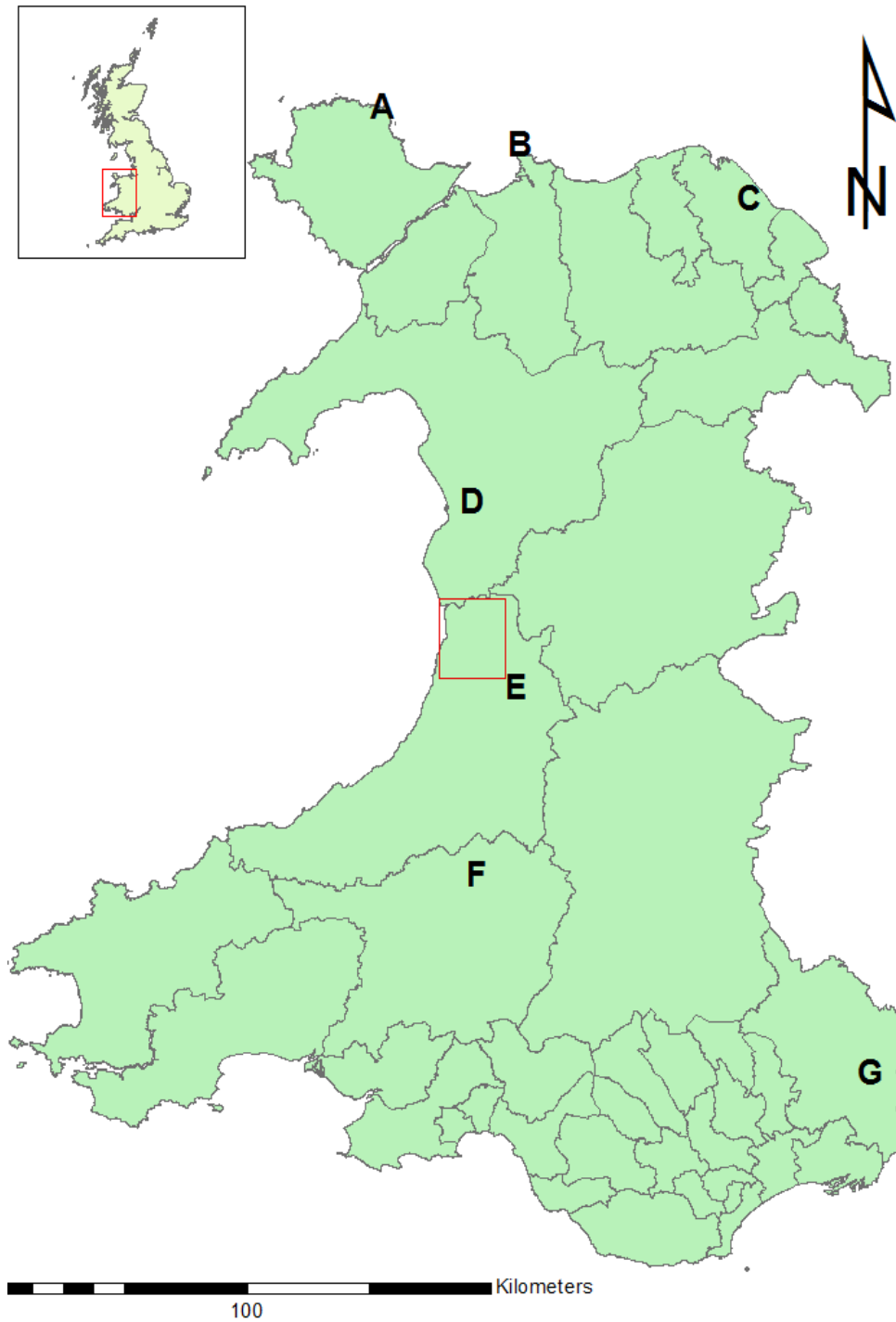


## Chapter 2 Background

### Introduction

The last fifty years have seen an increased interest in archaeo-metallurgy, its origins, and the technological advances through pre-historic to the Classical periods. This has often been due to metal artefacts being well preserved and with the attachment of a metal value (Thornton and Roberts 2009). Evidence of the earliest known metal rich ore extracted for smelting (pyro-metallurgy) suggests that it originated in the Near East during the Chalcolithic (Copper Period), *ca.* 7000 yrs. BP (Barker *et al.*, 2007; Hauptman *et al.*, 1986; Hauptman, 2007; Grattan *et al.*, 2007; Hunt *et al.*, 2007; Levy *et al.*, 2002; Pyatt *et al.*, 2001, 2002, 2005). But it was not until the British Bronze Age *ca.* 4500 yrs. BP that Britain and Ireland saw the beginning of pyro-metallurgy (Cunliffe, 1974; O'Brien 1995). Subsequently, exploitation during the Bronze Age, Iron Age and Roman periods targeted the metal rich mineral deposits found throughout Britain. Wales was no exception, with rich deposits of metal bearing ores, yielding copper (Cu) at the Great Orme, Llandudno and Parys Mountain, Anglesey; lead (Pb) in the Llanrwst ore fields of North Wales; lead, zinc (Zn), copper and silver (Ag) in the Central Wales Ore fields, gold (Au) in mid Wales and rich iron deposits on the Welsh borders and the Forest of Dean in the south east of Wales [see Figure 1].

From the onset of ore extraction and smelting, artefacts have been left in or near prehistoric and classic period industrial centres. Wider evidence of ancient metallurgy can be found within soils, lacustrine sediment, fluvial peat, and arctic ice cores. The natural geochemistry of these systems may have been altered by natural fluxes or anthropogenic inputs (Abrahams 2010; Grattan *et al.*, 2002, 2007; Shotyk *et al.*, 1997; Mighall *et al.*, 2002 Hong *et al.*, 1994, 1997). These geochemical archives have been successfully used in parallel with artefact typology to research prehistoric to historic metal exploitation (Timberlake, 1987, 1988, 1994, 1995, 2003, 2004, 2011; Jenkins and Lewis, 1991, Mighall and Chambers, 1997; Lewis, 1996; Mighall *et al.*, 2002, 2009; Timberlake *et al.*, 2004), developing our understanding of the historic development and overall importance of metallurgy.



**Figure 1.** Centres of ferrous and non-ferrous metal rich ore deposits throughout Wales.

**A.** Parys Mountain Anglesey. **B.** The Great Orme, Llandudno. **C.** Llanrwst ore fields **D.** Dolgellau gold belt  
**E.** Central Wales Ore field. **F.** Pumpsaint (Dolaucothi gold mines) **G.** Borders and the forest of Dean. The red box in North Ceredigion has an abundance of Roman and Iron Age settlements and forts include the sites selected for this study.<sup>1</sup>

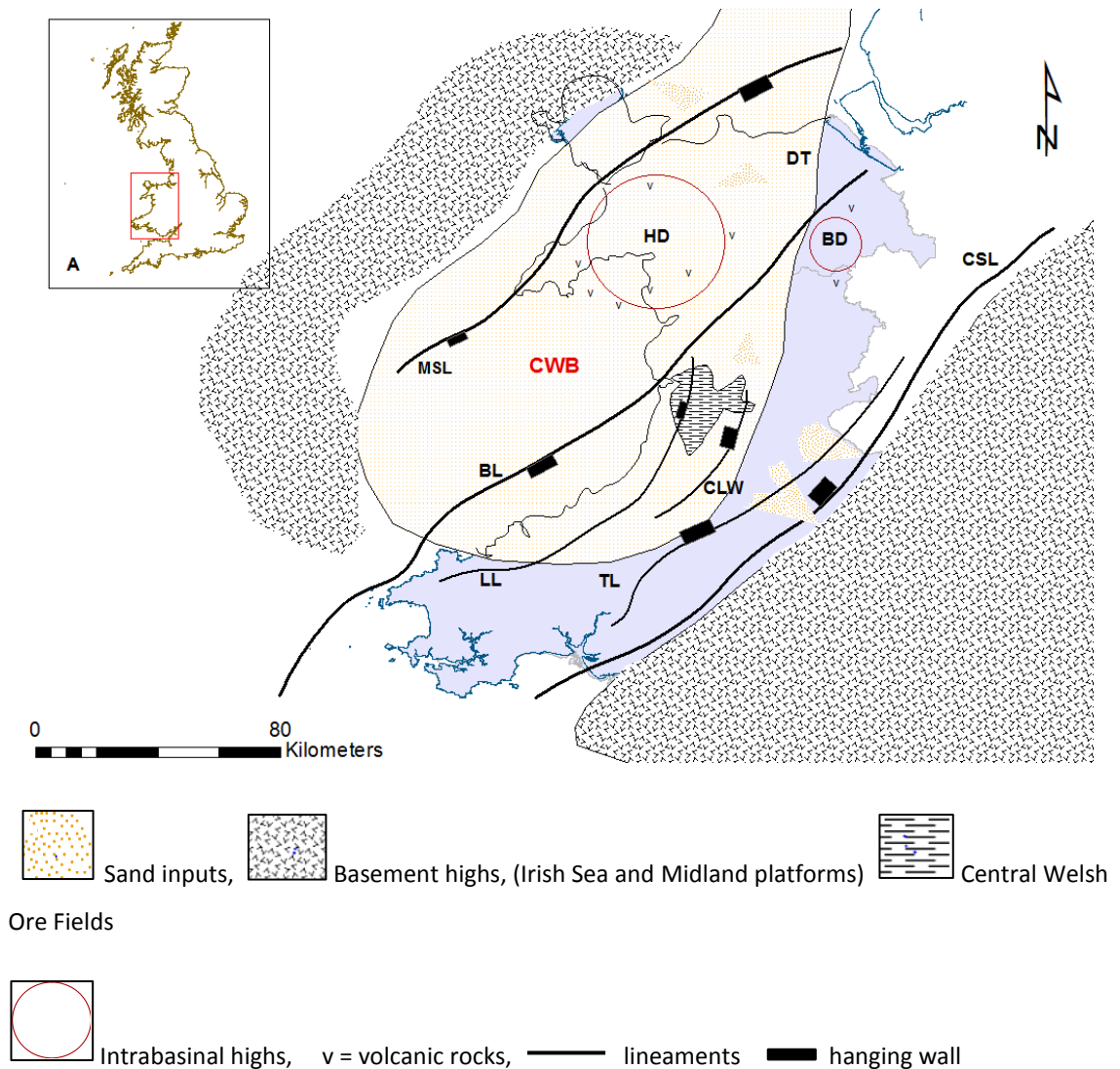
During the Late Bronze Age into the Iron Age, a parallel period of hill fort development took place throughout Northern Europe. This may have been ongoing since the Late Bronze Age. Of *ca.* 4000 forts that have been identified throughout Britain (Hogg, 1975) > 1200 are situated in Wales (National Museum Wales, 2015), although some of these could be termed defended farmsteads or enclosures (CADW, 2015). However, sites are found in a range of locations from the coastal fringes, hinterlands and eastern border with some specific nucleation of Iron Age sites, (see section 2.8 Figure 8 and Figure 9).

There is evidence of metal ore exploitation and metal production from the Bronze Age (Jenkins and Lewis, 2001; Mighall *et al.*, 2009; Timberlake 1998, 2003, 2011). Geochemical and typological analysis have successfully identified and dated evidence for pyro-metallurgy within many Iron Age settlements in Wales (Musson, 1991; Mighall and Chambers, 1997; Quinnell *et al.*, 1994; Crew, 2002). However, North Ceredigion's Iron Age hill forts have produced little evidence of contemporaneous Iron Age metallurgical workings. Here, there are only a few 'presumed' iron rich slag finds that have been uncovered (Murphy 1988; Driver, 2005). The continuum of Classical Roman period metal exploitation has left significant evidence in North and South Wales, with geochemical and typological evidence in Mid Wales' peatlands (Mighall *et al.*, 2002, 2009).

The abundance of metal ores throughout Wales is apparent, with copper being targeted during the Bronze Age and possible during Iron Age periods. It has left contamination of copper, zinc and lead around mining and smelting sites. The following section details lodes and content within North Ceredigion.

## **2.2 Structural geology and mineral assemblages in Mid Wales**

The Welsh Basin developed during the breakup of Gondwanaland in the late Ordovician period, forming a trans-tensile mobile zone situated on the Northern margin of the Avalonian terrane. During the late Ordovician, cessation of major volcanic activity gave way to turbidite influxes in a deep marine environment. Glacio-eustatic rise in sea level during the late Ordovician and Silurian created phases of anaerobic and dysarobic mud deposition (Benchley and Rawson, 2006). Subsequent to this, there was strong influence by syn-sedimentary half-graben development [see Figure 2]. The shallow marine shelf was immediately east of the Tywi Lineament and a NW-facing slope-apron developed when the lateral sediment supply rates were high relative to the sloping seafloor. Conversely, when supply rates were comparatively low the sea-floor slopes above footwall crests were reversed, the ponded mini-basins then developed above the hanging wall of the adjacent lineaments to the west of the Central Wales Lineament and the Llangranog Lineament. The complexity of the development of the Welsh Basin is described in full by Benchley and Rawson, (2006).



**Figure 2.** A simplified schematic diagram of the Welsh basin with the Late Ordovician–early Silurian tectonic setting of the host rocks of the Central Wales Orefield.

The Central Wales Basin (CWB) lies in a trans-extensional mobile zone between the Menai Straits Lineament (MSL) and the various elements of the Welsh Borderland Fault System which include; the Tywi Lineament (TL) and Church Stretton Lineament (CSL). Other lineaments and troughs within the Welsh basin include the Bala Lineament (BL); Central Wales Lineament (CWL); Llangranog Lineament (LL) and the Denbigh Trough (DT). Intrabasinal highs include the Berwyn Dome (BD) and Harlech Dome (HD).

Re-drawn from: James, (2011) and Woodcock, (2000).

The Welsh basin is made up of three mini basins, [see Figure 3], which are the accumulation sites of turbidite sandstones (James, 2011). These are now inliers of Ordovician Lower Llandovery and Ashgill/Caradoc undivided mudstone and slate, with some sandstone situated in northern Ceredigion. These are surrounded by the Silurian

Upper Llandovery and Mid Llandovery undivided mudstone, slate and sandstone (Hutt, 1974).

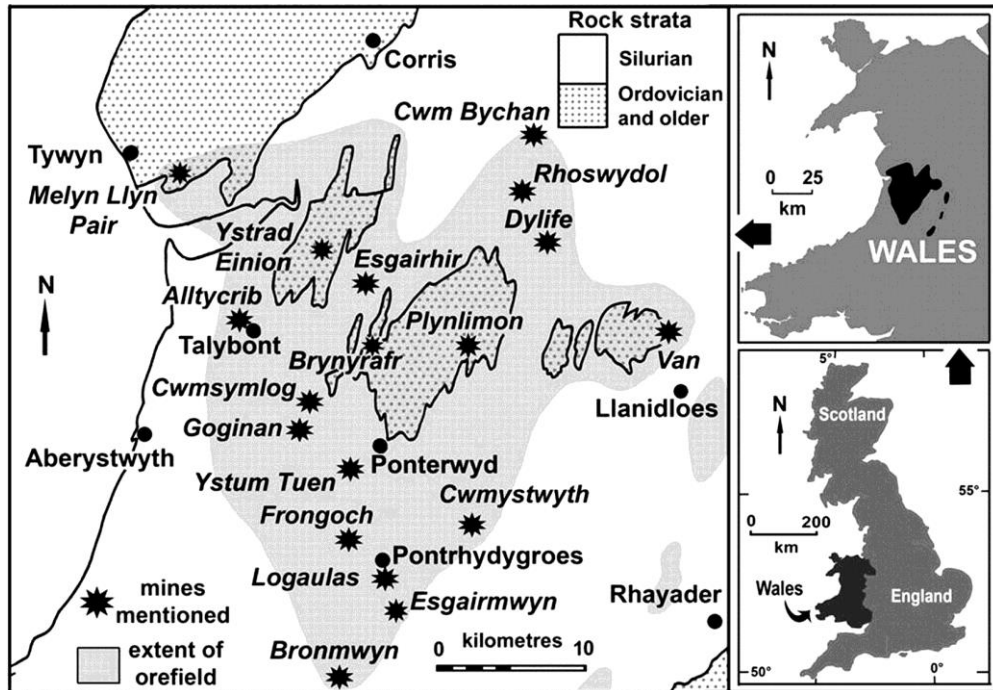
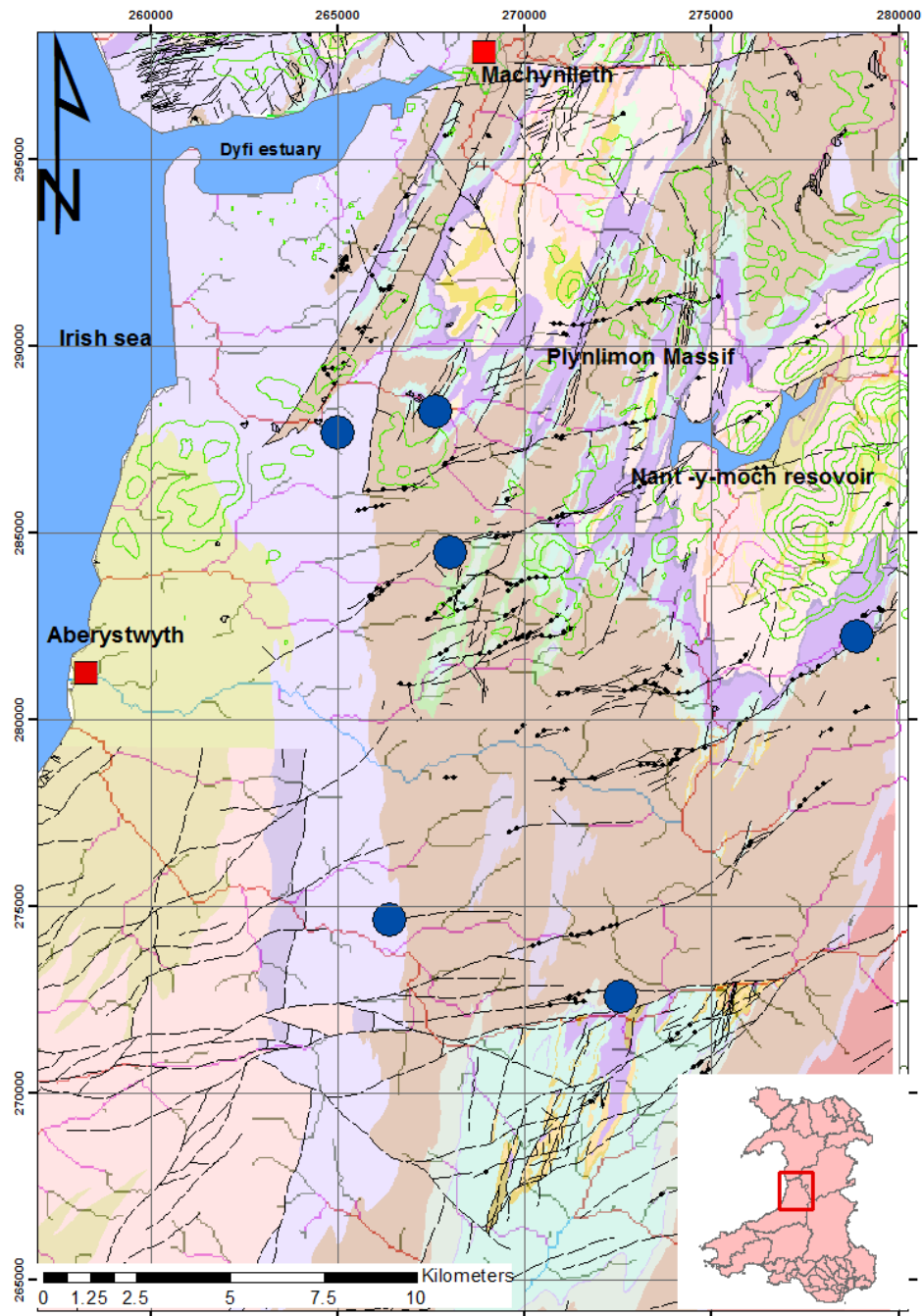


Figure 3. Central Welsh ore field with inliers. Source: James, (2011).

By the end of the Silurian period the Welsh Basin was an active extensional basin which faulted and subsequently fractured sedimentary lithology derived from turbidity flows. Sphalerite, chalcopyrite and galena formed in these host rocks as mineral rich fluids crystallised to the vertical or inclined fractures in the interbedded greywackes, siltstones and shale forming the lower part of the Frongoch Formation (Phillips, 1972).

## Main lodes and site locations



**Figure 4.** Geology, map of the mineral lodes and key in relationship to the site locations. Source: Edina (2013).

The geological map of the Cambrian ore fields with the fractures and lodes, sites for this study are indicated in blue

## Key for geology, towns and survey sites



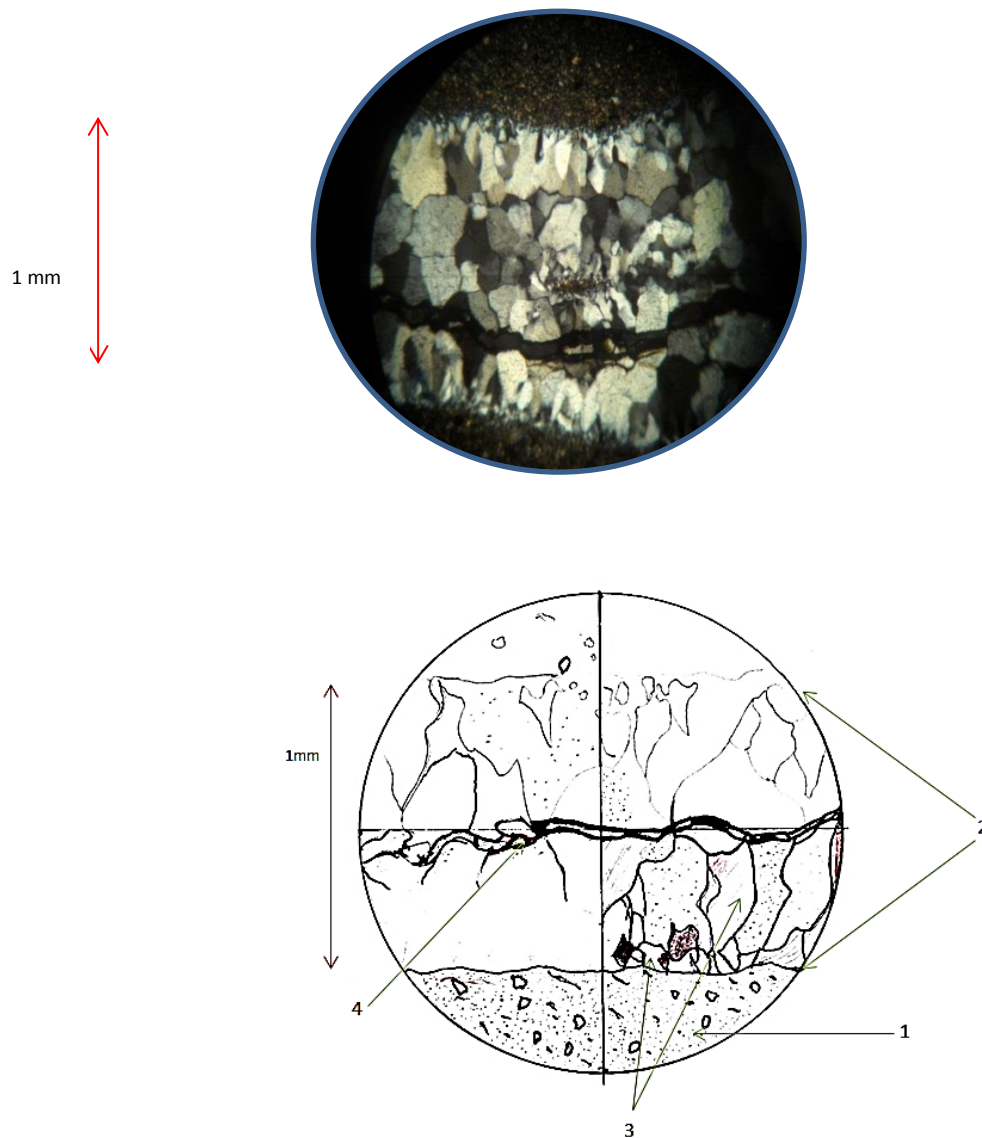


### 2.3 Mineralisation

The Central Welsh Ore field which developed within the Welsh Basin extends from Machynlleth in the north, to Tregaron in the south, and from Aberystwyth in the west to Llanidloes in the east (Phillips, 1972). It is termed a 'polyphase mineralised terrain' in which the paragenesis comprises twelve discrete mineral assemblages. These fall into two groups: 'early complex' A1; and 'late simple' A2. Many fractures (lodes) carry assemblages from both groups in crosscutting relationships that are indicative of repetitive fracturing and mineralising events (James, 2006). There are three main discrete inliers with different degrees of mineralisation situated east to west from Machynlleth to Llanidloes. Here, mineral deposits were formed by the recirculation of fluid inclusion and the scavenging of minerals from country rocks from the Welsh Basin *ca.* 440 Ma [ $\pm$  40 Ma yrs.]. Pore fluids show zonal nucleation as quartz deposited on brecciated or slightly re-crystallized wall rock.

Chalcopyrite, sphalerite, siderite, galena and barytes formed within these primary deposits (Phillips, 1972; James, 2006); however, galena and sphalerite often formed directly onto rock fragments (Phillips, 1972).

This thin section image and drawing, [Figure 5], taken from Grogwynion mine near Castell Grogwynion shows the formation of quartz and other minor impurities on the host rock, often a seam of metal rich deposit with infill in the space between the gangue [quartz and impurities] typical of the regional mineralisation.



**Figure 5.** Photograph and thin section drawing of the regional mineralisation.

1. The mineralisation is 73% of well sorted greywacke which contains sub rounded 20% quartz and 5% muscovite with some minor mineralisation.
2. The anastomosing vein is *ca* .1mm with 90% mineralisation. In cross polarised light (xpl) there are some grey and cream interference colours which fade to extinction every  $90^{\circ}$  [this fading is undulous].
3. The quartz grades inward growing in a dog tooth manner with the larger *ca*.0.5 mm nearer the centre and the smaller  $< 0.1$ mm on the crystallised wall
4. Some of the inner most section is unfilled or brown (iron)

## 2.4 Mineral assemblages

### 2.4.1 Sphalerite (ZnFe)S

Sphalerite has a tetrahedral and dodecahedral crystal system with a cubic shape. The chemical composition is zinc sulphide (ZnFe)S, commonly formed with quartz and galena as in many of the mineral lodes of the Cambrian Ore Fields. It is normally visually identifiable by its density and reddish brown to black colour with a non-metallic lustre. It contains a range of other elements as impurities, particularly iron, which affects its colour. Cadmium, if present in sufficient amounts in ground water or as dust dispersed from old mine tailings can constitute a groundwater geo-hazard, (British Geological Survey, 2012).

To place the mineralisation into a geological context is difficult, but it shares similarities to Mississippi Valley Types (MVT) where the mineralisation is formed in areas of shallow water sedimentation separated by shale-rich basins which are similar to the turbidites of the Welsh basin. The later fractures have allowed uprising solutions to form mineral lodes (N. Pearce, pers. comm. 2011).

Sphalerite is widely distributed in the Cambrian Mountains and was extensively mined over many areas. However, unlike copper, lead, gold and silver, zinc was not extracted commercially in Europe until *ca.* 260 years ago, and then primarily by William and John Champion, who devised processes to recover the metal from smithsonite and later from sphalerite ore, also referred to as ['blende' or 'black jack']. Ore was mined in many areas of Wales, most notably in the Halkyn-Minera and Llanwrst orefields of the Northeast and the Central Wales Orefields. Later exploitation retrieved sphalerite from early lead mining spoil at Grogwynion until *ca.* 1904 (Palumbo *et al.*, 2009). After refining zinc was use in commercial zinc plating processes.

#### 2.4.2 Galena (PbS)

Galena, a cubic crystalline ore, is widely distributed in the Cambrian ore fields, and has a similar geological context to that of Sphalerite (Haggerty *et al.*, 1996; N. Pearce, Pers. comm., 2011). The colour, density and perfect cubic cleavage of galena make it easily identifiable. However, there are two varieties that are less easily distinguishable. These are 'steel-ore', which looks like broken cast iron on fracture-surfaces and a foliated ore which has a streaky fibrous appearance. Both can be found in Wales and have often been formed by recrystallization and shearing respectively. The process of shearing affects galena due to its soft ductile properties, with other more brittle sulphides tending to suffer cataclasis [deformation of the brittle ore] by movement along a mineralised fracture, or by compressive deformation.

Galena occurs in abundance in the mining area that stretches from Machynlleth in the north to the Llandovery-Carmarthen district in the south, and as far east as Caersws, Rhayader and Llanwrtyd Wells. The mineralisation occupies a series of mainly ENE-trending fault-fractures that have experienced repeated episodes of movement and mineralisation. Galena deposits range in size from small lenses to thick ribs often over 1 metre wide (James, 2011).

Lead, which is extracted from galena, has a long history of economic importance in Wales. Exploitation of Pb dates back to the Roman period and possibly to the late Iron Age, with later industrial-scale mining activity for this mineral recorded during the 16<sup>th</sup> - 19<sup>th</sup> centuries, peaking during the 19<sup>th</sup> Century (Bick, 1988, 1993). Some of these locations, such as the Van mine had international importance during their operating period. But mining declined during the 20<sup>th</sup> Century with very little activity taking place after the Second World War (Museum of Wales, 2012). Some deposits contained prolific mineral inclusion assemblages of argentine tetrahedrite ((Cu,Ag)<sub>10</sub>(Fe,Zn)<sub>2</sub>Sb<sub>4</sub>S<sub>13</sub>). The high silver [Ag] content was exploited in early Roman and later 17<sup>th</sup> -18<sup>th</sup> Century mining periods (Mason, 1997), with some deposits yielding *ca.* 1000 ppm of silver (Hughes, 1981). Records of the outputs from later exploitation are given in Bick (1974, 1988), while the ore mineralogy is covered by Raybould (1974) and Mason (1997).

### **2.4.3 Chalcopyrite (CuFeS<sub>2</sub>)**

Like galena and sphalerite, this tetragonal ore is widely dispersed in the Cambrian ore fields. Its chemical composition is copper iron sulphate and is identified visually, both in hand specimens and in polished sections by its brassy appearance (Mason, 1997).

Chalcopyrite is the local principal ore of copper and occurs in many primary ore deposits, from medium-temperature mesothermal lodes, porphyry-style mineralisation to low-temperature MVT deposits. It also occurs as a diagenetic/low-grade metamorphic mineral. Like many sulphides it tarnishes when exposed to air with the colours varying, but often including blues, greens and purples. Its un-weathered rich golden yellow colour can attract attention in freshly-broken rock samples due to the small flecks in quartz gangue that are often referred to as fool's gold. (National Museum of Wales, 2012).

Chalcopyrite was an important mineral to the Welsh mining industry for centuries; it was the main economic mineral extracted from Parys Mountain Copper Mine. At the Great Orme mine near Llandudno, the deeper 19th Century workings exploited the secondary ores of malachite in the oxidised zone. The majority of metalliferous mineral veins known to exist in Wales contain chalcopyrite in trace to major deposits, or the mineral occur as fine disseminations within the host rock. (National Museum of Wales, 2012).

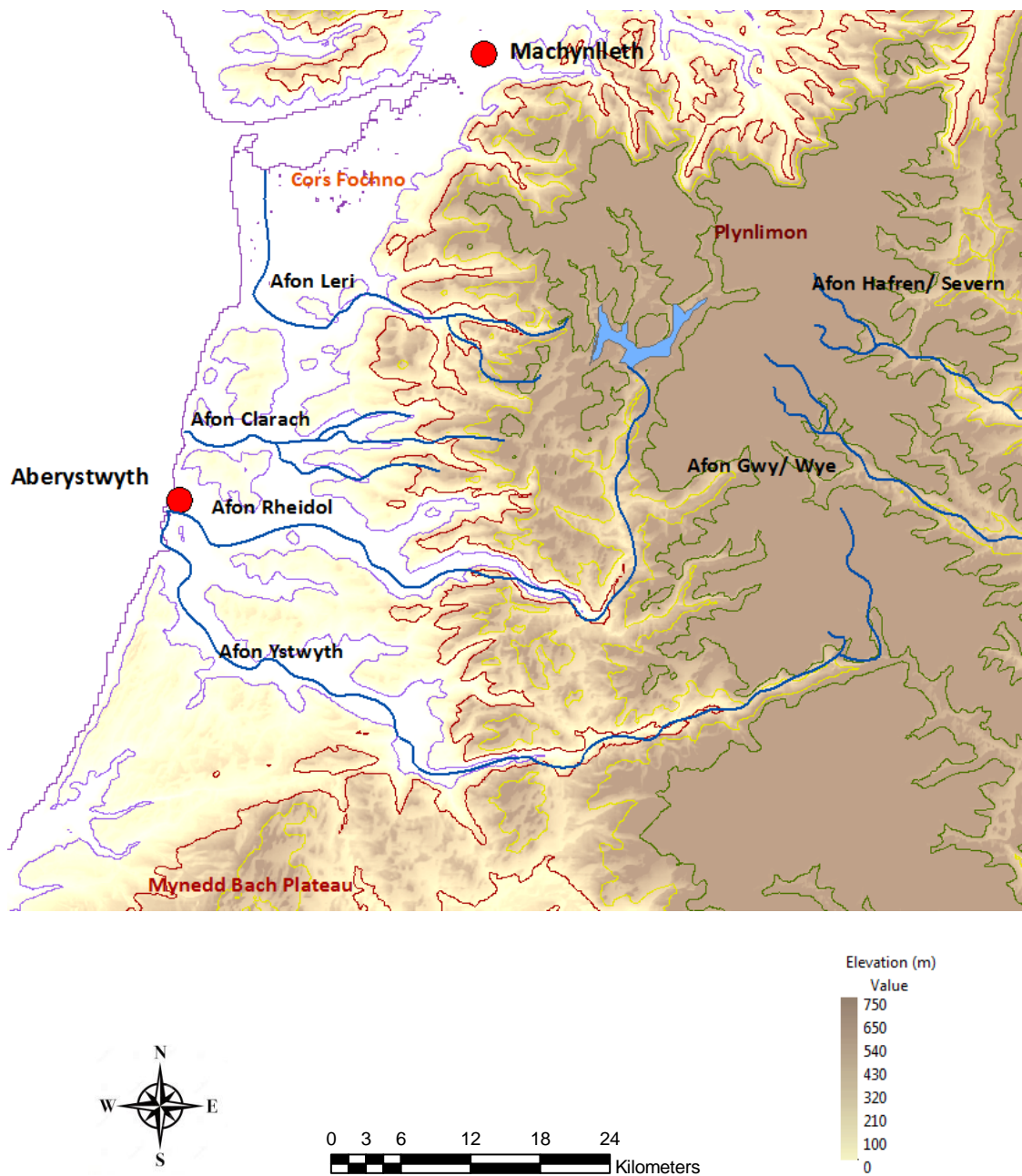
### **2.4.4 Iron ore**

There are numerous deposits of iron ore in North and South Wales, albeit varied in their mineral formation and extraction. These range from oolitic and pisolitic deposits in Silurian sedimentary mudstones situated in north-west Wales, to limestone hosted clay ironstone in many South Wales coal measures. Oolitic ores are also found in the river systems often washed from limestone-rich deposits. Haematite (Fe<sub>2</sub>O<sub>3</sub>) ore found outside the margins of the South Wales ore fields is similar in composition to ore from the Forest of Dean (North, 1962). Most of these ores were exploited during the 17<sup>th</sup> Century; however they were of poor metal quality with a low iron concentration (Timberlake, Pers. comm., 2013)

Ore for iron production during the Iron Age and later periods up to the industrial age was often sourced from bog iron deposits. These form as a soft porous hydrated iron oxide limonite ( $\text{FeO}(\text{OH}) \cdot n(\text{H}_2\text{O})$ ). It is formed by the precipitation of iron from freshwater in wetlands after the water has passed through iron-rich sedimentary rocks. It can be both chemically or biochemically oxidised to its ferric form. In aerobic soils it gives a characteristic red colour sometimes welling up to the surface with an oily looking precipitate on the water's surface. The overall process can be accelerated by microbial activity where iron is reduced to the ferrous form in an anaerobic environment. Iron oxide may have a characteristic grey or grey-green colour; here, the ore minerals are hydrous ferric oxides. These are mainly hydro-goethite ( $\text{FeO}(\text{OH})$ ) or siderite  $\text{FeCO}_3$ , dependent on the local geology. Iron content can be variable but weathering of the local lithology reduces other elements often creating an iron-rich ore (Paynter, 2006). Thus, abundant iron ore sources suitable for Iron Age technology to exploit are to be found throughout Wales.

## **2.5 Landscape, climate and agriculture**

North Ceredigion has a diverse landscape, with a variable western coastal boundary stretching from the Dyfi estuary in the north to the coastal village of Llanon, 30 km to the south. This coastline gives way to a hinterland of sloping hills and mainly east-to-west oriented valleys. Further east the Cambrian Mountains create a natural upland barrier. This includes the Plynlimon Massif in the north-east and Mynedd Bach Plateau to the south [Figure 6].



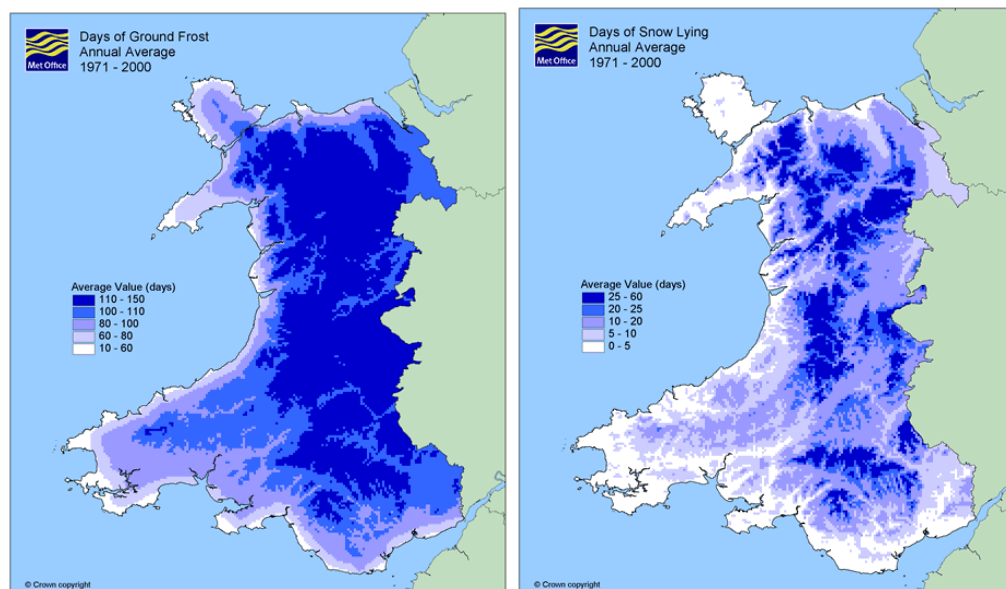
**Figure 6.** Main rivers, peatland and upland areas of North Ceredigion. Contours at sea level, 100m, 200m, 300m and 400m.

The upland areas are catchments for the rivers Rheidol, Ystwyth and Clarach which flow west to Cardigan Bay and the Afon Leri situated to the north which flows directly into the Dyfi estuary. Holocene alluvial landscapes often contain rich cultural and environmental records including evidence of historic metal exploitation (Macklin *et al.*, 1994, 1996, 1997; Foulds *et al.*, 2014). The two major peatlands of Cors Fochno (Figure 6) and Cors Caron are situated in the north and south of North Ceredigion respectively. Cors Fochno 12 km south-west of Machynlleth has buried geochemical evidence of

metal enrichment suggesting both Bronze Age and Roman metal exploitation (Timberlake and Mighall, 2013), but no evidence of Iron Age metallurgy.

## 2.6 Climate

Since the end of the last glacial maximum *ca.* 20 k yrs. BP the climate affecting Britain and northern Europe has varied between warm and cool. The Younger Dryas (Loch Lomond Stadia) 12.9 – 11.5 ka Cal. BP was the last major cold period. It was followed by shorter cooler and warmer periods which may have had a lesser impact on the upland areas of Britain (Hughes, 2002). Today Ceredigion benefits from warm maritime air keeping the coastal and hinterland region up to *ca.* 9 km inland free from prolonged frosts or lying snow during the winters (Met Office, 2014). These conditions may be similar to the mid and late Iron Age period, but it is postulated that possible climatic perturbations may have caused periodic abandonment of hill forts during the early Iron Age and this is considered to have been one of the reasons for hiatuses in Iron Age fort development (Cunliffe, 1994). Alternative theories are discussed later in this chapter.



**Figure 7.** Days of ground frost and lying snow. (Metoffice 2014).



## **2.7 Agriculture**

There is evidence to show clearance and regeneration of upland areas during the late Bronze Age – Iron Age transition, with transhumant grazing and cereal crops often grown from the lowlands to above 450 m (Dark, 2003).

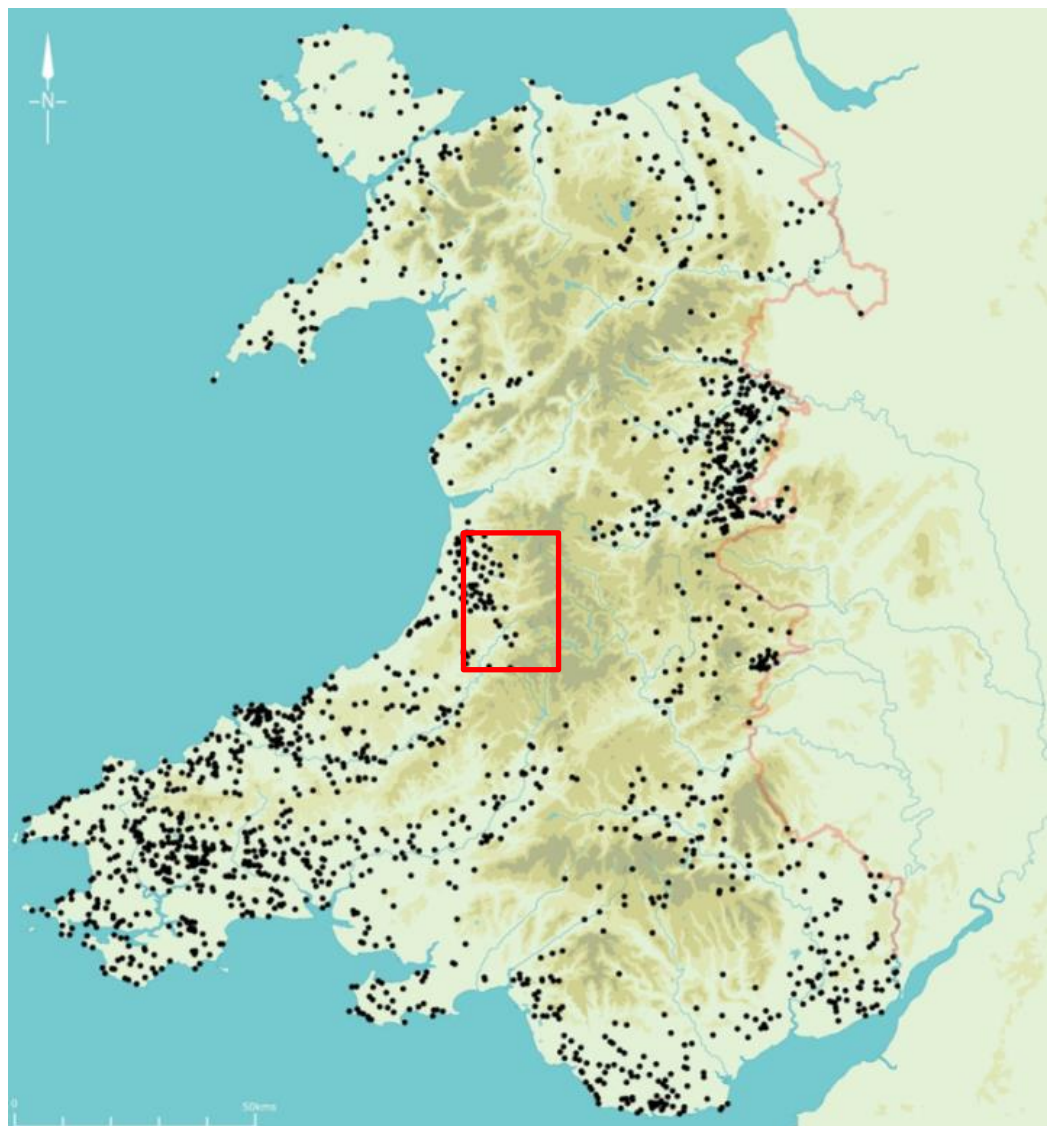
Later land improvement to some central areas of the hill forts was carried out using modern farming techniques (Overton, 1996). Since then, further agricultural work on these sites has been limited at most of the scheduled hill forts. Some may have been too difficult to work on due to their position and access. But possibly one of the main reasons for the limited upland pasture improvement is the limitation on the peaty soils ability to retain nitrates or phosphates (Cuttle and James, 1995). Thus, it is presumed agricultural practises were limited to the lowland, more fertile soils. However, alternative palynological records suggest upland agriculture may have expanded during the late Bronze Age - early Iron Age transition (Moore and Chater, 1969; Dark, 2006); this also contradicts the idea of hill fort abandonment.

There is some evidence of medieval use of hill forts, but it was limited to some Anglo-Saxon re-use of these settlements in England (Williams, 1999), but little is known of any late medieval use of these sites. Since these hill forts were made scheduled sites the only other work that has been carried out is limited grass and bracken clearance often as a consequence of livestock grazing. Importantly for this study the limited use and lack of land improvement may have left some geochemical evidence within hillfort soil archives.

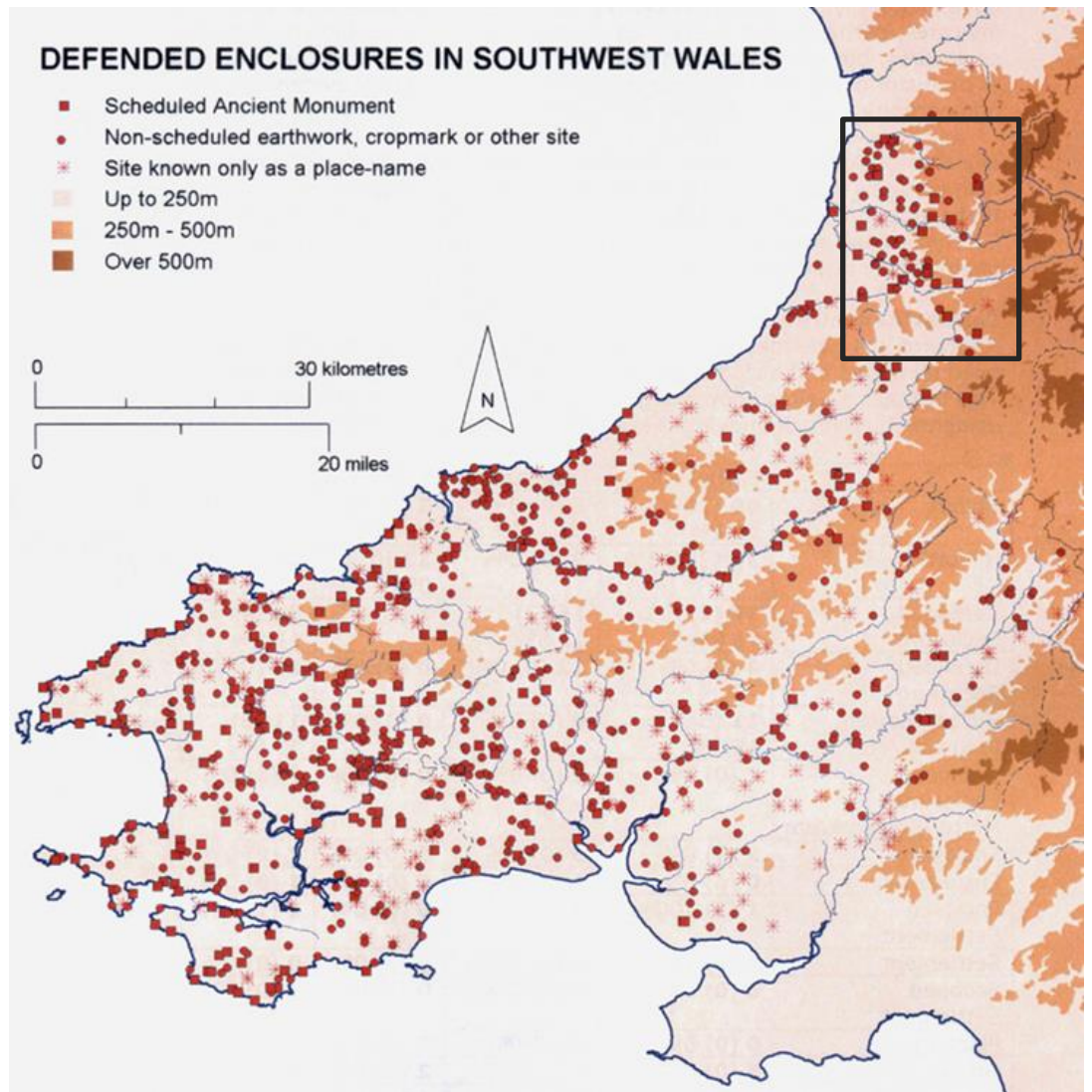
## **2.8 Distribution, architecture and purpose of hill forts**

Hill forts are widely distributed throughout Wales [ Figure 8 and Figure 9], with a greater density across the more fertile lowlands of West Wales and the South Wales coast and hinterlands (Hogg, 1979). Other areas with increased density are the borders of modern day Shropshire and Powys, and the Mid Wales coast and hinterland, [see Figure 8]. Hill forts and settlements were constructed from the Late Bronze Age until the onset of the Roman period *ca.* 2800 – 1970 BP (Cunliffe, 1991; Collis, 1984;

Henderson, 2007). The term 'hill fort' describes a structure on an elevated position (hilltop, inter-land or sea-promontory) with one or more earthworks (univallate, bivallate or multivallate), ditches and ramparts forming enclosures from 1 - 20 hectares in size. These were often developed using the natural geology and topography. This term can be generically applied to any upland or lowland settlement of the Iron Age including defended farmsteads and enclosures (Hogg, 1975).



**Figure 8.** Distribution of Iron Age hill forts and defended enclosures in Wales. Source: DAT (2013). The red box indicates all of the research sites for this study.



**Figure 9.** Defended enclosures in west and south West Wales. Source: RCAHMW (2013). The black box indicates all of the research sites for this study.

Hill forts are often termed as defensive structures; Avery (1986) describes them as the ‘The ultimate defensive weapon’ but many Welsh hill forts were overlooked by higher ground suggesting that defence was not their only purpose (Cunliffe,1991). Their principal use may have been to store produce, protect against theft of livestock, or as summer sites for occupation and upland farming, possibly until the Middle Ages (Harding, 2012). Their use as summer dwellings (*hafods*) for summer transhumant practice released more fertile lowland areas for crops around the main lowland dwellings (the *hendre*) (Davies, 1985; Driver, 2005). Driver (2005), also comments on hill fort architecture and how it may have provided symbolic status for chiefdoms. The

initial view of hill forts would have reflected the chiefdom's importance through the grandeur of gated bastions and façades. Castell Grogwynion translates to the fort of White Pebbles which may refer to how it was embellished, possibly with quartz and it is also interesting to note this was often the lode bearing gangue (Driver, 2005).

Overall, evidence of metallurgy from many Iron Age sites may have been lost in the modern landscape due to land improvement. But in Wales, a high percentage of hill forts situated in Ceredigion may still contain soil geochemical evidence of metallurgy that may add to the understanding of their social, environmental and quasi industrial history.

## **2.9 Sites of known metallurgy in mid and north Wales**

### **2.9.1. Bronze Age metallurgy**

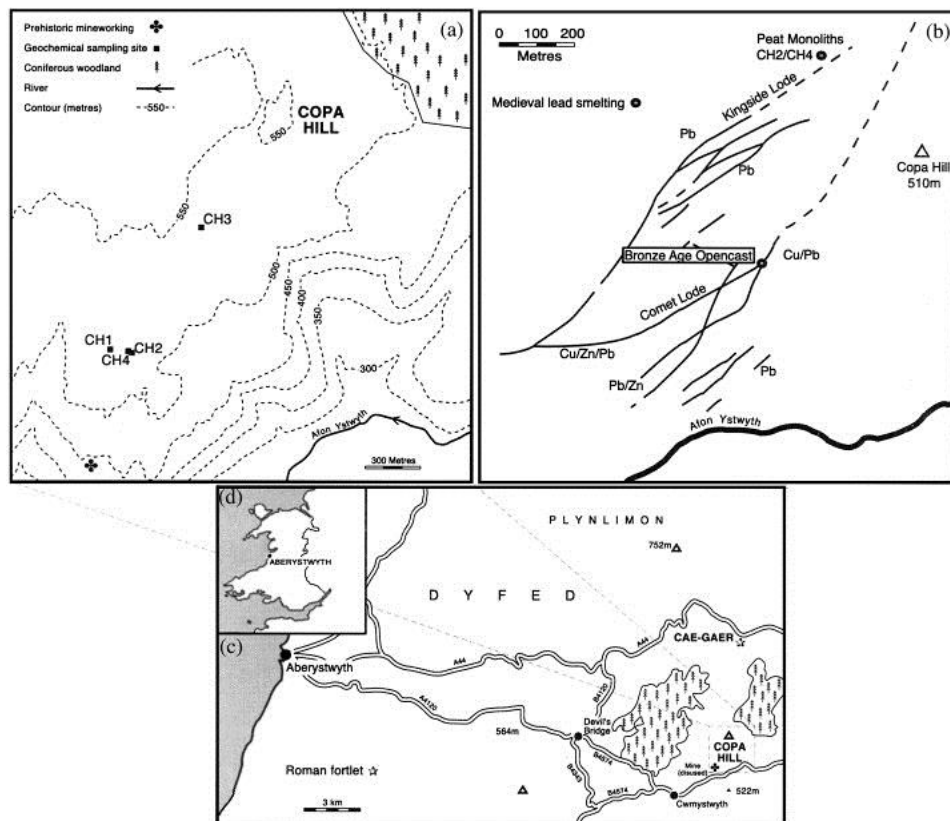
There are numerous sites with evidence of Bronze Age metal exploitation in Wales. With Bronze Age tools and artefacts similar to other mining and ore smelting paraphernalia found globally (Adams, 2009; Andrews, 1994; Craddock, 1995; Crew, 2002; Driver, 1995, 1996a, 2005, 2009; Barker *et al.*, 2007; Bick, 1974; 1988; Giles, 2007; Musson *et al.*, 1992; Pickin and Timberlake 1988; Timberlake and Switsur, 1988; Timberlake, 1995, 2001, 2003), research suggests the Cambrian Mountains and North Wales have been a source for non-ferrous metals used from the Bronze Age, Roman [see Figure 11] and later medieval periods (Musson *et al.*, 1992, 1994; Jenkins and Timberlake, 1997, 2001; Crew 2002; Mighall, 1997, 2009 and Timberlake 1994, 2004, 2011).

It is notable that many metal artefacts have been dated to the Bronze Age (Mighall *et al.*, 2002), with important culturally crafted artefacts that include, the 'Mold cape', found in North Wales in 1863 by working quarry men, [see Figure 13]; the Banc Ty'nddol sun disc from Copa hill Cymystwyth found in 2002 [see Figure 10] (Timberlake, 2004); the Burton hoard found at Acton, Wrexham 2004; the Rosset hoard found in 2003 in South Wales and the St Mellons and the Manorbier hoards found in 1983 and 2010 from West Wales. These are some of the many finds catalogued by the Museum of Wales, Cardiff and the British Museum (Museum of

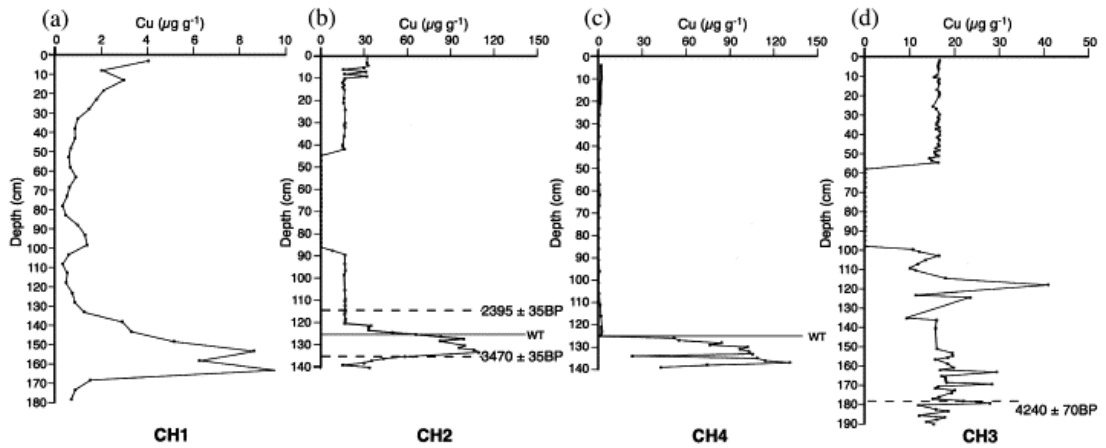
Wales, 2014; British Museum, 2014). It therefore seems reasonable to suggest there was Bronze Age metal working and intricate crafting of the metals throughout Wales.



**Figure 10.** Tyn'nddol sun disc '39 mm in diameter' found at Banc Tyn'nddol, Cwmystwyth by S. Timberlake in 2002) crafted from Welsh alluvial gold. Source: EMRG (2014).



**Figure 11.** Location and schematic of Cwmystwyth open cast copper mine and the location of the monolith samples. Source: Timberlake *et al.* (2002).



**Figure 12.** Depth models of increased copper signal in peat monoliths. **CH 2** and **CH 3** carbon dated at a depth of 133–134 cm  $3470 \pm 35$  Cal BC  $1883\text{--}1687$  GrN-17636. Source: Timberlake *et al.* (2002).



**Figure 13.** The Mold Cape discovered in 1833 and possible produced between 1900 – 1600 BC. Source: British Museum (2014).

These metal rich hoards containing artefacts, and the Tyn’nddol sun disc from Copa hill, Cwmystwyth, suggest that Ceredigion was an important centre for metallurgy. This evidence is further strengthened by the evidence of fire setting and quenching with

frequent finds of hammer stones; a wooden water launder [see Figure 14] with handles for hammer stones, antler tools for picking and *ca.*5000 tonnes of pre-historic mining waste from the excavation of copper ore at Cwmystwyth mine [see Figure 11] (Hughes, 1984; Timberlake, 1990a, 2004; Andrews, 1994; Jenkins and Timberlake 1997; Anguilano *et al.*, 2010). It must also be recognised that copper continued to be used throughout the Iron Age period, with copper and bronze utilised for decorative and utility items (Cunliffe, 1991). However, is there isotope evidence for the source of these metals, and if so are there local to the finds?

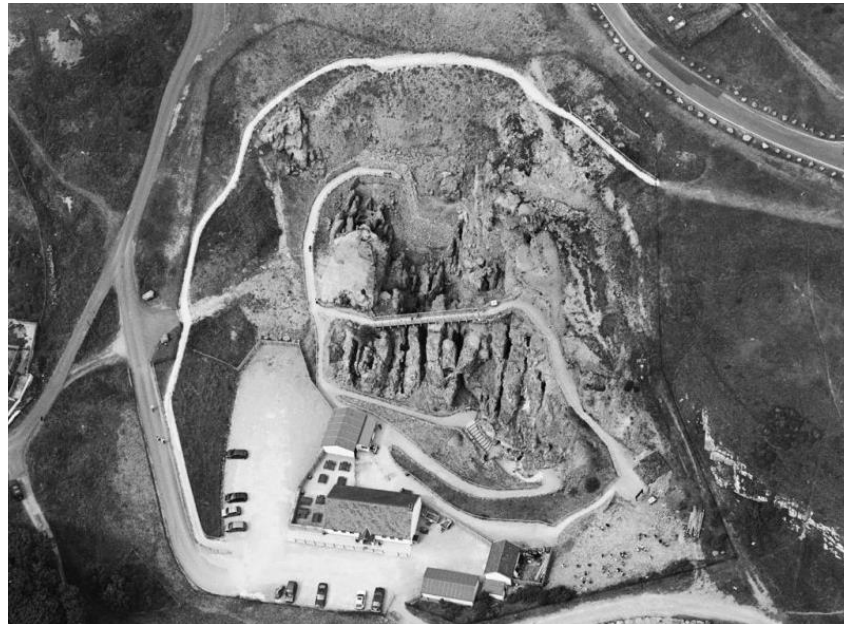


**Figure 14.** This image of a wooden drain launder found during excavation of a Bronze Age copper mine at Copa Hill, Cwmystwyth, during the 1990s. It is radiocarbon dated to *ca.* 4000 yrs BP and provides evidence of copper mining at Cwmystwyth. Source: National Museums and Galleries of Wales (2014).

The main area of copper exploitation was at the comet lode at Cymystwyth located on a high scarp slope at 480 m OD. In addition to Bronze Age evidence at Cwmystwyth, Timberlake (1994) postulates that the Early Bronze Age Twll y Mwyn mine, 15 km north-west of Cymystwyth and 1 km north from Banc y Darren, would have had exposed outcropping mineralisation. This lode was within only a few meters of the Iron Age Banc y Darren hill fort. Is it possible that Bronze Age exploitation was also carried

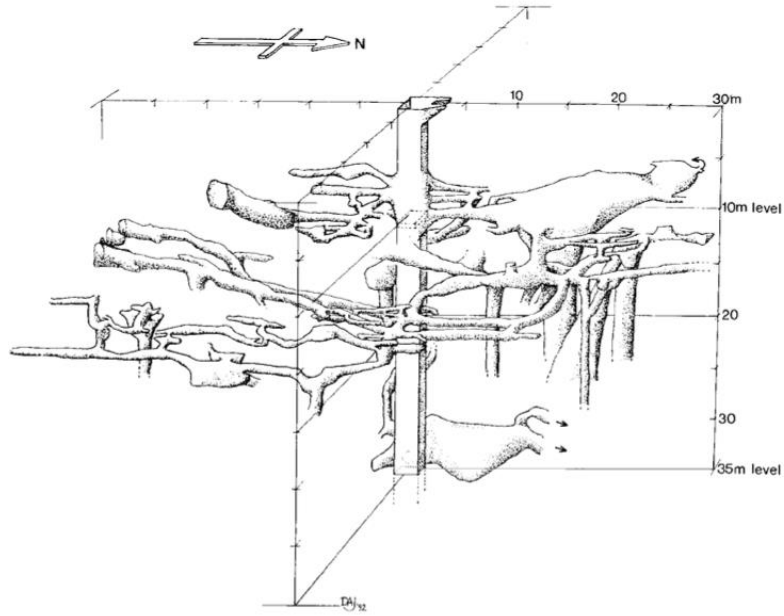
out here prior to the development of this fort? Further evidence of use of this area is seen with the Bronze Age burial cairns, which predates the hill fort development. The wealth of information provided by the artefacts from these hoards adds to evidence of Bronze Age metallurgy, and continues to build a larger picture of metal exploitation in North Ceredigion prior to the Iron Age period.

In North Wales, the Great Orme limestone outcrop, [see Figure 15] has surface and subsurface workings containing evidence of ore extraction and smelting dating from the EBA onwards.



**Figure 15.** Aerial image of the Great Orme copper mine. Source: RCAHMW (2014)



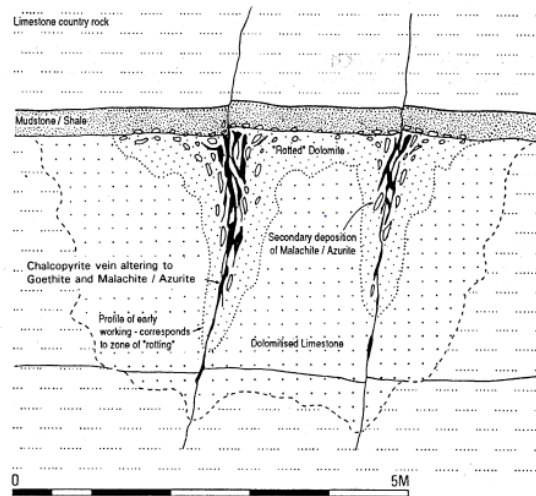


**Figure 16.** A simplified schematic of the sub surface Bronze Age workings and the Vivian shaft, Great Orme near Llandudno. Source: in Ixer (2001).

Replacement or secondary mineralisation of malachite and azurite [see Figure 17] was organised vertically and horizontally, concordant with bedding of the lithology. Initial working has been dated to the late Bronze Age, 2950 Cal. BP, with the limestone outcrop worked for its ores intermittently until the nineteenth Century (Lewis, 1996; Ixer, 2001). It may have contained the only large secondary mineralisation lode to have been worked in Wales from the Bronze Age onwards. Similar, but smaller deposits were also found near Llanidloes, on the east of the Cambrian Ore Fields (Timberlake, 1990a).

Great Orme was analysed for its geochemistry and the smelting distribution of copper using pXRF Spectrace 9000 (Jenkins *et al.*, 2001). Even though it is regarded as a portable instrument, it was difficult to use due to its weight and the required environmental licences for the decaying isotopes. These were even further complicated by its susceptibility to inclement weather (Timberlake, pers. comm., 2012). This method mapped the spatial distribution of Cu over the prehistoric and later Roman workings at Great Orme. The results were useful in the context of the period of archaeology, which suggested some similarities to the various artefacts of bone, antler and stone tools typical of the Bronze Age period. Evidence of the use of these tools is

seen on the rotted dolomite with pick marks in the underground workings *ca.* 7 m below the surface where the secondary ore lode formed [see Figure 17].



**Figure 17.** Section through mineralised fractures indicating oxidised ores and the relationship between the rotten dolomite and morphology of the early workings. Source: Lewis (1994).

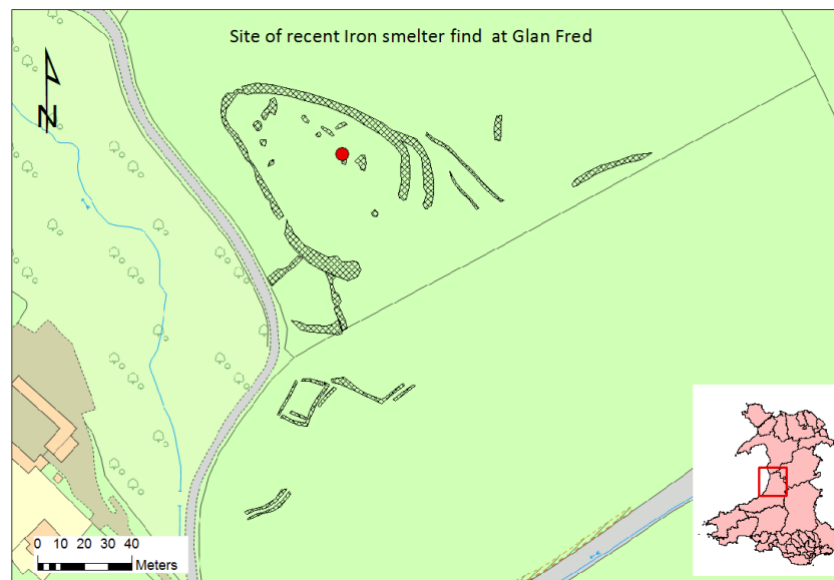
Many of the tools survived in the alkaline conditions formed within the dolomitic limestone and have subsequently been used in the correlation of typology to the radiocarbon dates. Using techniques such as pXRF has enabled fast track geochemical mapping at a known site of ore extraction. There is also evidence of smelting at this site, which, if further surveyed, may create a useful template in assessing other sites in Ceredigion (Jenkins, pers. comm., 2013).

Parys Mountain situated in the North east of Anglesey, has further evidence of prehistoric workings in areas unaffected by later large scale mining. It was initially identified by Oliver Davies for the British Association for the Advancement of Science in the 1930s, and dated to the Roman Period. Timberlake (1988), working with the early mines research group (EMRG), re-discovered Davies' original excavation. The radiocarbon dated charcoal remnants retrieved from fire debris dated the activity to *ca.* 3500 Cal. BP, 'the Mid Bronze Age' (Amber *et al.*, 1991). This correlates with other prehistoric mining sites in Southern Ireland, central and North Wales. Overall limited evidence remains for any prehistoric mining from this site, from which only hammer and cobbling stones were identified (Timberlake, 1994; Craddock and Craddock, 1996). It may be that the exploited lode also contained secondary mineralisation in the

gossans above copper-rich portions of 'The Great Lode', which were initially reported by Lentin in the nineteenth century (Ixer and Budd, 1998). The mineralisation may have been easy for the Bronze Age miners to extract, similar to the Great Orme and Llanidloes secondary lodes. All of this evidence continues to build a widening picture of the spatial and temporal scale of prehistoric to historic metallurgy in North and Mid Wales.

### **2.9.2 Iron Age metallurgy**

It is possible that Cors Fochno and Cors Caron [Borth and Tregaron peatlands] or other similar sites with optimum conditions for bog iron formation, were sources for iron ore in central Wales. Work on an Iron Age site in the Ceredigion lowlands uncovered a smelting hearth on a lowland fringe hill fort at Glan Fred, 7 km North of Aberystwyth. The iron slag remnants with charcoal assemblages have been radiocarbon dated to the medieval period (Jones, 2013 unpublished). The nearby peat deposits at Cors Fochno and other smaller wetlands may have provided raw material. The alternative, but unlikely source for raw materials may have been from the Frongoch mines where supergene hematite occurs at several localities as thin bright red coatings on leached brecciated mudstone from the oxidation zones of the lead-zinc (Pb-Zn) lodes (Raybold, 1974). One of the other finds at Odyn Fach, 2 km from Glan Fred, was found prior to the construction of a new a gas pipe line which also crosses Caer Lletty Llywd hill fort 7 km to the north of Aberystwyth. Work was undertaken to assess if any archaeology was present within the enclosure. The excavation cut across the outer section of the earthwork revelling rubble and earth filled ditches. Only one small piece of Iron smelting debris was uncovered (Murphy, 1988).



**Figure 18.** Glan Fred Iron Age defended enclosure site of a recent Iron Age smelter find dated to the Medieval Period.

A further find at Pen Dinas (Elerch), also presumed to be iron rich was found by Driver (1998) only 3 km to the east. Whether these iron rich slag finds were made during the period of fort occupation is still unclear (Timberlake, 2011; Crew, 2002). Does this suggest a nucleation of sites with some evidence pointing to Iron production? Unlike the site at Glanfred, where the datable evidence points to medieval production, these other finds have not been found alongside charcoal remnants which could have been used to date these finds.

The question remains, was metal production within North Ceredigion contemporaneous to other parts of Wales during the Iron Age (Cunliffe, 1991; Driver, 2005). But without chronological markers or further evidence of smelting, then an assumption that Odyn Fach and Pen Dinas (Elerch) were used for metallurgy during the Iron Age or even the later medieval period is questionable.



**Figure 19.** Slag find from Pen Dinas (Elerch) 1998 by T Driver. .Source: RCAHMW (2013).

However, other sites in Wales have produced evidence of Iron Age smelting. Crew (2002), used a geophysics survey to assess the Iron Age sites at Crawcwellt, located in the Snowdonia region of North Wales. Here, iron slag and spoil produced by prehistoric smelting were identified. As well as Crew's research, many hill forts sites in Wales that have been excavated contain evidence of prehistoric iron smelting. Both the Breiddin hills sites situated in the Welsh marches, described in Musson (1991), and the contemporary site at Rhuddlan Clwyd in North Wales, where Quinnell *et al.* (1994), catalogued evidence containing Iron Age activity. Both excavations produced artefacts including iron pieces, smelting bowls, and hearths. These finds are not near to known iron deposits and bog iron may well have used as the ore source. While this is only conjecture, the evidence of metallurgy processes is compelling.

Even though the hill forts in Ceredigion have had research carried out on their structure, stature and defensive capabilities (Driver, 2005), apart from the finds at Odyn Fach and Pen Dinas (Elerch) which may suggest evidence of Iron Age metal working, none has yet been recorded at any other Ceredigion site. This includes some of the larger sites of Castell Grogwynion, Caer Lletty Llywd, Pen-y-Bannau and Pen Dinas. The latter is a coastal site near Aberystwyth and is one of the largest Iron Age hill forts in Ceredigion. It was excavated by C. Daryll Forde from 1933 – 7 producing limited finds from the Iron Age and later periods with no on-site evidence of metallurgy. It may have been due to the limited area covered during the two main

excavations through the ramparts (Forde, 1938; Avery, 1986; Driver, 2005). One of the sites surveyed in this study, Banc y Darren, has been previously excavated through the rampart section to develop further understanding of its construction methods (Timberlake and Driver, 1996a). Apart from some minor finds of pottery, no metal artefacts were found. But lead found in the exposed section of the one of Banc y Darren's ramparts, and with the large deposits of galena ore nearby, it is not unreasonable to consider that mining and possibly smelting may have occurred here during the Iron Age. If isotope analysis connects this to the local lode, it may suggest lead exploitation. Furthermore, if smelted here it would be one of only a few lead smelting sites in Wales that relate to the Iron Age (Timberlake pers com, 2014).

### **2.9.3 Roman and medieval period metallurgy**

Lead was an important commodity for the Romans for use in sanitary engineering and piping, with much of the lead processed in Britain used for this purpose (Rich, 1994). The evidence of lead and copper exploitation during the Roman period is supported by finds of lead pigs and copper cakes in North and South Wales. Six inscribed lead pigs indicate they were from what is now modern day Flintshire. These also detail the evidence of de-silvering silver bearing a stamped mark 'EX Arg or EX Argent', (North, 1962; Oddy, 1983; Craddock, 1995).

The suggestion is that many of the lead and silver rich lodes in Wales were important enough to warrant the use of the network of forts and fortlets located near many of these mineral assets. This is supported by a series of forts found in North Ceredigion, with evidence 7 km N.N.E of Cwmystwyth at Cae Gaer, 12 km from Aberystwyth at Trawscoed on the Sarn Helen Roman Road, and west of Cwmystwyth at Esgairperffedd (Hughes, 1981). However, Hughes (1981) was dismissive of any Roman evidence found at Cwmystwyth in his publication on 'The Cwmystwyth mines', but further evidence of Roman workings was put forward suggested by Timberlake in Craddock and Lang, (2003) detailing leat and hushing developments which are synonymous with Roman period metal exploitation. This paper further described early mining processes in Cwmystwyth.

Further Roman smelting evidence in the North Ceredigion landscape is seen on the fringes of Cors Fochno, where a smelting bole underneath a medieval timber track way was discovered by the Dyfed Archaeological Trust during 2004, with further proxy evidence in the peat geochemical record also supporting this evidence of industrial Roman smelting (Mighall *et al.*, 2008), [see Figure 20 and 21].

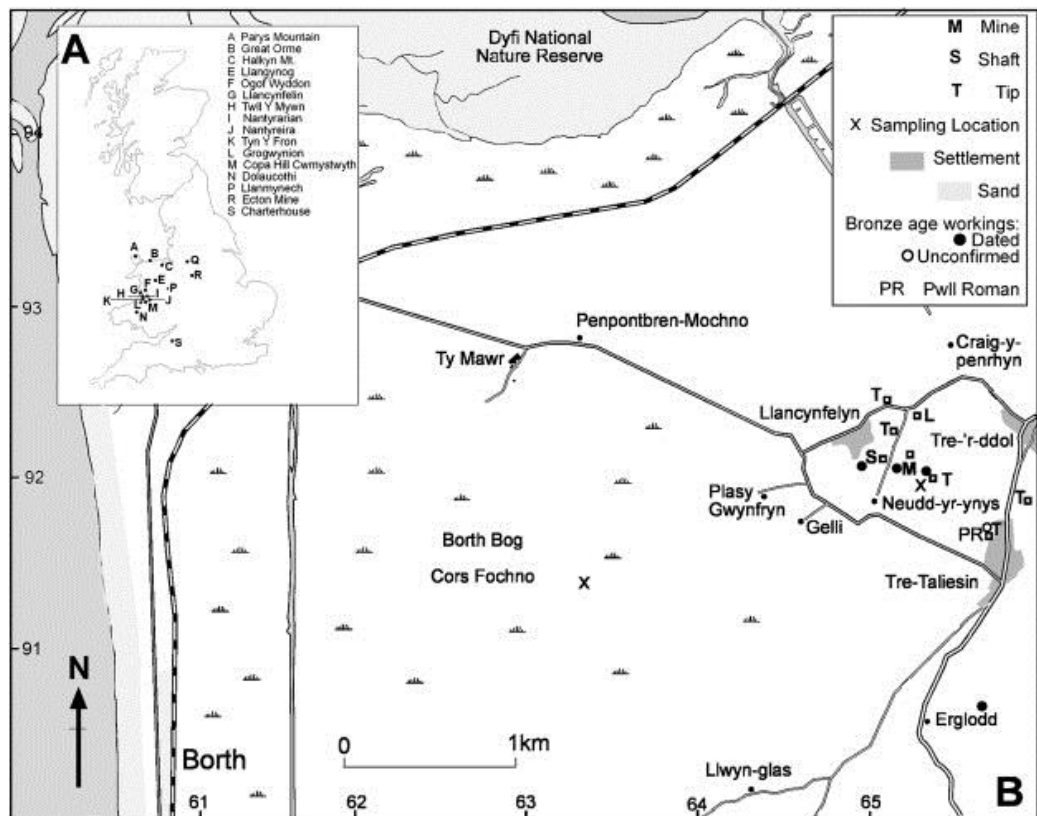
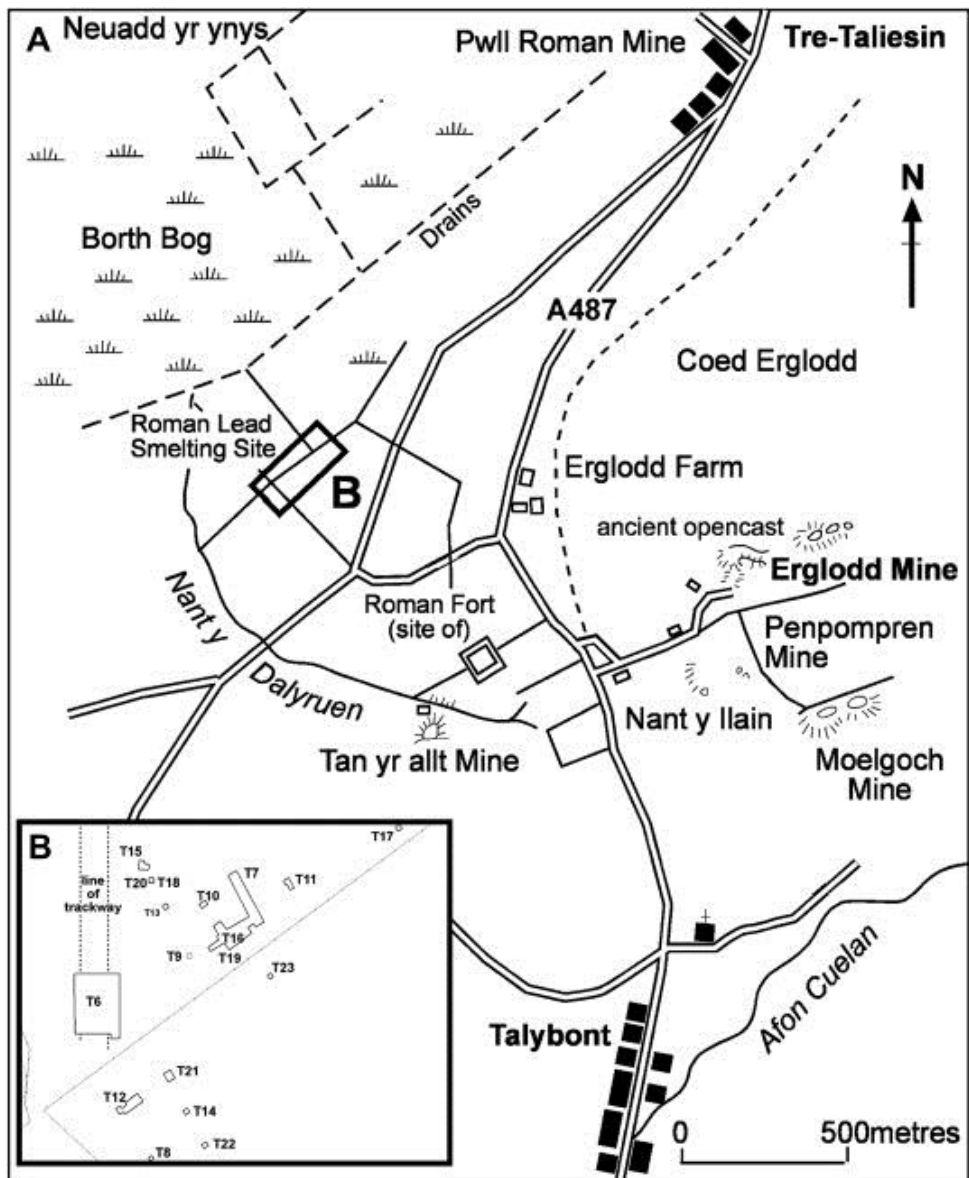


Figure 20. Location of the study centre within Cos Fochno near to Llancynfelin. Source: Mighall *et al.* (2008).



**Figure 21.** Location of Roman smelting site and plan of the trench dug for the archaeological excavation.

Source: Mighall *et al.* (2009).





**Figure 22.** Roman smelting evidence at Cors Fochno. Source: Dyfed Archaeological Trust (2013).

Again, evidence of smelting at Cors Fochno demonstrates the exploitation of local ores possibly sourced from the Erglodd mine which may also have been protected by a Roman fortlet situated less than a 1km to the west [see Figure 22].

Work at Abermagwr on a recently excavated late Romano-British winged villa situated near Trawscoed Roman fort, provided a geochemical archive that may have been left from the working or processing of local ores. Davies and Driver's (2011) work on this settlement questions whether metals found within the excavation of the villas have also been sourced from local ores. To further explore the potential link between these settlements and metal exploitation, this study also developed work previously undertaken at Abermagwr in an attempt to further the understanding of the Roman exploitation of the areas metal lodes. Results from these surveys may also address the key question posed by Driver (2005) as to whether there is any relationship between metallurgy and Iron Age hill forts in North Ceredigion.

Medieval smelting evidence has been identified at Cwmystwyth. Exploitation of the Comet lode yielded Pb from the rich galena ore. Apart from the peat monolith geochemical evidence of earlier Bronze Age exploitation (Mighall *et al.*, 2009) and the assessment of artefacts and their typology (Timberlake, 1994), recent work by Anguilano *et al.*, (2010) investigated this site using a geophysics survey, a similar

method employed at Crawcwellt (Crew, 2002). It revealed between 6 – 10 smelting sites as geophysical anomalies, identifying deep heating, i.e. dipoles which are typical smelting evidence. Again, this shows the evidence of metal exploitation from periods prior to, and after the Iron Age period. It also highlights the lack of, or at best, some limited circumstantial Iron Age evidence of iron slag finds which have yet to produce proven artefacts from Iron Age smelting in North Ceredigion.

Further evidence from the excavations at the Cistercian Abbey at Strata Florida (8 km South of Cwmystwyth mines) have produced charcoal fragments which were radiocarbon dated to 1030 – 700 Cal. BP. (Timberlake, 1994; Sables 2012 unpublished). These charcoal finds are also associated with metallurgical artefacts. Current work at the abbey is utilising geophysics, LiDAR, AAS, and ICP-MS and artefact typology to evaluate remaining evidence of lead smelting bowls (Sables, pers. comm. 2012). Whether some of these smelting sites may be earlier or later than the medieval period is still being discussed.

Overall further research is needed on sites in Wales where clear cut evidence is hard to find from the mixed developments and remaining spoil tips around sub surface and the open cut mining sites. But the datable metallurgical evidence suggests the ores exploited from Early Bronze Age were copper, during the Roman period copper, lead and silver. However, is this reflected at nearby Iron Age locations within North Ceredigion, or is it possible these sites were re-used during later periods when a re-emergence of metal exploitation was seen in the Middle Ages, prior to the industrial scale mining seen during the 17 – 19<sup>th</sup> centuries? These points are key to this study in exploring the metal/Iron Age relationship, by creating an understanding of the location of lodes, ore exploitation and where metals have been produced.

## **2.10 Summary**

This chapter has outlined the regional mineralisation of Mid Wales, the climate and agricultural during the late Bronze Age and Iron Age periods. Period and development of hill forts and the history of pre-18<sup>th</sup> Century AD metal exploitation in Wales.

## Chapter 3: Site description

### Introduction

Iron Age Hill forts and smaller defended enclosures are widely distributed throughout Wales, in a variety of shapes and sizes from small [ $<1$  ha] to larger [ $> 4$  ha]. In North Ceredigion the upland and lowland sites were developed near to the many metal ore bearing lodes. Many of these were exploited during the Bronze Age. It is also suggested that many hill forts were modified during their occupation (Driver, 2013). This chapter describes the sites and locations chosen for the study, outlining the chronology, surficial and bedrock geology and what research has been carried out at these sites.

#### 3.1 Iron Age hill fort and Roman settlement chronology

The overall chronology of the development of Iron Age defended enclosures and hill forts is not fully understood (Cunliffe, 1991), while in contrast the understanding of the Romano-British period has been widely documented with archaeological research and recorded accounts which indicates a more structured and governed society during the Roman occupation of England and Wales from 44 - 440 AD than previously (Millett, 1992).

The chronology of the Iron Age in Britain is fully described by Davis and Lynch (2000) but a brief summary of the Iron Age and Roman period is as follows;

Late Bronze Age to Iron Age transition	2900 - 2540 BP
Early Iron Age to the Mid Iron Age	2540 - 2400 BP
Mid to late Iron Age	2400 - 2170 BP
Late Iron Age to Roman period	2170 BP- 1940 BP (44AD)
The Roman conquest and occupation of Wales	44 AD – 380 AD

**Table 1.** Suggested chronology from the Bronze Age until the Roman occupation. Source: Davies and Lynch (2000).

Ceredigion and the Central Wales Ore fields were occupied during the Bronze Age and how evidence of mining in the quasi-industrial sites that were exploited. In contrast, the Iron Age period does not contain much evidence of pyro-metallurgy. All that physically signifies the presence of this period of occupation is the hill fort structural archaeology found from the coastal fringes into the upland regions of Wales. It is possible that many of these structures were initially developed during the Bronze Age. It is also possible that the remoteness and the lack of land improvement in upland sites may have limited the degradation of these earthwork structures. In contrast to these upland sites, the lowland sites have mostly disappeared due to land improvement affecting both Iron Age and Roman settlements and infrastructure.

Vertical and oblique aerial photography in the 1950s identified crop marks and led to the rediscovered of many lowland and upland sites in Wales (Driver, 2013). More recently the use of light detection and ranging (LiDAR) has enabled heavily vegetated or wooded areas to be surveyed, often uncovering further sites of some antiquity.

### **3.3 Hill fort and settlement construction and metal lodes**

With much of North Ceredigion's landscape rich in metal ores, the question is whether Iron Age hill forts were specifically positioned to both protect and exploit these. This is a question that has not been considered in previous literature. Archaeological surveys have often used the geochemical and palynological archives to support the hypothesis that Iron Age hill fort development possibly started during the cultural shift from the Bronze to Iron Age periods. This correlates with the reduction in woodland cover over Britain (Cronin, 1993; Mighall *et al*, 2002). Furthermore, the choice of upland sites may have been influenced by availability of materials for hill fort development, but possibly for the ability to view and control trade routes, hill fort approaches and to defend livestock and other assets (Driver, 2005, 2013). In contrast lowland sites and enclosures were placed within the more fertile lowland and hinterlands for agriculture and transhumant practice, and are considered to have been developed later in the Iron Age (Davies and Lynch, 2000; Driver, 2013).

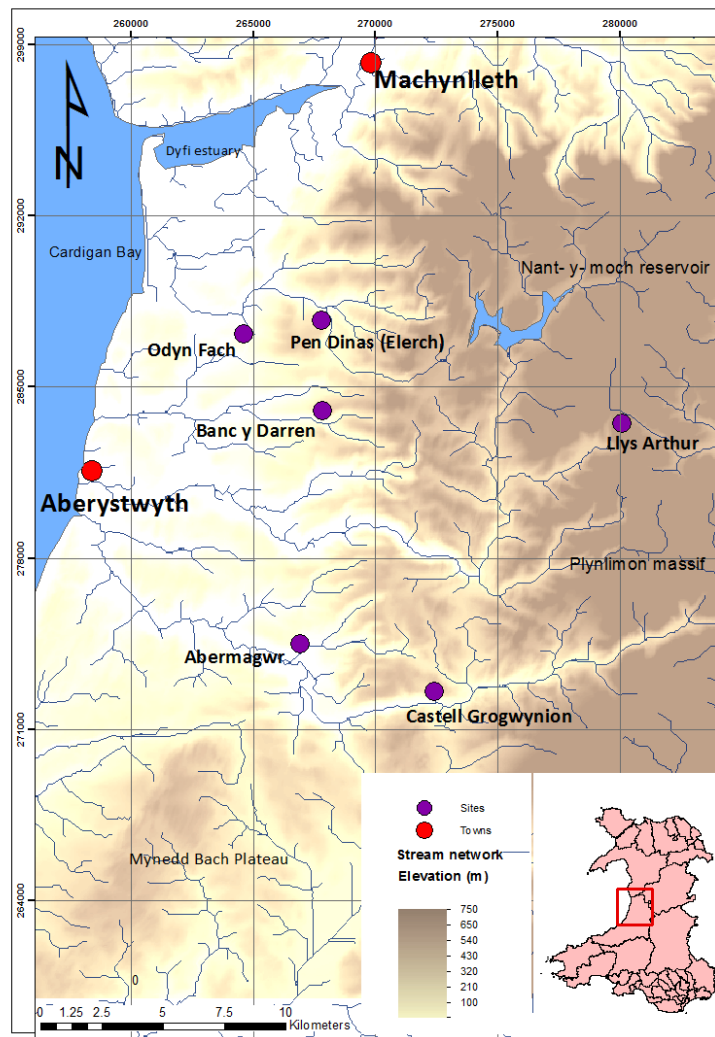
The Bronze Age culture has left a legacy of mining and smelting evidence with crafted metal artefacts found in Ceredigion and Wales (Timberlake, 1990), indicating the mineral lodes were widely exploited during this period (Bick, 1974, 1988; Picking and Timberlake, 1988; Timberlake, 1997, 1988, 1994, 1995, 2001, 2003, 2011, 2013; Mighall *et al.*, 2002, 2008, 2009). So why during the cultural shift between the Bronze and Iron Age was the exploitation of metal rich lodes not continued into the Iron Age? Only some minor circumstantial evidence uncovered during more recent survey excavations suggests later exploitation of copper, lead and iron (Murphy, 1988; Driver, 2005), but these are yet to be proven as Iron Age. However, is there further evidence still within these settlements that can establish a continuum of metal exploitation?

There are theories that attempt to explain the lack of metallurgical evidence in North Ceredigion. It has been suggested hiatuses in hill fort occupation possibly affected construction, which may have been influenced by deteriorating climatic conditions, during the late Bronze Age Iron Age transition (Van Geel and Renssen; 1998; Driver, 2013). Some settlements are postulated to have been affected by large scale abandonment during this period and only reoccupied when conditions improved. However, Masson (1991) suggests that in the east of the Cambrian Ore Fields, the Breiddin Hills sites and Rhuddlan Clwyd in North Wales, were not abandoned, and contain evidence of metallurgy from this period, although an alternative hypothesis on climatic deterioration suggests this assessment is at best ambiguous (Dark, 2006; Tipping, 2002; Tipping *et al.*, 2008), and that this deterioration of the climate was not contemporaneous with the suggested earlier abandonment of hill forts in Ceredigion.

Cunliffe (1991) suggests that until a more comprehensive and detailed investigation is carried out of cultural and datable evidence, the interpretation of hill fort chronology will remain difficult (Gwilt and Haselgrove, 1997). Driver (2013) argues that low land enclosures can be significantly different, even within small geographical areas.

In contrast, evidence of Roman period metal exploitation can be found in Mid Wales. There is evidence of lead smelting at Penguelan Copa Hill and Erglodd Roman Fort near Cors Fochno (Borth Bog), which correlates with lead enrichment in the peat profile (Mighall *et al.*, 2000, 2002; Timberlake *et al.*, 2003a). However, other sites in Ceredigion still need further investigation to ascertain if they were also used for pyro-

metallurgy. This may further add to the existing evidence found at Cors Fochno and Cwmystwyth (Timberlake, 1998; Mighall 2002, 2008). This parallels Roman evidence of lead pigs and copper cakes found in both North and South Wales (North, 1962), nearer to the main centres of governance at (*Segontium*) Caernarvon, (*Deva Victrix*) Chester, (*Isca*) Caerleon, and (*Moridunum*) Carmarthen.



**Figure 23.** Site locations in Mid Wales; Iron Age (IA) and Roman Period (RP).

1. Pen Dinas (Elerch) (IA). 2. Odyn Fach (IA). 3. Banc y Darren (IA). 4. Llys Arthur (RP).

5. Abermagwr (RP). . Castell Grogwynion (IA)

### 3.4.1 Pen Dinas (Elerch)

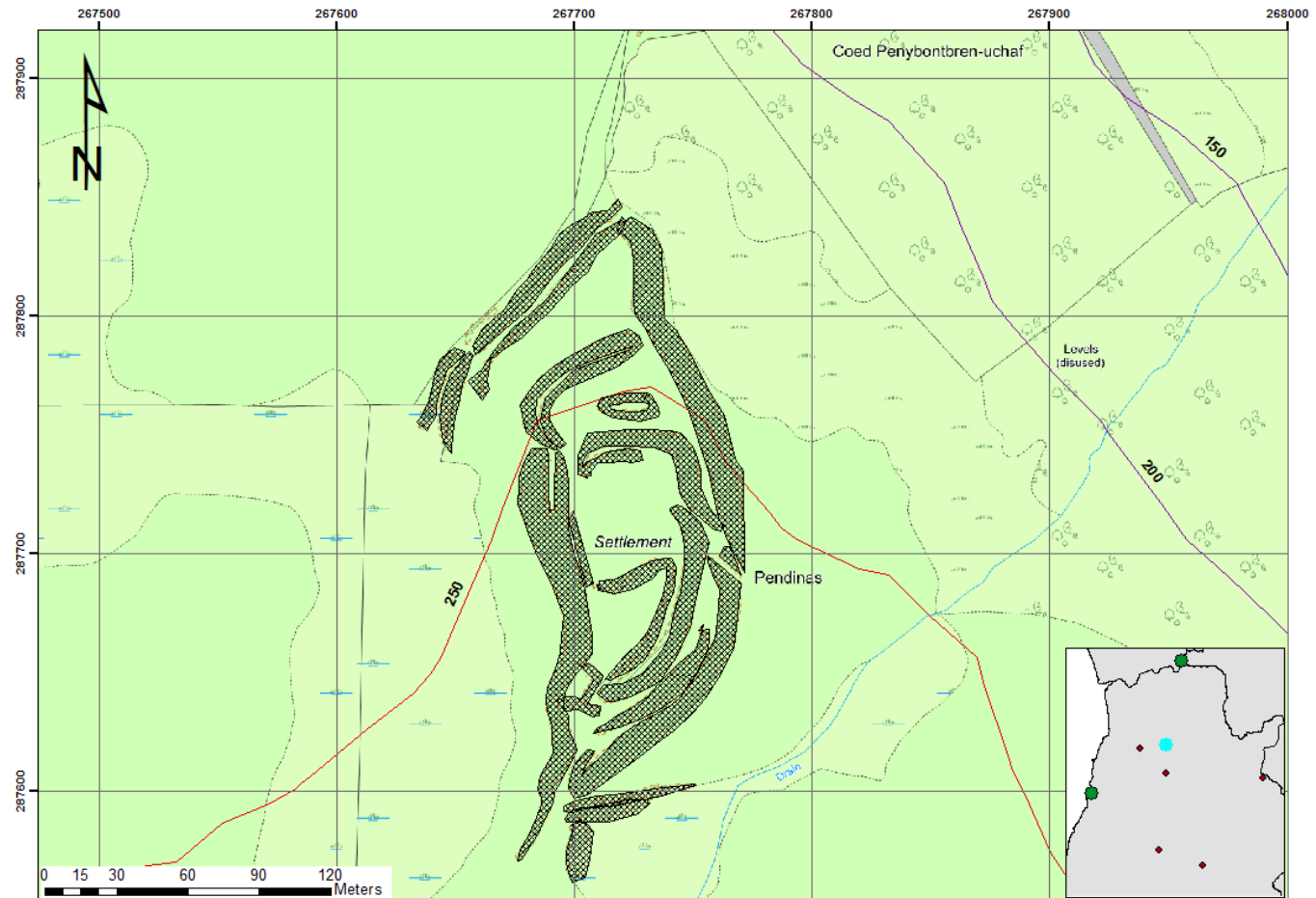
<b>Pen Dinas (Elerch) (Iron Age)</b>	Upland defended fort possibly Mid to late Iron Age 2400 -2190 BC
<b>Geographical coordinates</b>	Grid reference SN 6772 8767
<b>Elevation OD</b>	279 m
<b>Area (approximate)</b>	200 x 70 m = 1.4 hectares
<b>Geology bedrock</b>	Ordovician-Silurian age. Derwenlas formation (DLF), (S1), Cwmere formations (CMR), Devils bridge formation (DBF) and mudstone siltstone and greywacke
<b>Surficial geology</b>	Limited Devensian till, peat to the west and south east

**Table 2.** Pen Dinas (Elerch): geographical and geological details.

This scheduled site is situated 7 km north of Aberystwyth with a view of Banc y Darren 5 km to the South. The fort is 800 m south of more recent mining locations, which exploited the Allt-y-Crib lode for argentiferous galena and copper rich chalcopyrite. Further mining locations are situated south of the hill fort adjacent to the course of the Afon Leri (Hughes, no date).

It is flanked by peatlands to the west and south east, which may control run off from the plateau. Whether or not these peatlands were cut during the Iron Age period is unclear, but it is possible that they have been harvested in more recent years for fuel.

The Derwenlas Formation lies on the eastern edge of the hill fort, and the Brynglas formation with interbedded mudstone and sandstone is situated 500 m to the north. The Devils Bridge Formation is adjacent to the western approach [see Chapter 2].



**Figure 24 .** Pen Dinas (Elerch) (highlighted in blue on the insert) outline of the ramparts and inner section of the hill fort. Contours in meters show the steep valley to the North east. Source: after RCAHMW (2013).



Pen Dinas (Elerch) is classed as a defensive Iron Age hill fort, structurally developed around a promontory outcrop. The main gate at the southern end of the fort is littered with glacial boulders, suggesting that these were used for the gateway construction, with another gateway situated on the NW side.



**Figure 25.** Google Earth image of Pen Dinas (Elerch) with peat mires to the west, south and east. The very steep north-east perimeter falls 100 metres into the Afon Leri creating a formidable approach. The main bastion gateway situated at the southern approach is circled in red. Source: Google Earth (2013).



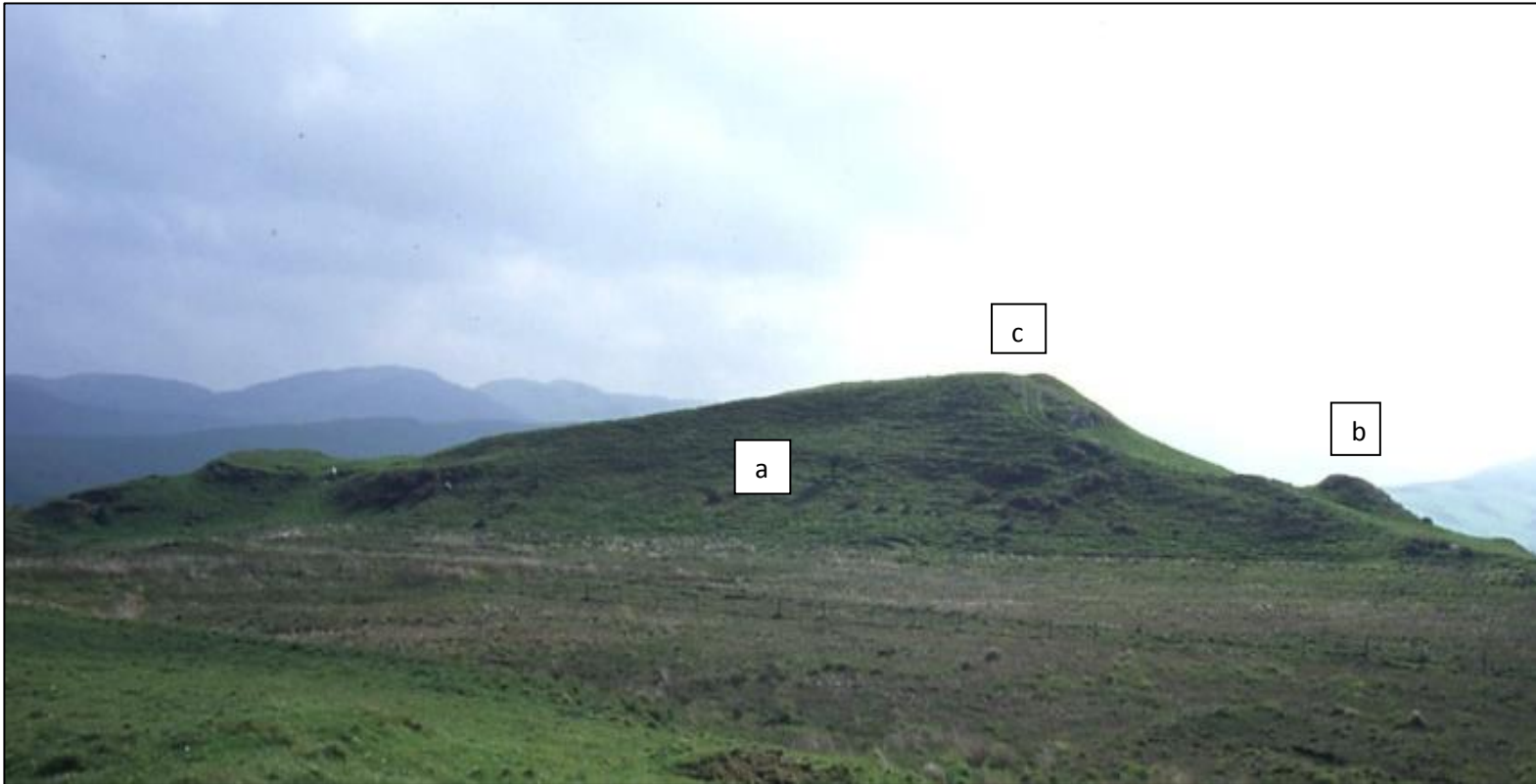
**Figure 26.**View of the South west bastioned gateway with the Plynlimon uplands in the distance (sheep to the right of the right hand side bastion for scale).

Steep revetments on the western slope overlook the seaward route, which may link Pen Dinas (Elerch) to other hill forts sites located at Caer Lletty Llwyd, Odyn Fach and Glanfred 3 km to the west.

The complex earthwork remains suggest multiple phases of development during the late Iron Age period (Hogg, 1994; Driver, 2013). The only research carried out on this hill fort has mapped the fort's footprint, showing how the internal spaces were possibly organised and providing evidence of hut platforms within the upper compartment. Artefacts and other finds are limited to just one piece of presumed iron slag in 1998 by T Driver (Davies (1998), [see Figure 27], which has been misplaced. But the presence of slag is not always an indication of local smelting. Slag found in the fort at Rhos Tryfan North Wales near Caernarvon was more likely to have been created by a forge than a smelting hearth (North, 1962). But this sample does appear to resemble metallurgical slag and maybe associated with the recent find at Glanfred, (see page 33 and Figure 18). Apart from the slag-like find, three sling shot stones and a pottery sherd were found around the SW gate (Timberlake and Driver, 1997), all of which are now in the Ceredigion Museum in Aberystwyth.



**Figure 27.** Image of iron slag uncovered from the western revetments at Pen Dinas (Elerch) by Dr T Driver In 1998. Source: RCAHW (2013).



**Figure 28.** View of the western side of Pen Dinas (Elerch) hill fort, with one of the peat deposits in the foreground. Note the steepness of the western stone built revetment (a) and the bastion gate way to the right (b), and the more recent vehicular tracks to the right of the highest point (c). These may follow a former route into the internal section.

### 3.4.2 Odyn Fach (Small or little kiln)

<b>Defended enclosure (Iron Age)</b>	Defended enclosure, date unknown; possibly late Iron Age 2400 - 2150 BP
<b>Geographical coordinates</b>	Grid reference SN64668769
<b>Elevation OD</b>	75 m
<b>Area (approximate)</b>	63 x 40 = 0.252 hectares
<b>Bedrock geology</b>	Ordovician – Silurian age. mudstone formations, s
<b>Surficial geology</b>	Devensian glaciofluvial deposits of sand and gravel with Devensian till.

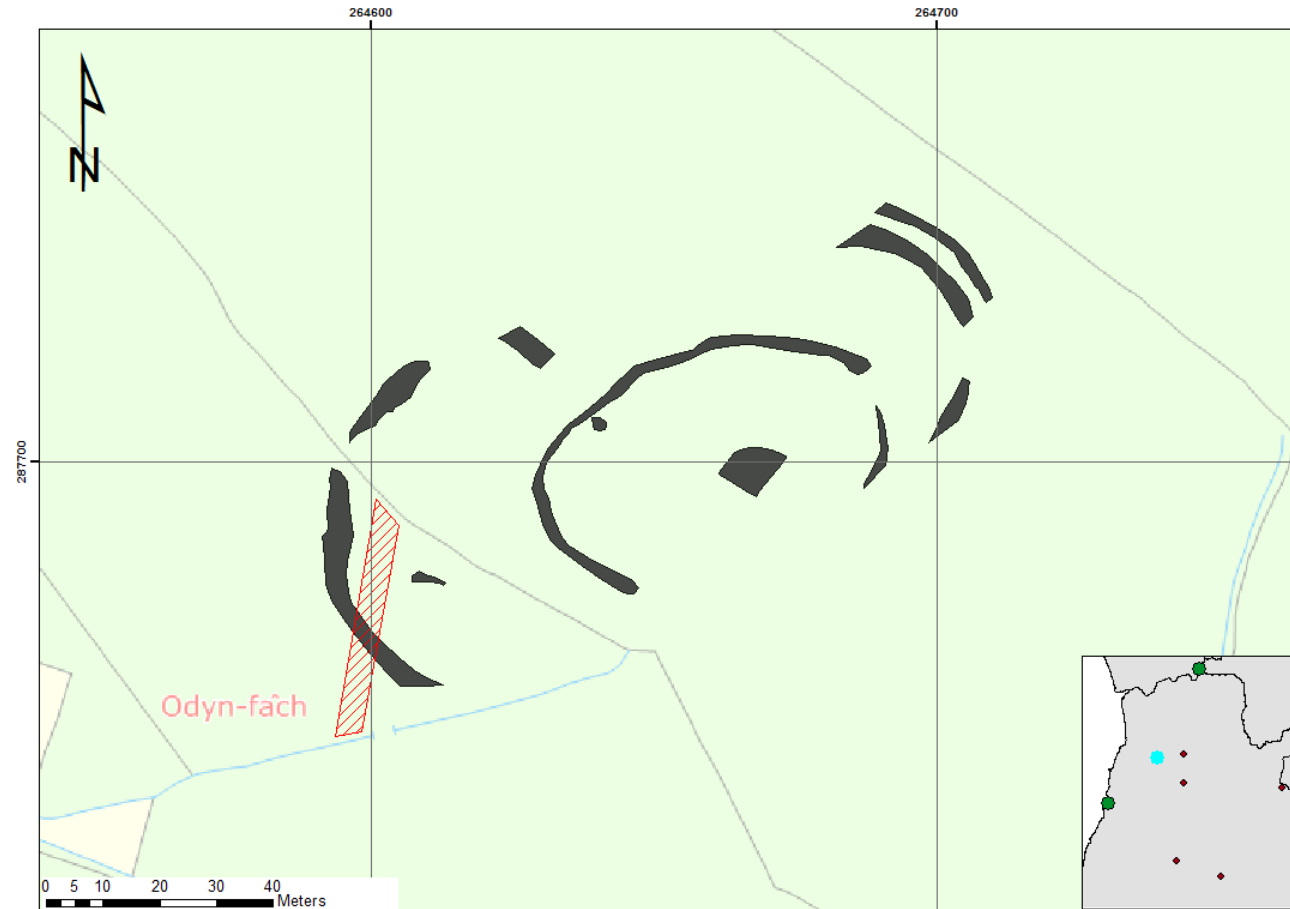
**Table 3.** Odyn Fach: geographical and geological details.

Odyn Fach is an unscheduled site described in RCAHMW's database (Coflein) as a defensive Iron Age hill fort, but more typically defined as a defended enclosure or farmstead. It is situated on a small raised tump (mound or tumulus) to the east of the A487 main road between Aberystwyth and Talybont. The proximity to Caer Llety Llwyd *ca.* 600 m, Glanfred *ca.* 1 km and Pen Dinas (Elerch) *ca.* 3 km suggests that it may be part of a larger hill fort group (Driver 2013). Odyn Fach translates to 'Small or little Kiln' and may suggest a later use of the site, but this is difficult to establish. However, during the Iron Age period these smaller enclosures were more often associated with agriculture and transhumant practises.

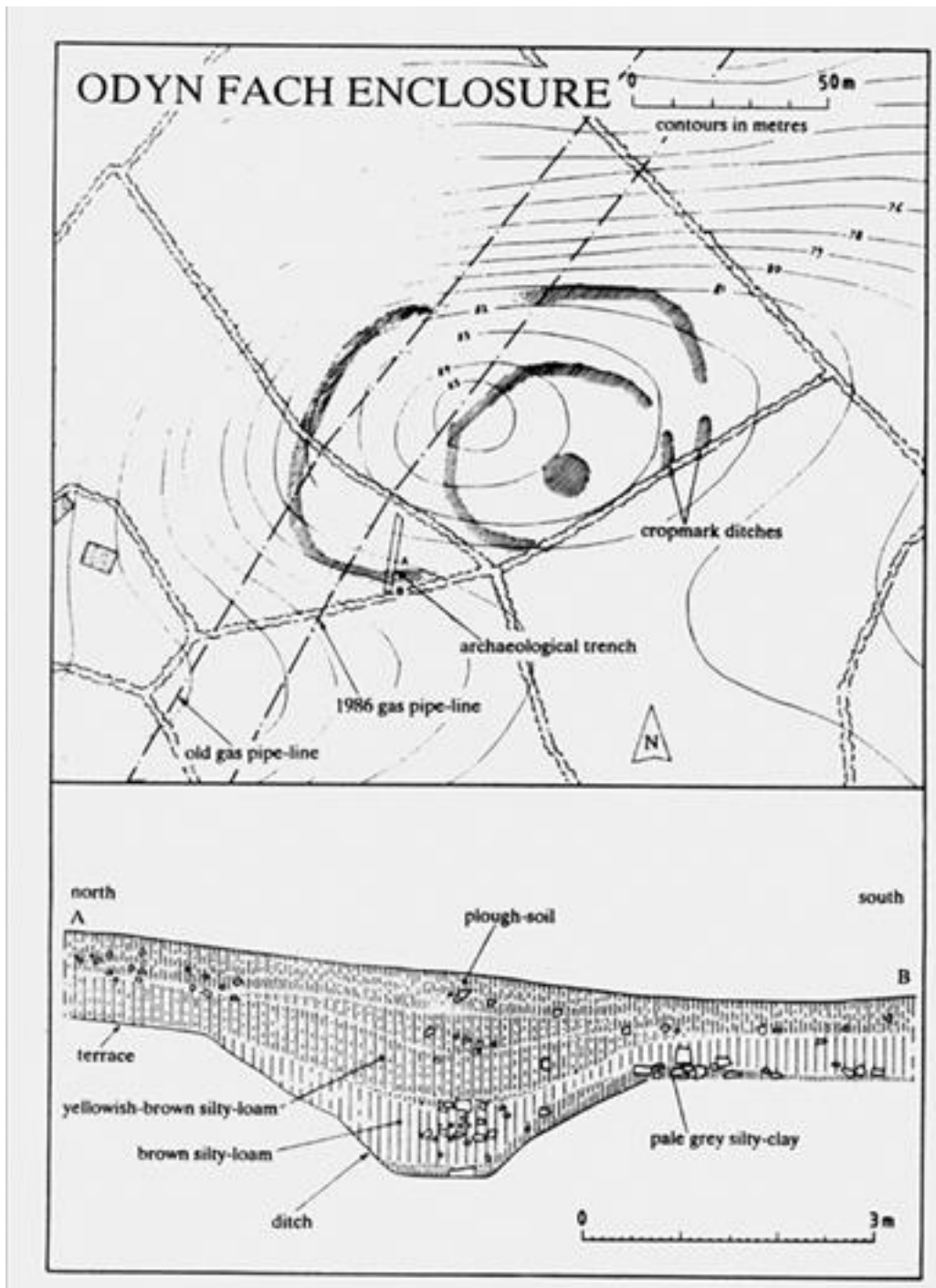
Any evidence of its former construction has been lost to land improvement, but drought-induced crop marks revealed a bivallate enclosure on the site with one house platform outlined within the interior. The tump's soil organic horizon was modified by the addition of soil from the nearby orchard of Maesnewydd farm in 1993, to increase the soil depth for grazing quality (Morgan, pers. comm., 2013). Apart from a small excavation by Murphy (1988), financed by British Gas prior to a new gas pipeline, no further work has been carried out on this site.

Murphy's (1986) excavation revealed a 4.3 m wide, 1.5m deep ditch situated between the bivallate earth works. Iron slag was unearthed at the bottom section of the excavation [see Figure 30] (Murphy, 1988; Hogg, 1975), but has been misplaced, as has

the slag find at Pen Dinas (Elerch) However, this may also be similar to the explanation of the slag like find from Pen Dinas (Elerch) offered by North (1962).



**Figure 29.** Outline of Odyn Fach crop mark ditches situated near Talybont, Mid Wales indicated in blue on the insert. Murphy’s 1986 excavation is highlighted by the red hatching to the western edge of the site. Source: after RCAHMW (2013).



**Figure 30.** The excavation plan drawn in Murphy (1986) for the Dyfed Archaeological trust. Source: RCAHMW (2013).



### 3.4.3 Banc y Darren

<b>Banc y Darren</b>	Upland defended fort, possibly Mid to late Iron Age 2400 -2190 BC
<b>Geographical coordinates</b>	Grid reference SN 67908302
<b>Elevation OD</b>	271m
<b>Area (approximate)</b>	123 x 63 = 0.75 hectares
<b>Geology bedrock</b>	Ordovician-Silurian age. Devils Bridge Formation (DBF), Rhayader Mudstone Formation (green beds) (RMFG), mudstone siltstone and greywacke
<b>Surficial geology</b>	Colluvium and mining detritus with made up ground.

**Table 4.** Banc y Darren: geographical and geological details.

Banc y Darren, a scheduled upland defended hill fort is situated 9.5 km ENE from Aberystwyth on a promontory set on the hill's spine, between the Nant Silo and Nant Peithyll valleys.

To the north-west an open cut mine is set to the west of the hill fort clipping the north-west earthworks. It is postulated mining took place here from pre-history. Later exploitation incorporated adits and shafts which date from the Roman period until ore extraction finally ceased in the 18th Century (Bick, 1988, 1992).

The precipitous northern approach is fringed by woodland with stands of *Quercus petraea* [sessile oak] and *Pinus sylvestris* [scots pine]. To the south, east and west the topography is steep, ca. 20 % but still permits access to the hill fort though a series of constructed earthworks. These would have defended the west gate, one of the three possible entrances, with the others situated to the north and east. The hill fort has uninterrupted views to the coastal hill fort of Pen Dinas near Aberystwyth, north 7 km to the hill fort of Pen Dinas (Elerch), and south and east to the Mynedd Bach Plateau and the Plynlimon Massif respectively. Geologically it is situated 3 km South of the Camdwr fault and on one of the polyphase mineralisation lodes in the Ordovician – Silurian period host lithology with mesothermal polymetallic properties similar to the Frongoch lode containing argentiferous lead and zinc ore (Bick, 1992).

Excavations by the Early Mines Research Group (EMRG) on the gateway ramparts during 2006 uncovered galena (lead ore) which may have been used as infill. However, it does not demonstrate early mining or metallurgical processes. What it may suggest is Iron Age inhabitants identified galena ore and possibly some smaller quantities of chalcopyrite ore (Timberlake and Driver, 2005).



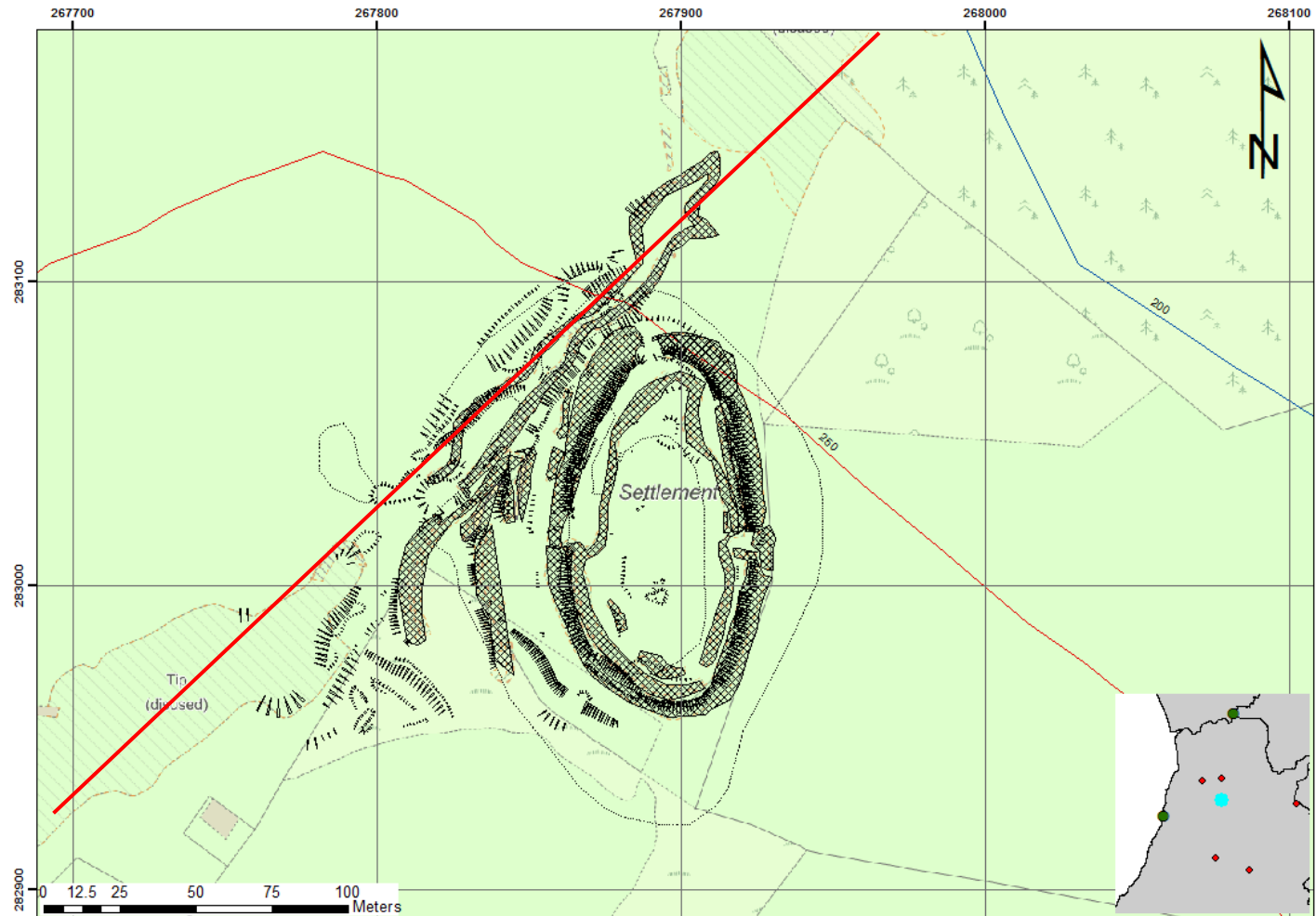
**Figure 31.** Banc y Darren 2005 excavation by Timberlake and Driver showing earth works and stone foundation. Source: RCAHMW (2013).



**Figure 32.** Banc y Darren 2005 Excavation by Timberlake and Driver through the west rampart showing the depth of construction at the site of the galena find. Source: RCAHMW (2013).



**Figure 33.** Banc y Darren is set upon the ridge between Nant Silo and Nant Peithyll. This photograph looks west to Clarach bay, Borth and Cors Fochno, situated north of Aberystwyth. The mineralised lode runs SSW to NNE along the straight red line from Darren South to Darren east. Source: RCAHMW (2013).



**Figure 34.** Banc y Darren (highlighted blue within the inset). Note the outline of the open cut mining to the north west of the fort indicated in red. This continues south-west through the hamlet of Banc y Darren to Darren Farm and north-west down the precipitous hill side into Nant Silo valley and the Twll y Mwyn mine workings.

Evidence of mining is evident in the extensive but now vegetated spoil tips to the NNE towards Cwm Darren and SSW to Darren farm. The workings possibly date from prehistory and continued into the Roman and medieval periods. Later 19<sup>th</sup> Century mining used deep shaft and level workings to exploit the silver rich lead from the Darren lode (Bick, 1988). Prehistoric mining is suggested by a collection of hammer stones found at Twll y Mwyn mine situated to the north east of Banc y Darren, near Pen-bont Rhydybeddau, uncovered by Pickin and Timberlake (1988) (see Figure 36), but no other evidence has been identified.



**Figure 35.** Google Earth image of Banc-y-Darren showing the extent of open cut mining ca.1 km running SSW to NNE touching the north-west edge of the hill fort. Source: Google Earth (2011).



**Figure 36.** Twll y Mywn mine.

A. View towards Twll Y Mywn and Cerrig yr Wyn mines from the open cut mine on the Northern section of Banc y Darren. The mines are now only identified by remaining gullies and vegetated tips. B. illustrates the cache of hammer stones found at the open mine, hole or pit of Twll y Mywn. Source: Early Mines Research Group and Coflien (2014).

### 3.4.4 Llys Arthur

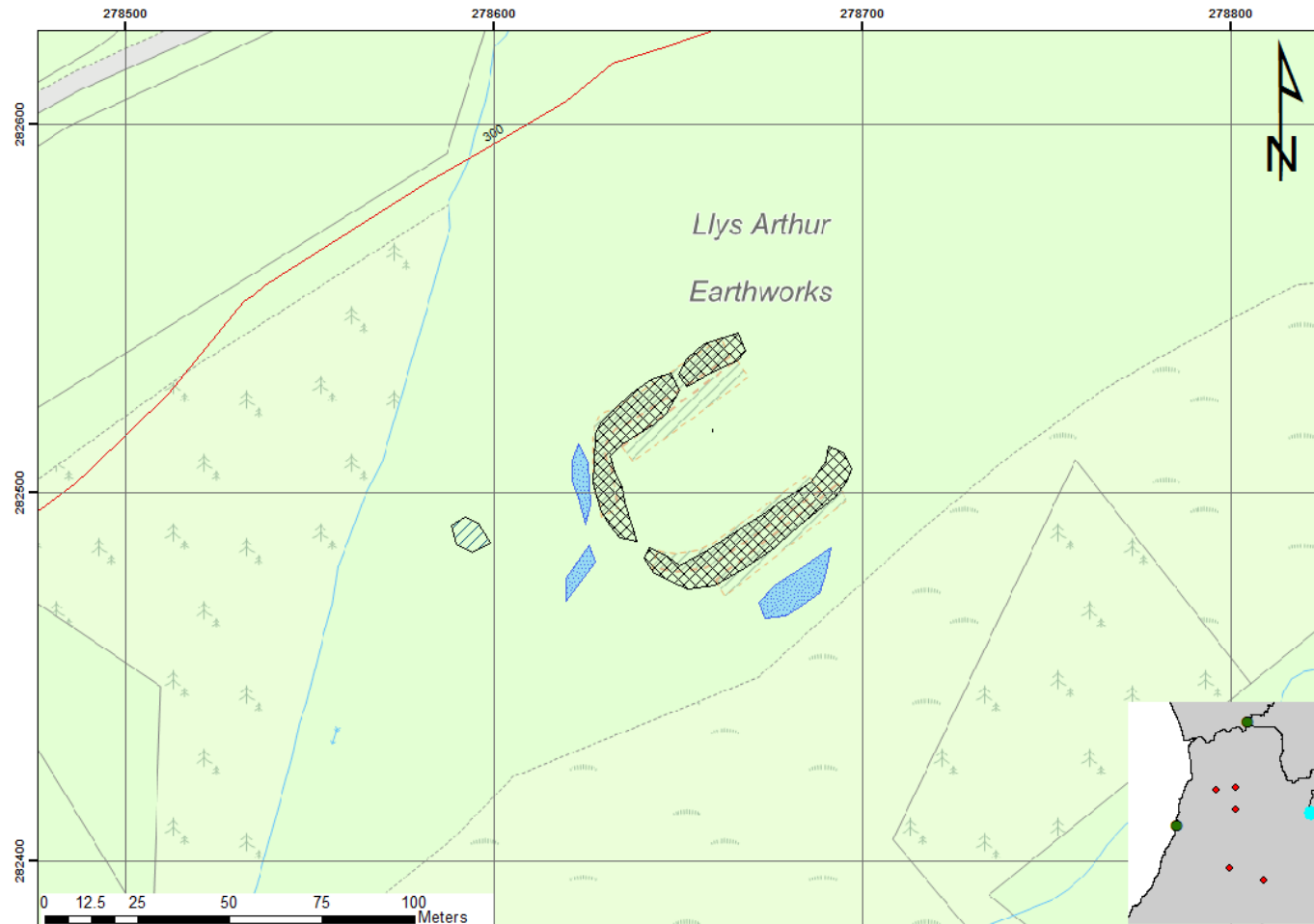
<b>Llys Arthur</b>	74 AD – Medieval period*
<b>Geographical co-ordinates</b>	Grid reference SN7865882505
<b>Elevation OD</b>	289m
<b>Area</b>	60 x 55 m = 0.3 hectare
<b>Bed rock geology</b>	Ordovician – Silurian age. Cwmere formation (CMR), Derwenlas Formation (DLF), Rhayader Mudstone Formation (RHF) mudstone, slates and conglomerate of the upper Mid and lower Llandovery groups
<b>Surficial geology</b>	improved pasture, with Alluvium (ALV) and River Terrace Deposits (RTDU)

**Table 5.** Llys Arthur: geographical and geological details.

Lying at the head of the Afon Castell valley *ca.* 2.1 km due east of Aberystwyth and adjacent to the Castell fault, Llys Arthur is situated on relatively level improved pasture on alluvial deposits. The Nant Coch Mawr (stream) flows south 50 m from the western edge of the fort's earthworks to join the Afon Castell, which eventually joins the Afon Rheidol near Ponterwyd. The course of the Nant Coch Mawr was altered between the 1960s and 1980s possibly to control flooding over this improved pasture. Evidence of overbank flooding and a braided palaeo stream can be seen *ca.* 40m to the north-west of the fort. It has possibly caused erosion to the northern edge of the earthworks [see Figures 38 and 39]. Furthermore there is also evidence suggesting the re-routing of the land drain that appears to run along the old path of the river from the north-west edge of the fort (Edina, 2013).

The site has caused debate as to whether it is Roman or Medieval. Arguably, its rectangular features are common to Roman period marching camps with an outer ditched enclosure. These smaller marching camps were often created along main marching routes. However, its proximity to Cae Gaer, the larger Roman camp 3.5 km to the east, suggests its purpose may have been for other reasons. Lewis Morris' map denotes it lying near to the now deserted farm of Llest Troed Rhiwwiddon. It is less than 1 km from the potential Roman ruin of Fagwry-fawr farm, and even less to Esgair Lle mine. The possible name association with Ogofwyddon, near Machynlleth 25 km to the north, suggests some association with metallurgy. Whatever the case, its narrative is steeped in folk lore (Timberlake, no date; Coflein, 2014).



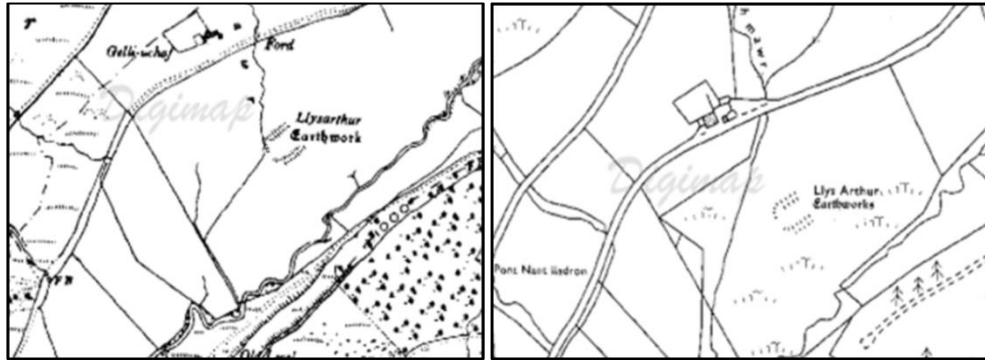


**Figure 37.** Outline of Llys Arthur. See inset for location to other sites highlighted in blue. The earthworks have rounded corners to the western perimeter with the eastern end corners possibly lost to land improvement.

It is also argued the site may have started as a Roman marching camp possibly associated with the larger Roman Cae Gaer site 4 km to the east. It is suggested Llys Arthur was later developed into a medieval moated site. What distinguishes Roman sites are their rounded [card] shaped corners (Phillpott, 1998), which are present on the earthworks here. Along the Southern earthwork is a defined depression possibly associated with a water feature suggesting a later medieval influence? The site is only 400 m west from the Esgair Lle [Great West Van] lead mine described as a post medieval industrial mine which was exploited for the lead ores. However, it has been suggested that prehistoric mining was carried out in close proximity, but with only circumstantial evidence noted by Wilies (2002) in (Coflein, (2014)). This evidence may have been uncovered near the Foel Wyddon shafts *ca.* 1 km north east of the Esgair Lle. However, this area has now been levelled by continuous land improvement and civil engineering projects improving the A44 trunk road.



**Figure 38.** Aerial photograph showing the fort outline and surface sediment debris following a summer flood in 2006. Source: RCAHMMW (2014).



**Figure 39.** The Nant Coch Mawr (stream). The left hand map from the 1960 show the stream path clipping the north-west edge of the fort, and the right hand map shows the straightened course. Source: Edina historic maps (2014).

As with many other sites in this area, very little research has been carried out apart from site description and aerial photography by the RCAHMW.

### 3.4.5 Abermagwr Romano-British villa

<b>Abermagwr villa</b>	Roman period 250 AD - 380?
<b>Geographical position</b>	Grid reference SN 66887418
<b>Elevation OD</b>	63m
<b>Site area</b>	The total site within the double ditched perimeter = 1 hectare
<b>Bed rock geology</b>	Silurian - Devils Bridge Formation (DBF), Borth Mudstone Formation (BMF)
<b>Surficial geology</b>	improved pasture with underlying alluvium and Devensian till

**Table 6.** Abermagwr: geographical and geological details.

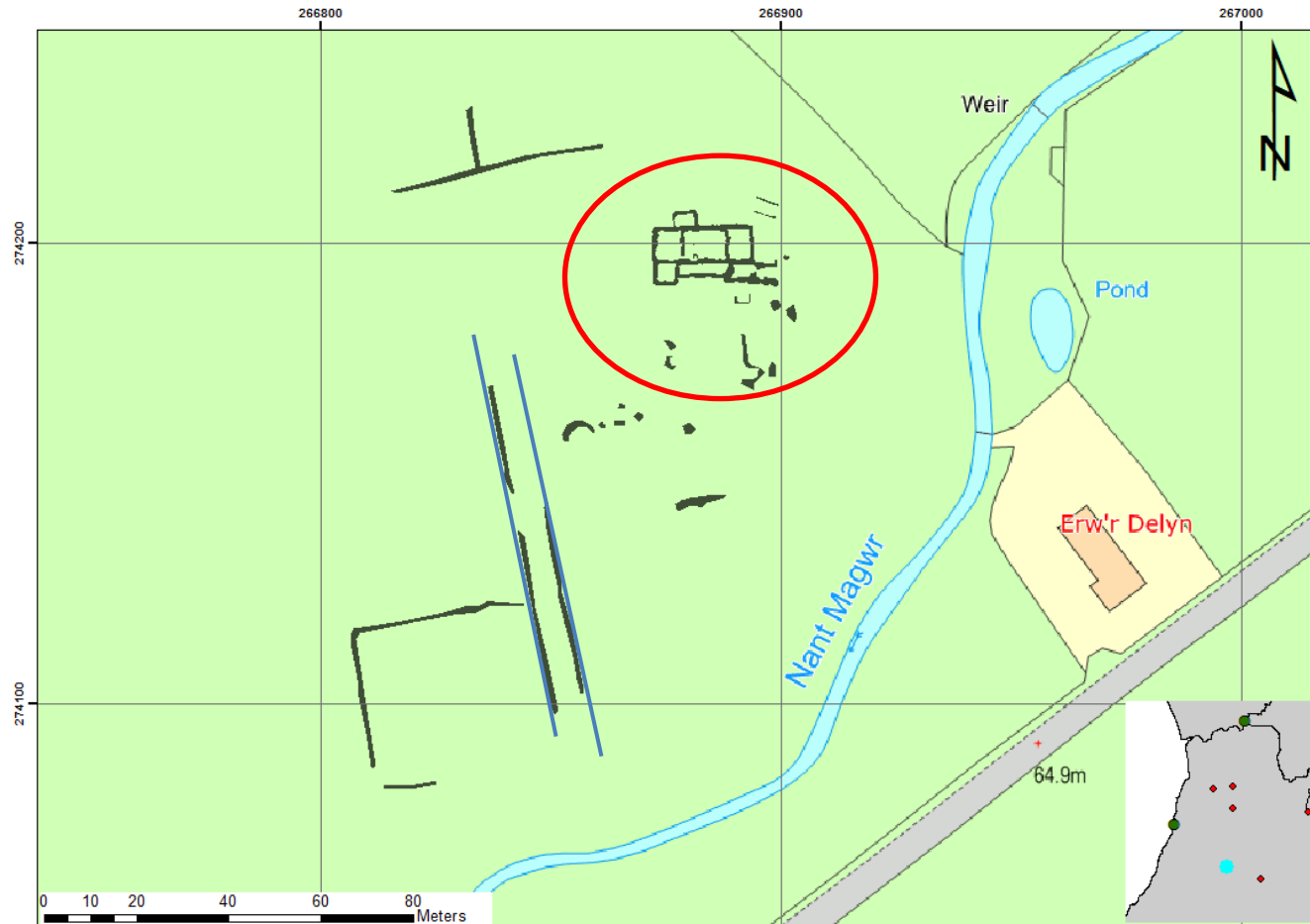
Situated 1 km north of the Roman fort at Trawscoed and 5 km west of Castell Grogwynion and the Frongoch and Grogwynion lead mines, the Romano-British villa is typically of a late winged design with a double ditched perimeter. It was initially identified by Cambridge University aerial photographers when the crop marks outlined the villa and the double ditch perimeter during the 1979 summer drought. It subsequently was documented in the RCAHMW aerial photographic survey of Wales. The 2011 excavation dated and categorised this site as a late Roman domestic site of the 3<sup>rd</sup> or 4<sup>th</sup> Century AD. It is possibly the most western high status late Roman villa site in Wales or Britain (Davies and Driver, 2011).

Abermagwr Villa reflects the high quality found in other Roman villas commonly found in the South of England. The construction of Abermagwr is described as: “built with local stone, with slate roof, glass windows and fronted by a court yard of cobble stones”. There is speculation as to whether an upper floor existed, which was most likely to have been constructed with a timber frame and finished with plaster walls (Davies and Driver, 2011). The upper floor would have added extra rooms to the eight identified in the villas foundation footprint.

Any surface features have been lost to land improvement, but initial geophysical survey and later excavations during 2010-11, uncovered ditches, fire pits and artefacts which included coinage and glassware. From these finds the site date was revised to

*ca.* 250 AD (Davis and Driver, no date), as coinage dated to Severus Alexander *ca.* 224 AD is considered not to have been circulated after 250 AD. These coins were amongst other finds which included other coinage, glassware, lead sheets, gaming counters and worked roofing slates (Davies and Driver, 2012). These were uncovered in four of the eight rooms identified in the villa's foundation, which was partially excavated during 2011.

The exposed ground floor surface revealed numerous fire pits, possibly with some associated with its initial occupation, but many more possibly created after its primary occupation, later abandonment, and eventual dilapidation. Evidence of this is given by the roof beams, which were scorched and collapsed into the building's interior (Davies and Driver, 2011). The roof slates and lead sheets, suggest that local materials were possibly used in its construction. But subsequent stone robbing has taken much of the foundation and wall stones probably to build post-Roman dwellings nearby.



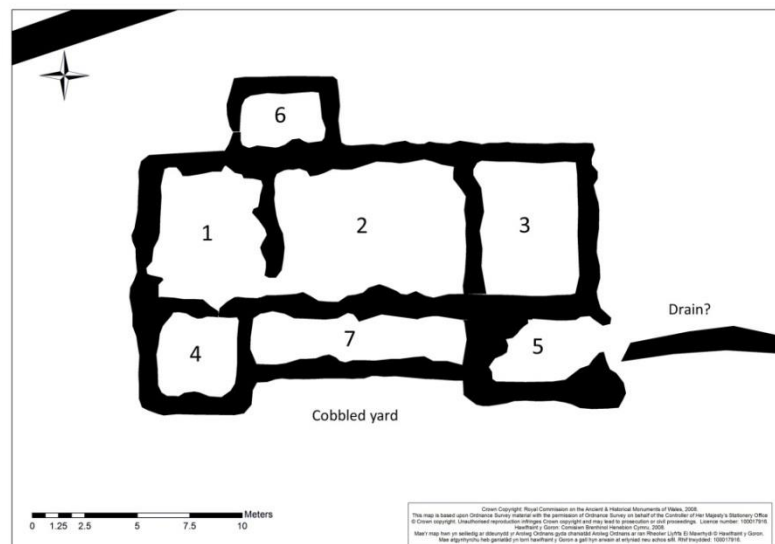
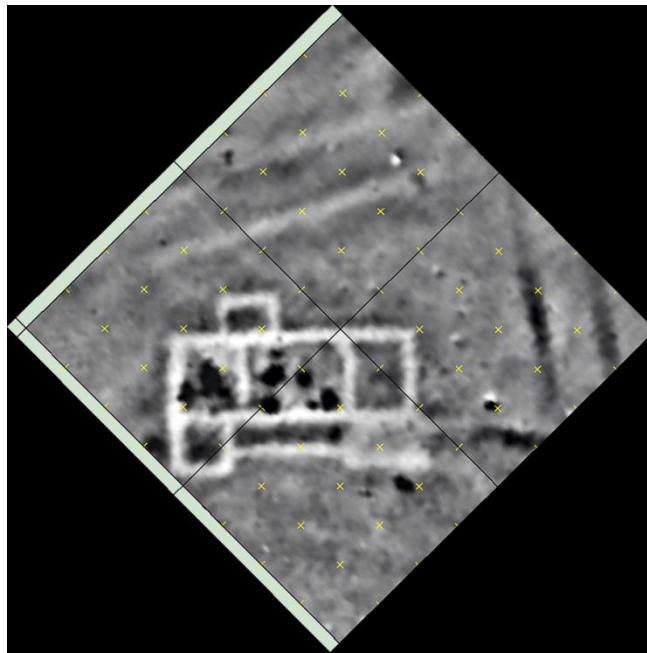
**Figure 40.** The villa's location with regard to other sites is highlighted in blue within the insert. Source: after RCAHMW (2014).

The villa is outlined by the red circle; other features may or may not be associated with the villa, but the two parallel lines indicated in blue are part of the double ditch enclosure.

**Geophysical survey of the villa and surrounding double ditched perimeter**



**Figure 41.** Geophysical image of the villa's outline with a more defined path of the double ditch perimeter. (RCAHMW 2013).



**Figure 42.** Geophysical low resolution plan of the villa's rooms. Source: RCAHMW (2013). (Note the double ditch outline to the top of the villa and the black marks on the Middle image indicative of deep burning, possibly hearths).

Further focus on this site will explore some of the fabric used for the construction and may elucidate the villa's overall use of metals. For example, did the site lend its self to a small metal workshop and how may this link to the wider context of metallurgy and ore exploitation?



### 3.4.6 Castell Grogwynion

<b>Castell Grogwynion (Castle of the white pebbles)</b>	Upland defended Iron Age hill fort continued development suggesting the forts has a long and complex history (Date unknown) but probably within the periods 2800 BP– 150 AD
<b>Geographical co-ordinates</b>	Grid Reference SN72107249
<b>Elevation OD</b>	260 m
<b>Area</b>	180 x 100m = 1.8 hectares
<b>Bedrock Geology</b>	Situated in the Middle of the north and south spall on the Ystwyth fault. Both Ordovician and Silurian geological period; (S1) Claerwen Group, Cwmere formations of mudstone siltstones and greywacke, Devils Bridge formation (DBF): with thinly interbedded turbidites, sandstone and mudstone. To the South and west Rhayader Mudstone pale green turbidite mudstone with predominantly burrowing hemipelagites and scattered units with laminated hemipelagites and Monograptus Sedgwickii Shale Member (MSW).
<b>Surficial geology</b>	Minimal, with thin colluvium from an eroding outcrop

**Table 7.** Castell Grogwynion: geographical and geological details.

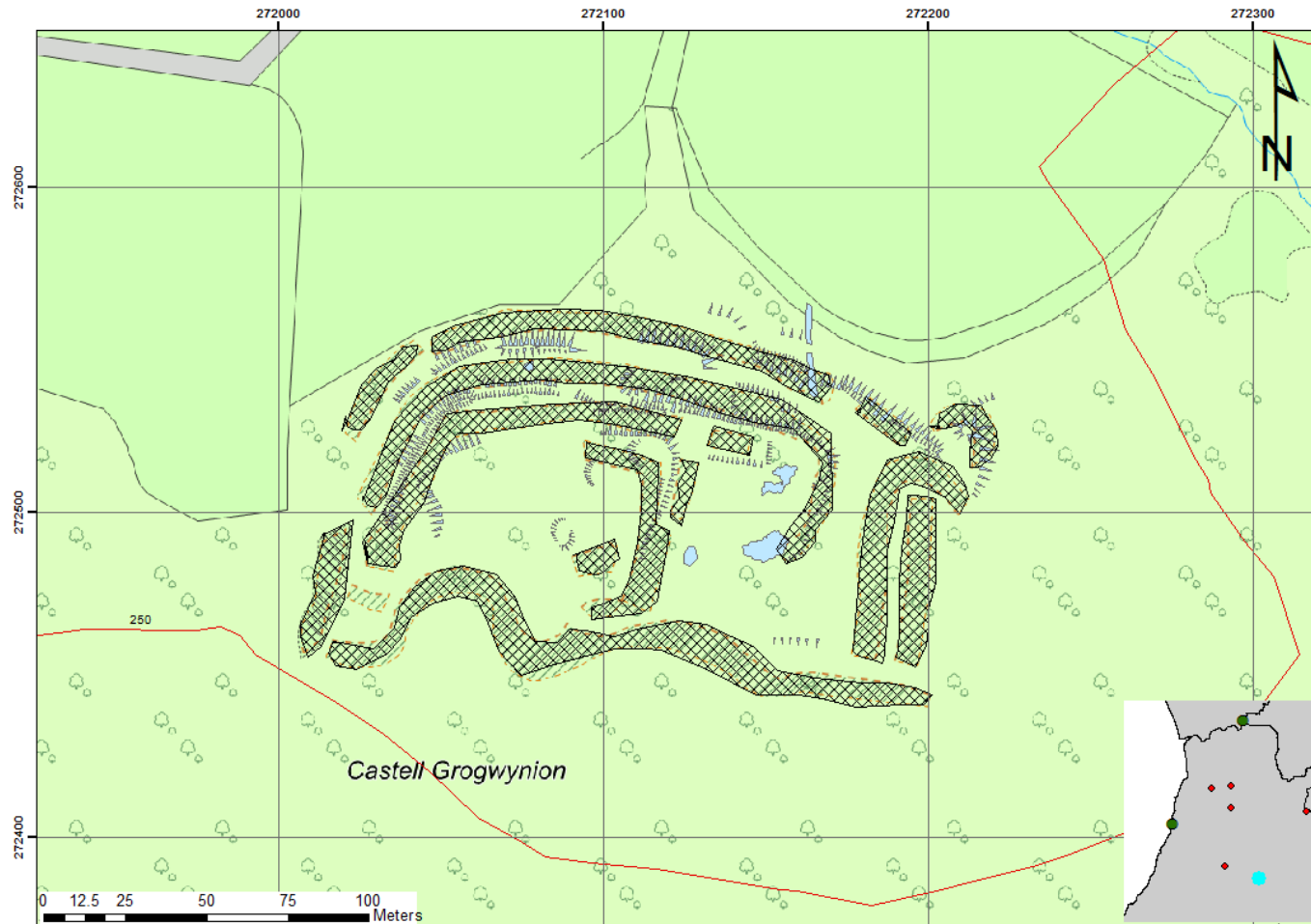
Situated *ca.* 16 km due east of Aberystwyth, the site is perched on a platform above the steep northern side of the Ystwyth Valley between the spall in the Ystwyth Fault which contains complex underlying geology. The Ystwyth River runs east through Aberystwyth into Cardigan Bay. The hill fort commands views east and west along the Ystwyth river valley, and *ca.* 6 km to the south east across the Afon Ystwyth sits the Iron Age hill fort of Pen y Bannau.

The precipitous west, east and southern approaches are covered with stands of *Quercus petraea* [Sessile oaks], *Quercus robur* [English oak], *Betula pendula* [Silver birch] and *Pinus sylvestris* [Scots pine]. The northern approach is less steep, and would have been the hill fort's entrance, defended by earthworks and a bastion gateway situated to the lower north eastern section of the hill fort.

Less than one kilometre to the west, the Frongoch Lode is just one of a series of mineralised veins that collectively form the Central Wales Orefield. It is located on a major, ENE to WSW trending fault and breccia zone. At the Grogwynion Mine, the lode

has been exposed and exploited for lead, and to a lesser extent zinc, from the vein which is comprised of sphalerite and two galena lodes (Bearcock *et al.*, 2010).

Bedrock geology is of the Ordovician and Silurian period (S1), with Claerwen Group, Cwmere formations of mudstone siltstones and greywacke, Devils Bridge formation (DBF): with thinly interbedded turbidites, sandstone and mudstone, Rhayader mudstone with further pale green turbidite mudstone with predominantly burrowing hemipelagites, and scattered units with laminated hemipelagites. Surficial geology is minimal, with thin colluvium from the eroding outcrop covered with a thin organic soil horizon.



**Figure 43.** Outlines of the ramparts and ditches and the interior of Castell Grogwynion hill fort set to the northern edge of the escarpment 145 m above the Afon Ystwyth.

The approach from the north and west sees a formidable looking set of ramparts, which, on closer scrutiny, are false multivallations (the natural topography which has been extended by man-made earthworks extending to the east) (Driver, 2005). The steep south perimeter falls 150m to the river valley. A waterfall cuts through the forested area of Coed Maenarthur to the east into the Afon Ystwyth [see Figure 45].

The initial development of this fort was probably on the west of the outcrop, the highest point of the hill fort, which contained two smaller compartments. One of these may have been used as a lookout, with views along the Ystwyth Valley [see Figure 45].

Further construction took place to the east of the rocky outcrop which initially demarcated the western section [see Figure 44. adding further terraced sections which were accessed from an eastern entrance through the bastion gateway. The internal organisation of the modified eastern section consists of three main terraces in a stepped configuration orientated east to west and rising 19 m in height from the bastioned gateway. A further northern platform is enclosed within the false ramparts, possibly developed after the eastern phase was completed.



**Figure 44.** Looking south-west to Castell Grogwynion with the terraces well defined and the false multivallate ramparts. The rocky outcrop dissects the site and rises *ca.*30 m higher than the bastion entrance highlighted in blue. The round house platforms were situated on the terrace on the left of the outcrop circled in red.



**Figure 45.** Google Earth image of Castell Grogwynion highlighted in red and looking west showing the course of the Afon Ystwyth through the deep valley, with a steep forested area to the south and north. Source: Google Earth 2013.

On the terrace to the eastern side of the outcrop there are two or possibly three round house platforms. On the northern perimeter there is evidence of some antiquarian test pits possibly dating from the early 20<sup>th</sup> Century, and a trial pit which runs north to the site's perimeter. Apart from this and later work by Driver (2005) on the architecture and regional identity of this hill fort, little research has been carried out on this site.

### **3.5 Soil**

The soil of each site can be generally categorised as shallow with limited development. The upland sites of Castell Grogwynion, Pen Dinas (Elerch) and Banc y Darren are peaty podzol soils which are mineralogical and dominated by quartz, chlorite, plagioclase, feldspars and illite micas (Loveland, 1984; Langan *et al.*, 1996). By contrast, lowland sites have often developed on either alluvium or colluvium high in the lithogenics made up of the weathered lithology of local origin dependent on the catchment.

### **3.6 Summary**

This chapter has outlined the locations and surrounding landscapes of Odyn Fach, pen Dinas (Elerch), Ban y Darren, Llys Arthur, Abermagwr and Castell Grogwynion, with a brief description of the soil, surficial and bedrock geology and the ore lodes which have been exploited nearby. It has discussed specific problems with the understanding of the overall chronology of the sites within Wales identifying how they may have been developed during their possible sporadic occupation. It has also identified previous work carried out within and proximal to the sites which may have relevance to this study's aims. This includes work on systematic site surveys, excavation and/or aerial reconnaissance and uncovered artefact that have been used to determine site chronology and use.

## Chapter 4: Methodology

### Introduction

The aim of this study is to understand if a relationship with metallurgy exists between North Ceredigion's Iron Age and Roman settlements, which may be similar with settlements of a similar type in other ore rich areas on the North East Atlantic fringe. However, the permits granted by CADW required a non-intrusive and non-destructive method of detection and analysis of soil and sediments of the selected scheduled sites. If these initial surveys produced evidence of metal enrichment well above the expected background levels, further applications for more intrusive sampling could be considered by CADW.

All analytic techniques used in this study are described and justified in this chapter in a stepwise progression. These included field walking, Remote Light Detection and Radar (LiDAR) analysis, acid digestion and analytic methods used include Atomic Absorption Spectrometry (ASS), Inductive Coupled Plasma Mass Spectrometry (ICP-MS), geophysics, Portable X-Ray Spectrometry (pXRF) *in situ* and *ex situ* analysis in tandem with Differential Global Positioning System (DGPS), laboratory, excavation, typology and laboratory isotope analysis, these were combined with desk based work using Computer Aided Design (CAD), ArcMap, Sigma plot and statistical applications.

#### 4.1. Field walking

Reconnaissance by field walking over all of the sites gave an overall understanding of the topography and how these sites were initially organised and how they may have been subject to later development. This was carried out in methodical 5 m swathes also enabling the assessment of where pXRF sample would be undertaken, but also enabled the identification of areas and features that were unsuitable for sampling. These included outcropping lithology and steep areas unsuitable for habitation. It also enabled the identification of where it was feasible to gather background geochemical data for site control points which would be used to compare later *in situ* and *ex situ* sampling. Also a photographic record of the internal platforms and external



earthworks and approaches were taken for later reference, description and illustration.

#### **4.2 LiDAR Imagery and GIS mapping**

Light detection and ranging (LiDAR) can enable fine ground surface detail to be exposed. It can provide both a digital terrain model (DTM), showing surface and ground objects and a digital surface model (DSM) where all the vegetation is removed. The process requires raw LiDAR data, which was only available from Environment Agency Geomatics for this area. It was rendered using integrated processes in both Arcmap and Arcscene which create maps, perform spatial analysis and manage geographic data. These can produce an Arcscene 3D expression of the upland hill forts selected (Davies, 2011). Using azimuth light direction control within Arcscene the 3D modelling software was used to identify any discrete land forms in, or nearby the selected upland sites. However, it was not used for the lowland Iron Age and Roman sites as these were identified by the crop marks from aerial photography during previous summer droughts, as little or no visible archaeological or earthworks remain. However, LiDAR may have also shown these sites to some degree. There are many other comparable systems for this process but Arcmap was considered the more complete and integrated system for this study. Furthermore, ArcMap platform is a cartography tool which enables 2 D Ordnance Survey surface maps or outline maps to be integrated with CAD drawings and DPGS coordinates. These can also be used to integrate the geochemical data collected from the site and laboratory analyses into the ArcMap platform within attribute files. These data can also be used for inverse distance weighted interpolated maps (IDW) which can model concentrations of the elements copper, lead, zinc and iron to identify probability of increases in metal deposition. The ArcMap platform can also be used to import maps from Edina. These included geological and geographical maps for basic reference to bedrock, surficial geology, faults and mineral lodes, and also historic maps to assess changes in the landscape of alluvial systems and mass movement at the sites surveyed.

The DraWinG (dwg) files stored two and three dimensional designs and data are often used in AutoCAD. These were supplied by the RCAHMMW and contained recent surveys of the hill forts used for this study (Coflein, 2013). All of these processes have been applied in this study to help interpret and illustrate outcomes at the sites surveyed.

### 4.3 Soil, sediment and other sample preparation

The elements that were exploited during and since the Bronze Age are copper, lead, zinc, silver and Iron, but what elements remain within environmental archives from prehistoric and classic period pyro-metallurgy can be related to the lack of mobility of the heavy metals used and by-products of extraction, ore processing and smelting during these periods. Therefore, understanding is needed of chemical, biochemical and physical bonding of elements that can either create mobility or immobility in specific environmental conditions. For instance, the release of iron and manganese from sediments can be due to the dissolution of ferro-oxides and hydroxides in the surface sediment (Alloway, 2013). Arsenic (As) (arsenite As<sup>3</sup>) can attach to these free oxides and become mobile in wet environments (Fuge, pers. comm. 2012). This often removed evidence of iron artefacts if in oxidising environments. However, this is not the case with Pb and Cu and some arsenic speciation's like arsenate As<sup>5</sup>, which can become immobile in peat or other anoxic environments. Even low pH soil will retain lead and copper longer than cadmium and zinc (Merrington and Alloway, 1994; Alloway, 1995). Therefore, these elements are normally environmentally consistent and are subsequently good target elements for this study as they may indicate potential pyro-metallurgy locations.

Taking *in situ* pXRF sampling is considered qualitative, so further analysis by atomic Adsorption Spectrometry (AAS) and Inductive Coupled Plasma- Mass Spectrometry (ICP-MS) on supplementary soil samples collected during both phases of pXRF sampling were conducted for element identification and a comparison of element concentrations to pXRF. But the soil samples required preparation before these processes could proceed.

Preparation for wet analysis requires sediment or soil to be prepared to a homogeneous aliquot. Single or multiple acid digestions renders remnant metals into solution (Davidson, 2013). Additional chemicals may create aliquot homogeneity and can also be required to keep specific elements in solution. Sample handling and the

equipment used are described in Hoenig and Kersabiec (1996), but a brief description is given here.

All soil and sediment samples were catalogued and stored in separate re-sealable polythene bags at an ambient temperature of *ca.* 15 °C, with minimum exposure to light prior to preparation. Soil samples were dried at 110 °C for 24 hrs and disaggregated with standard pestle and mortar with the material passed through 180 µm nylon sieve yielding < 180 µm fraction. Hydrofluoric acid digestion required a finer fraction to < 60 µm, achieved by using an agate pestle and mortar for ores or pottery glazed artefacts required for acid analysis.

#### **4.4. Acid digestion**

Atomic Adsorption Spectrometry (AAS) required approximately 0.5 grams of prepared samples. These were placed into borosilicate boiling tubes and digested with 2 ml of 70% volume concentrated nitric acid (HNO<sub>3</sub>) analytic reagent grade. The digested samples were then placed on block heaters at 100 °C in a fume cupboard for one hour. Adding 18 ml of distilled water made a 20 ml aliquot [a ratio of 40:1 between solutes and sample]. All samples were mixed for *ca.* 10 seconds and left to settle for a further 12 hours. Finally, a further 10 % dilution gave the sub samples a ratio of 400:1 solute to sample.

Other variations in the acid digestions used in this study are outlined later in this chapter. These include hydrofluoric acid digestion for pottery glaze, hydrochloric acid digestion of galena ore, and finally the lead plate sections from the Abermagwr villa with various acid preparations prior to initial AAS and later ICP-MS analysis, the latter for isotope provenance. Galena samples were crushed by pestle and mortar disaggregating the quartz gauge. Using a microscope identified and select *ca.* 0.50 gram of galena fragments ready for acid digestion. The lead plate section was initially cleaned in 10 % HCl to remove surface calcification, then divided into cubes of 1-2 mm acid digested and analysed alongside blanks and certified reference material (GSG11), all using the same protocol for precision and accuracy.

Isotope analysis on the pottery, lead artefacts, galena samples and soils used either 0.1 or 0.5 grams +/- 0.05 % per sample these being placed in pre-labelled borosilicate boiling tubes. Ten millilitres of concentrated HCl was then added to all the samples and left for 12 hours on a hot plate at 110<sup>0</sup>C in a vented fume cupboard, and then left to dry for a further 12 hours. Adding 18 ml of 10 % HCl re-dissolved the samples with an additional 2 ml of diethylene triamene to retain any heavy metals in solution (Perkins, pers. comm., 2011). Finally, samples were placed on a hot plate to warm for 30 minutes. Solutes underwent a further dilution with milli-Q to 50ng/ml<sup>-1</sup>, to eliminate coating the ICP-MS detector cones with lead residue. The results were statistically manipulated with Excel and IGPET software to produce correlation graphs.

#### **4.5 Analytic methods**

Comparing pXRF with AAS and ICP-MS is normally done from an analysis of identical samples. As pXRF is often used *in situ* on a range of samples that may have differing moisture content, it is therefore prudent to prepare samples to meet the same conditions as would be appropriate for other analytic processes i.e. AAS or ICP-MS. Even though the latter will involve digesting with single or multiple acid combinations to produce an aliquot, it is important to sample at the latest possible stage of preparation to limit introduction of variance (Shefsky, 1997).

#### **4.6 Atomic Adsorption Spectrometry.**

Of the total samples analysed *in situ* by pXRF, *ca.* 10 % were collected as a supplementary soil sample and subjected to further analysis by the AAS for comparison to pXRF analyses, and also to calculate precision and accuracy and the lower level of detection (LLOD) and level of quantification (LOQ). Other artefacts were

also tested by both these methods. These comparative tests are outlined later in this chapter.

Detailed explanation of the ASS analytic process is given in Beaty and Kerber, (1978) but a brief explanation is as follows.

Developed in the 1950s, Atomic Adsorption Spectrometry (AAS) works on the basis of applying energy to a stable ground state atom, which absorbs the energy. This will cause an electron to move into an outer orbit shell. Thus, the atom is in an 'excited state' which is unsustainable. When the electron returns to its original position the excess energy absorbed by the atom is emitted, collected by the diode, pre-amplified and imaged as spectra. As each element has a unique atomic structure the amount of energy required to 'excite' an atom and the resulting amount of light energy emitted by an excited atom returning to its original ground state is distinctive. This characterisation can be used to identify individual elements through the integrated analysis software.

Software within the AAS detects how much energy is absorbed by the atoms present in the pre-prepared aliquot and introduced as an aerosol into the flame via a nebuliser. The AAS element hollow cathode lamp [specific to the element to be analysed] emits a beam through multiple lenses into a monochromator. Here, the detector identifies the element. This is processed by a photo multiplier or amplifier for both element type and abundance (Beaty and Kerber, 1978).

Using the Perkin Elmer Analyser 400 AAS requires a calibration curve to be set by sampling a range of prepared standards made up for lead, zinc, copper and cadmium specific to a range of element concentrations initially analysed using the pXRF. Using a single element cathode lamp for AAS analyses avoids problems of resonance wavelength interference which can occur when using the multi-element cathode lamp often associated with the copper 216.5 nm resonance line (Brown, pers. comm., 2014). The single element tube uses both wavelengths 217.00 nm and 283.31 nm, one having a more stable background but less sensitivity and *vice – versa*. Here, both gave similar results.

It is also noted that high levels of Fe > 10 k ppm creates interference (White and Miller, 1981) this can affect the values of copper and zinc (Billet, 2006).

Wavelength lines and standards used for Pb;

Pb 283.31: 5.0; 10; 20 and 50

Pb 217.00: 5.0; 10; 20 and 50

All standards are in µg/ml (equivalent to ppm)

Linear range can be an issue if the specific sample has a lower concentration than others in a suite of samples. Reducing element concentration through dilution can also introduce error that can affect outcomes of AAS analyses therefore it is advisable to keep handling to a minimum.

Other elements, wavelengths and standards used for calibration:

Zn 213.86: 1.0; 2.0; 4.0 and 6.0

Cu 324.75: 1.25; 2.5 and 5.0

Cd 228.80: 0.00; 0.5 and 1.00

All standards are in µg/ml (equivalent to ppm)

Arsenic, iron and manganese were analysed using ICP-MS, which is outlined next.

#### **4.7 Inductively Coupled Plasma –Mass Spectrometry (ICP-MS)**

The other elements iron, manganese and arsenic, were sampled using ICP-MS for the comparative analysis between AAS, pXRF and ICP-MS. Furthermore, it was also used for lead isotope analysis on soil, pottery and galena samples collected from Grogwynion mine for isotope provenance, details of which are given in section 4.10.

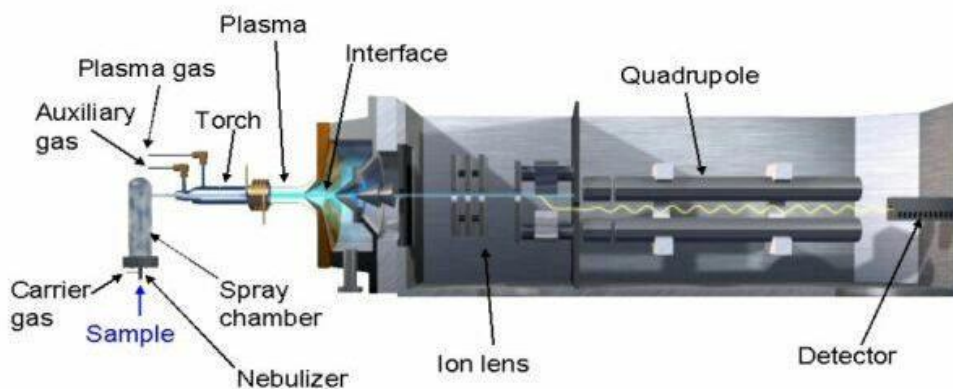
Developed in the 1970s ICP-MS analysis, alongside AAS, has become one of the benchmarks for environmental science (Houk *et al.*, 1980; Jarvis and Jarvis (1992) with ICP-MS analysis now routinely used in environmental studies. The technique is well

documented and detailed descriptions of ICP-MS and its applications can be found in Jarvis et al, (1992) and Primer, (2005). A detailed explanation of its operation can be found in Primer, (2005) through a brief explanation follows.

In contrast to AAS, ICP-MS is based on the principle that each element has a unique atomic mass, which can be used to characterise and identify individual elements and concentrations. As with AAS, samples are introduced in solution via a nebuliser. As it passes through the spray chamber the larger droplets are removed while being introduced into the plasma. The sample is then ionised at temperatures ranging between: 6,500 – 10,000 Kelvin (K). Sample ions pass into the mass spectrometer via the Ni cones, where neutral Argon separates from the ions by a series of ion lenses which form and direct the ion beam.

The focused beam of ions enters the ICP-MS that separates the mass of charged ions. Particular to this instrument is the quadrupole, but for higher resolution ICP-MS also uses magnetic sector based filters and the magnet flight tube. These are commonly used to identify isotopes of elements key to this study. Quadrupoles work using the principle that the mass charge ratio of the individually charged ions is equivalent to the mass of the ion. Variations in the electrical fields produced within the quadrupole separate the ions based on their mass, allowing a greater range of elements to be scanned by the instrument. Ions are detected by the electron multiplier, which measures the ions passing from the quadrupole. The size of the peak signal is directly proportional to the concentration of the element present in any given sample. Therefore, when the instrument is calibrated with known standards, quantitative data can be extrapolated from the sample (Primer, 2005).





**Figure 46.** Schematic of the internal parts of an Agilent ICP-MS.

Using this ICP-MS and a laser element further analytic work can be carried out to identify lead isotope signatures within lead enriched soils, spoil debris, galena ore and lead samples. Details of general soil sample preparation are given in the soil preparation section of this chapter.

Galena samples were crushed by pestle and mortar disaggregating the quartz gangue to separate the galena ore. A microscope was used to identify and select *ca.* 0.50 of a gram of the galena ready for acid digestion. The lead plate section was initially cleaned in 10 % HCl to remove surface calcification, then divided into cubes of 1-2 mm for acid digestion and analysed alongside blanks and certified reference material (GSG11) for precision and accuracy.

Isotope analysis on the pottery, lead artefacts, galena samples and soils used either 0.1 or 0.5 grams  $\pm$  0.05 % per sample which were placed in pre-labelled borosilicate boiling tubes. Ten millilitres of concentrated HCl was added to all the samples, which were then left for 12 hours on a hot plate at 110 °C in a vented fume cupboard, and then left to dry for a further 12 hours. Adding 18 ml of 10 % HCl with an additional 2 ml of diethylene triamine to retain any heavy metals in solution re-dissolved the samples (Perkins, pers. comm., 2011). Finally, the samples were placed on a hot plate to warm for 30 minutes.

Solutes underwent a further dilution with milli-Q to  $50 \text{ ng/ml}^{-1}$  to eliminate coating of the of ICP-MS detector cones with lead residue. The results were statistically manipulated with Excel and IGPET software to produce correlation graphs.

#### **4.7 Geophysical survey**

The Initial and the subsequent pXRF surveys at Castell Grogwynion identified high levels of lead, possibly indicating a former metal working area. The geophysical survey commissioned by the RCAHMW further investigated the lead anomaly. Using a caesium [alkali vapour] magnetometer commonly used in commercial archaeological prospection, sub surface data was collected from two platforms at Castell Grogwynion hill fort [see Figure 156].

At the base line set for each platform, the magnetometer was moved one meter perpendicular to the base line after every pass with a series of overlapping one metre swathes covering both platforms (Roseveare, 2013). The survey aimed to identify anomalies in the magnetic field without sensitisation to depth and avoiding the inability of other gradiometric configurations used in similar surveys to detect horizontal laminar structures. The geophysical survey identified anthropogenic features on both platforms which are discussed with all the other findings in the results, interpretation and discussion Chapters 5 and 6.

#### **4.8 Excavation**

The pXRF and supplementary soil samples correlated with the increased lead element concentrations suggested by to the geophysics outline of deep burning at Castell Grogwynion. This evidence was submitted to CADW for a trial excavation over the northern platform, along with the outline of the excavation method and final site

remediation. This was supported by data from the pXRF and geophysical surveys outlining the preliminary findings.

Scheduled site consent was given for a 25 square metre test excavation over the northern platform of the hill fort. This followed standard guidelines set out in, 'Introduction to Standards and Guidance in Archaeological Practical (SGAP) ([www.isgap.org.uk/docs/6](http://www.isgap.org.uk/docs/6)) 2014). The excavation was conducted between 6<sup>th</sup> - 10<sup>th</sup> October 2013 with two trial trenches hand excavated with members from the EMRG and the RCAHMW. All contents were dry sieved, with the findings and a full account of the excavation being given in Chapter 5.

#### **4.9 Typology**

During field surveys and subsequent excavations some artefacts were recovered. Their typology was appraised by experts from: the EMRG, Museum of Wales and RCAHMW and Wessex Archaeology. The information from these appraisals created further hypotheses that needed further geochemical and isotope analysis. These are outlined in the next section with a full account of these findings being given in Chapter 5.

#### **4.10 Isotope analyses of lead rich artefacts and soil.**

Identifying the isotope signature of pottery finds, soils and local ores was key to understanding the geochemical enrichment found at both Castell Grogwynion and Abermagwr.

Analysis of pottery sherds used methods outlined in this chapter and hydrofluoric acid digestion. As the lead content was primarily concentrated in the pottery glaze, samples of the glaze were taken using a small diamond burr grinder. They were then disaggregated to a fine powder < 60 µm using an agate pestle and mortar. Fine fraction of *ca.* 0.1 grams +/- 0.005 were added to PTFE beakers [one per sample] and washed in with milli-Q., with a further 5.0 ml of HCL added and mixed to homogeneous aliquot. All samples were dried for 24 hrs at 140 °C. After cooling a further 15 ml of HF and 4 ml

of perchloric acid (HClO<sub>4</sub>) were added and these samples were left to cool for 48 hrs. Samples were then returned to the hot plate at 140 °C until dry. The residue was tapped down and a further 2 ml of HClO<sub>4</sub> added. Samples were returned to the hot plate until dry. Finally 20 ml of milli-Q and 10 ml of concentrated analyte HCl were added, except for the standard (CRM) and blank, where only 2 ml were added. Details of these findings are given in Chapter 5.

After 24 hrs, samples were returned to the hot plate at 80°C until warm and clear. Samples were finally diluted to 500 ml in 'A' grade volumetric flasks with the standard CRM and blank made up into 100 ml flasks. All aliquots were stored in pre-decontaminated 125 ml and 60 ml clean labelled low density polyethylene (LDPE) bottles in 2% strength HCl. Prior to ICP-MS analyses these were further diluted with mill-Q to 50 ng/l<sup>-1</sup>.

#### **4.11 Whetstone analysis**

Using the Itrax core scanner [see Figure 47], provided high-resolution, elemental analysis, for the whetstone find from Pen Dinas (Elerch). It measured any subtle variations within the sandstone laminations or if any metal residue was left on the surfaces.

Itrax procedures are described by Croudace *et al.* (2006). Briefly, the Itrax scanner X-ray fluorescence uses a 3 kW molybdenum tube with the excitation voltage and current of the X-ray tube set at 30 kV and 30 mA, respectively. Dimension limits were set and the surface topography of both samples imaged. Radiographic parameters, including the scan increment (1000 µm) and dwell time of (10 sec) were used for the radiographic scan. The Q-spec program finds the elements selected for analysis and the spectral fitting parameters. The scanner navigator controls the movement of samples from under the X-ray beam for the X-ray line camera diode array to be calibrated with the radiographic scan. The XRF scans are then automated. Density and colour information is assessed through X-radiography and digital RGB (Red, Green and Blue) optical imagery.



**Figure 47.** Itrax core scanner. Source: Aberystwyth University web site (2012).

Aspects of the whetstone were sampled with the Itrax high-resolution XRF core scanner. Sample data for tin, silicon, iron, rubidium, strontium, arsenic, chromium, zinc, manganese and lead were separated automatically from the X-ray spectra using the Q-SPEC programme. Spectra were re-evaluated following scanning to further refine the background and/or elemental peak area fitting process during post processing. Details of these findings are given in Chapter 5.

#### **4.12 pXRF *in situ* sampling**

The range and depth of onsite investigation is variable in Britain and Ireland, with projects using traditional methodologies, and some introducing new and dynamic research concepts. Some have been successful in identifying specific research aims for metallurgical evidence or proxies that can be related to metal exploitation (Crew, 2002; Jenkins *et al.*, 1999, 2001; Mighall *et al.*, 2002, 2009). The application of *in situ* pXRF analyses to this study's investigation of surface soil geochemistry over the selected sites differs from the conventional methods previously used in pyrometallurgical enquiry. This application was determined by the conditions set out by CADW, whose governance of these sites deemed conventional excavation too invasive

without good evidence for granting these necessary licences. The application of pXRF to this type of enquiry fit CADW requirements and also ideas outlined in the National Heritage Science Strategy (NHSS) reports of 2006 and 2009, with a further proposed publication highlighting the development of science-based techniques for enhancing our understanding of the past (Williams, 2009). These publications' ideas combined with the evidence outlined in this chapter draw some parallels with this study's proposed method and application into investigating the Iron Age hill forts and Roman settlements of Ceredigion to understand their relationship with metallurgy.

Firstly, a brief history of x-ray spectrometry is outlined and how pXRF can be operated in both field and laboratory conditions, also how x-ray fluorescence determines both element identification and concentration.

The first use of X-Ray spectrometry dates to ca. 1910 when C. G. Barkla obtained the first emission spectra. H.G. Moseley advanced the application three years later by establishing the relationship between frequency and atomic number. But it was not until the 1950s that it was first commercially used (Jenkins, 1995). Wave length dispersive x-ray fluorescence (WDXRF) measures the wave length emitted by an element, but initially it was only possible to analyse one element per analysis. Advances with energy dispersive x-ray fluorescence (EDXRF) led to the development of multiple elements spectrometry. The use of XRF [x-ray fluorescence spectrometry] has progressed since the 1960s, with its analysis increasingly conforming to quantitative data required by many industrial and environmental disciplines (Jenkins, 1995; Janssens, 2013).

Development of pXRF equipment over the last two decades has concentrated on increased sensitivity, safety and portability. Its use has benefited ongoing multi-disciplinary land survey projects in the Near East (Adams, 2009; Grattan *et al.*, 2014), where it has enabled the recording of exploitation of metal rich ore, identifying mining and possible the earliest known sites where pyro-metallurgy has been recorded. These are situated in Southern Jordan near the Khirbet Nahas, and Khirbet Faynan. These were early centres of metal smelting and the research carried out there has provided a further understanding of the spatial spread and trophic pathways (Barker *et al.*, 2007;

Pyatt et al., 2000). The application of pXRF in these remote and often challenging locations highlights its value to ongoing research.

*In situ* analysis with portable pXRF equipment is being used extensively within industry for recycling, exploration, environmental monitoring, and to ground truth for LiDAR and other airborne platform based remote sensing techniques. It has changed industry's approach to geochemical assessment, and now *in situ* analysis is becoming a powerful tool in archaeology, capable of both site laboratory and artefact analysis. (Pantazis *et al.*, 2009; Melquiades and Appoloni, 2004), however, there is still some dispute to its real efficiency (Goodale *et al.*, 2012).

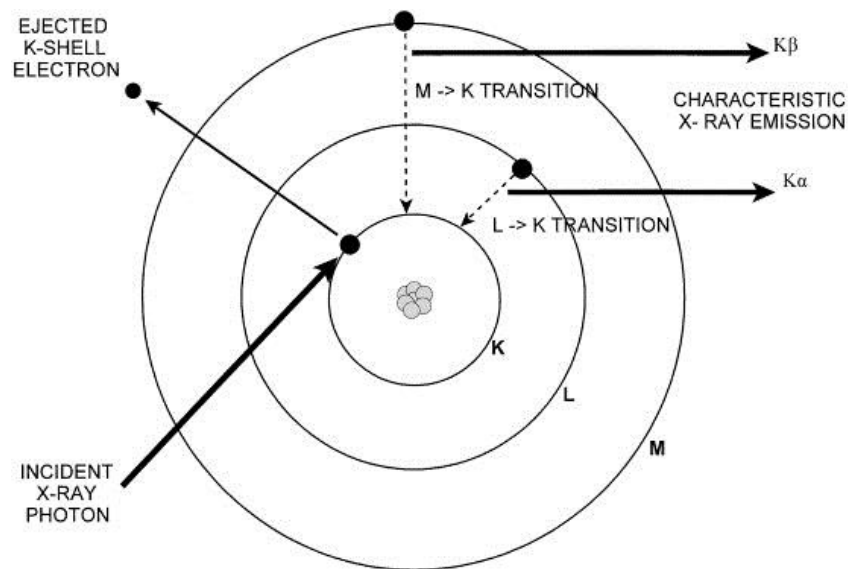
As pXRF is suitable for field work applications when looking for hot spots (discrete anomalies) it provides the use with a degree of flexibility in changing sampling strategies. It also reduces time spent gathering soil samples for wet analysis. Portable x-ray fluorescence has also been used extensively in other areas of archaeology due to its portability and non-destructive applications. Goren *et al.* (2011) used the pXRF in provenance studies of eighty one cuneiform tablets, grouping and indexing them by assessing their chemical properties. There is also increased use in obsidian artefact provenance. Nazaroff *et al.* (2010) compared similar pXRF equipment to a laboratory based Thermo/ARL Quant'X energy-dispersive X-ray fluorescence spectrometer. Outcomes suggest the portable Bruker pXRF used (similar to the Niton Xlt 700) can be used to provenance different obsidian sources by their geochemical properties (Speakman, 2012).

Other examples of its use have concentrated on metal ore rich locations in Britain, Europe and the Near East. These have left a legacy of anthropogenic derived contamination in the environment. With much of the river networks in North Ceredigion and the Swale catchment contaminated from the tailings and early mining processes from their local ore fields (Macklin *et al.*, 1994; Coultard and Macklin, 2003). Recently, postulated climate related flooding has re-mobilised contaminated river alluvium high in lead and zinc by vertical and horizontal bank erosion with the fine sediment transported downstream, it has eventually been deposited by overbank floods onto arable farm land. This has led to lead contamination of silage bales (livestock feed) by the flood waters (Foulds *et al.*, 2014). The transfer of lead rich

sediment has been linked to recent bovine morbidity and mortality due to high levels of lead ingested with the silage (Foulds *et al.*, 2014). Primary surveys with pXRF have not only been used to identify the areas contaminated by this event, but other similar riverine systems in England and Wales and eastern Europe which have analogous historic mining and contamination problems (Macklin *et al.*, 2006; Foulds *et al.* (2014). The later survey by Foulds *et al.* (2014) used pXRF for soil sampling, combined with AAS and ICP-MS analysis. This use of pXRF may become far more extensive for in situ analysis, as it has the benefits of speed, cost and provision of real time data (Carr *et al.*, 2008; Simpson *et al.*, 2006). Further use of pXRF identified high lead content in historic floodplain deposition near Aberystwyth; importantly in this case it prevented further public monies being spent on a small wetland infrastructure (Haylock, 2013, unpublished). Its application for this project will be in the assessment of the top soil for metalliferous enrichment that may yield evidence of metal use in Iron Age and Roman settlements in Northern Ceredigion.

Portable x-ray fluorescence is similar to laboratory-based XRF where the excitation of electrons by incident x-radiation causes the ejection of an electron from the inner K atomic shells. This creates a vacancy that is filled by electrons from the L or M outer shells, either  $K\beta$  or  $K\alpha$  or  $L\beta$  and  $L\alpha$  transitions. This leads to the emission of energy in the x-ray region of the electromagnetic spectrum equivalent to the difference in energy between the two shells photons. Subsequently, the surplus energy is emitted as a pulse of secondary x-radiation; this differing fluorescent energy and wavelength is the characteristic signal for specific elements. (Gill, 1996; Weltje and Tjallingii, 2008).



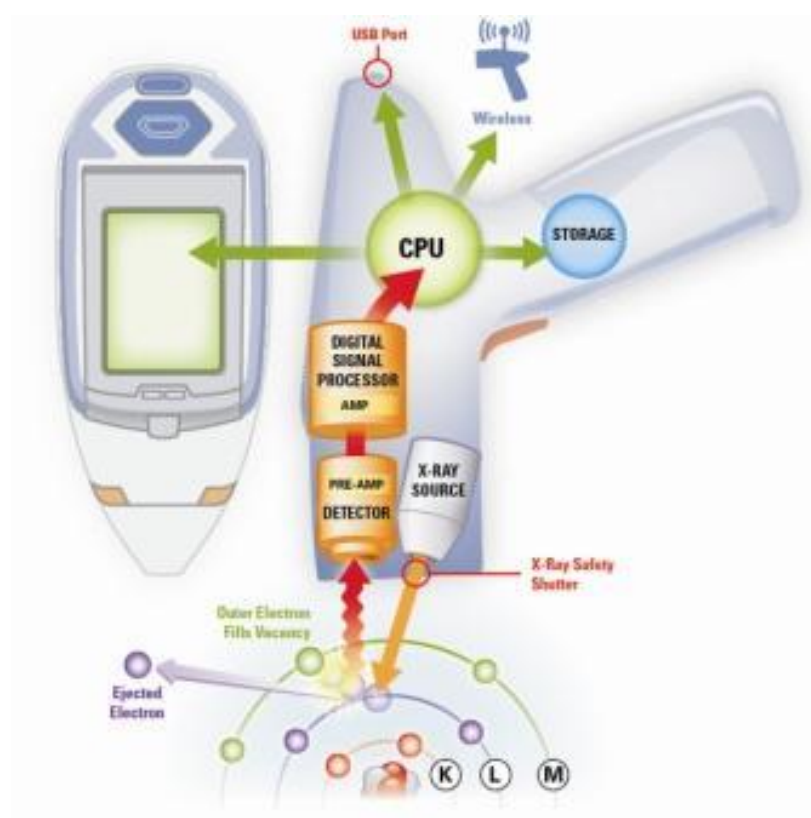


**Figure 48.** Mechanism for x-ray fluorescence of atoms (Kalnicky and Singhvi, 2001).

Miniaturisation of components has enabled the technology in different types of portable applications to advance, either as individual components set around an artefact, often used when items are difficult to move or fragile, or it can be used in the open field and *in situ* environments as a one piece tool - the hand held portable x-ray fluorescence pXRF. The latter contains an in-built x-ray emitter and x-ray detector connected to a central processing unit (CPU) and memory storage unit, with newer models having integrated global positioning systems (GPS) and Bluetooth.

Applications of earlier systems have been utilised within archaeological/soil sciences. Abrahams *et al.* (2010) study of an eighteenth century arable infield farmstead in the Central Highlands of Scotland had some success with the use of a Spectro X-lab 2000 XRF for simultaneous multi-element analysis. It established the differing geochemical makeup of arable or settlement areas by the analysis of the soil geochemistry, with the results considered as a possible template that could be used to assess other areas in the Central Highlands. Not only does this highlight the application of XRF to archaeological and particularly, geochemical research, but also shows how precision and accuracy of this type of equipment are becoming acceptable in the provision of both qualitative and quantitative evidence. Here, the complementary the use of discriminate statistic were also applied to the XRF data to interrogate and highlight the subtle differences.

For this study the Niton XLt 700 Analyser has been used to collect *in situ* and *ex situ* data from field samples and samples prepared in the laboratory for comparison to ICP-MS and ASS. The Niton uses a low power (1.0 W) X-ray tube in tandem with an Ag anode target and Peltier-cooled Si-Pin x-ray detector (Thermo Electron Corporation, 2012). Internal calibration is as per the instructions in the user guide (version 5.0 P/N500/905).



**Figure 49.** Schematic of the internal components of a pXRF, showing emission and detection of the x-rays and fluorescence. (Niton, 2013).

Within the Niton unit, integrated software algorithms, or the fundamental parameters [FP] interpret the fluorescence [secondary x-ray signal] into element identification and concentrations in ppb, ppm or % weight depending on which setting has been selected. The analysis mode can be set to: alloy, soil, bulk, metals or thin film and plastic mode, depending on the pre-installed software. Internal calibration uses an Ag anode target within the hand-piece. Fundamental parameters eliminate the need for site-specific calibration utilising theoretical mathematics to predetermine inter-

element coefficients rather than using matrix specific calibration standards (Kalnicky and Singhvi, 2001). Comparative testing by the National Institute of Standards and Technology Standards [NISTs] or similar approved standards can be used to compare pXRF against AAS and ICP-MS, for total extractable quantities accuracy and precision (Shefsky, 1997; Niton, 2013). Additional, integrated spectral analysis software can also be used to identify differing spectra that can be over-laid and compared, often identifying subtle differences in geochemical concentrations. However, element spectral overlap (interference) is an area of concern where some elements can give erroneous results e.g. antimony, cobalt and chromium need to undergo alternate analysis by AAS or ICP-MS when below certain thresholds, [see Table 13,14 and 15]. This problem is often due to the limitations of some of the equipment's internal filters or algorithms.

As outlined in the introduction using the pXRF, Niton XLt 700 Analyser conformed to the licenses granted by CADW, where non-invasive and non-destructive sampling was required.

The methods for *in situ* sampling were as follows. Sample points were pre-determined from the plan drawn from the reconnaissance field walking over all the usable areas of the sites. These sample points were a mixture of 2.5 and 5 m intervals with other multiple or single points added if it was considered these would add further data to the surveys outcomes [see Chapter 3]. The pXRF sampling used the standard soil mode setting for all *in situ* soil analysis and the Industrial bulk mode (Cu/Zn/Pb) for solid or rock samples or with geochemical levels > 1-2 wt. %. *In situ* sampling time was set at either, 120, 90, 60 or 30 seconds per sample.

pXRF sampling time	
sample size	time(seconds)
< 5	120 secs
6 - 25	90 secs
26 - 50	60 secs
> 50	30 secs

**Table 8.** pXRF sample times by sample numbers.

Initial pXRF analyses were taken on soil from underneath the turfed surface opened by a stainless steel shovel to negate cross contamination to a depth of 10-cm +/- 10%, leaving hinged turf sections to re-establish the divots.



**Figure 50.** Hinged turf exposing top soil. Source: RCAHMW (2013).

Preparation of the soil sample involved clearing any organic litter and soil was lightly mixed to create a homogenous matrix. The pXRF window [see Figure 51] was placed directly on the soil or sediment with the detector perpendicular to its surface and activated using two triggers set into the casing of the pXRF. During field sampling, element abundance in ppm and error +/- displayed on the integrated touch screen display. This helped to modify sampling strategies i.e. if data was consistently low or only showing element abundance at background levels, the resolution was decreased. Conversely, the resolution was increased in areas of high target element concentration.

#### 4.13 pXRF *ex situ* sampling

Supplementary samples were taken as the pXRF *in situ* data were collected using a stainless steel trowel and from the opened turfs. These samples were used to compare the pXRF data to ICP-MS and AAS for comparison and rigor. The samples were dried and milled [see 4.5] with the prepared samples re sampled with the Niton pXRF using the bespoke stand and automated software for controlled timing, geometry and recording. Details of these can be found at [www.nitonuk.co.uk](http://www.nitonuk.co.uk) or in the user manual.



**Figure 51.** Niton XLt 700 series analyser (pXRF). Source: [www.niton.com](http://www.niton.com) (2013).

Further pXRF analyses were conducted during re-surveys, where increased levels of copper, lead and zinc were identified. In tandem with *in situ* sampling, each analysis was geo-referenced with DGPS for location accuracy. Outcomes from pXRF analyses determined which, if any, sites warranted any further geochemical, geophysical surveys, or excavation that may produce metallurgical evidence.

#### **4.14 pXRF Operation and testing**

The use of pXRF complied with CADW's licensing requirement as being the only geochemical analytic tool that could carry out a non-invasive or non-destructive *in situ* survey of the selected sites for this study, with the aim of detecting metal enrichment of elements copper, lead, zinc and iron elevated above background levels.

The main variables that affect precision and accuracy for pXRF analysis can be characterised as:

1. Physical matrix effects (variations in the physical character of the sample)
2. Chemical matrix effect (absorption and enhancement phenomena). Spectral interferences (peak overlaps)
3. Moisture content, which affects x-ray transmission (Billets and Dindal, 2007; Kalnicky and Singhvi, 2001)
4. Poor operating protocol, geometry, timing and sample preparation.

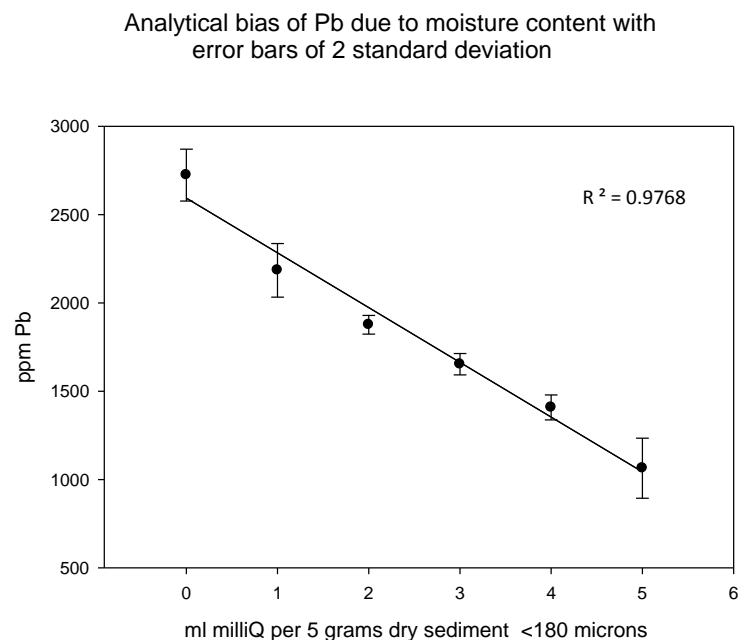
Some of these issues are corrected by Fundamental Parameters; others are subject to variability when using the pXRF *in situ*. Here, moisture, timing and comparative testing are outlined and the results interpreted.

#### **4.15 Matrix effect of moisture bias (methodology in the field)**

One of the environmental problems affecting pXRF is the amount of water content in soils which can affect pXRF analyses. The temperate climate of Wales is associated with high precipitation over upland areas often increasing the soil moisture content. It was considered to be an important factor and developing an understanding of this type of environmental bias was part of the hypothesis testing to determine whether the Niton XLt 700 pXRF was to be used *in situ* for soil and sediment analysis.

The supplementary soil samples taken during the surveys were later prepared for wet acid analysis by drying, milling and sieving to a fraction of < 180 µm. One sample selected with known concentrations of copper, lead, zinc, arsenic and nickel established by acid dilution and AAS was further homogenised by continuous mixing for 12 hours. Five sub samples weighing 5 grams each were placed in a zip sealed polythene bags labelled 1- 5.

MilliQ water was added in 1 ml increments to bags 1 to 5 with bag 5 having 5 g to 5 ml of MilliQ. To ensure total homogenisation the samples were resealed and manually manipulated for 20 minutes, and then left for 24 hours before further mixing for 6 hours for complete homogeneity. Each sample was analysed by the pXRF for 90 seconds 5 times with a mean of the 5 samples taken to assess the matrix effect created by water bulking. The results are shown in figures 52 – 56.



**Figure 52.** Water bias in Pb

Analytic bias of Zn due to moisture content with error bars of 2 standard deviation

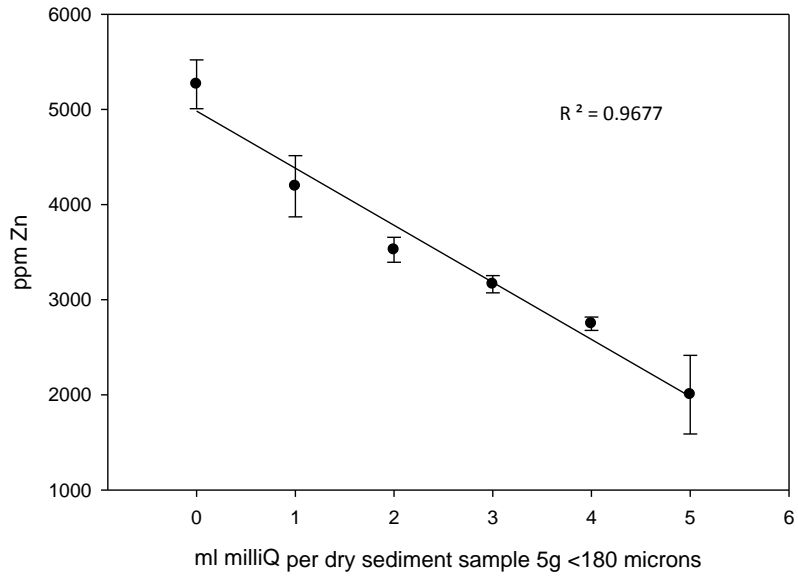


Figure 53. Water Bias in Zn

Analytic bias of Cu due to moisture content with error bars of 2 standard deviation

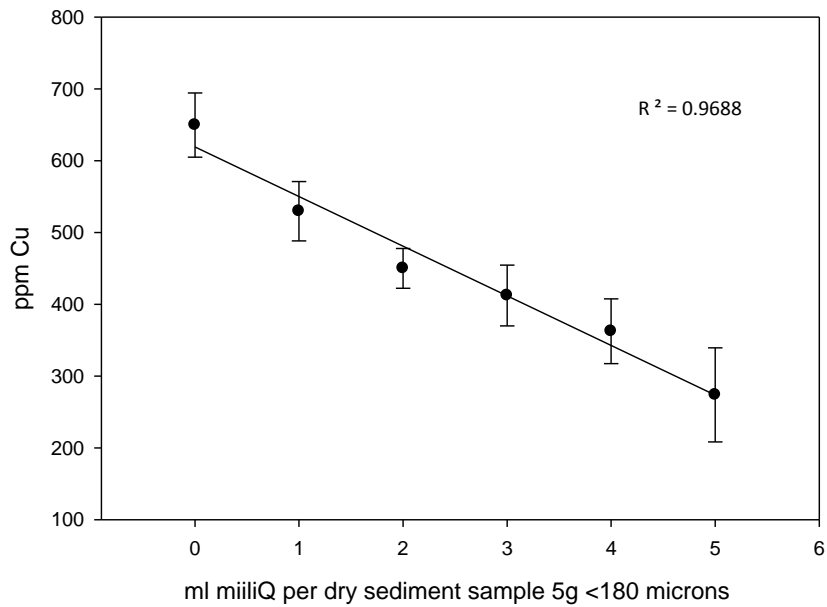


Figure 54. Water bias in Cu



Analytic bias of As due to moisture content with error bars of 2 standard deviation

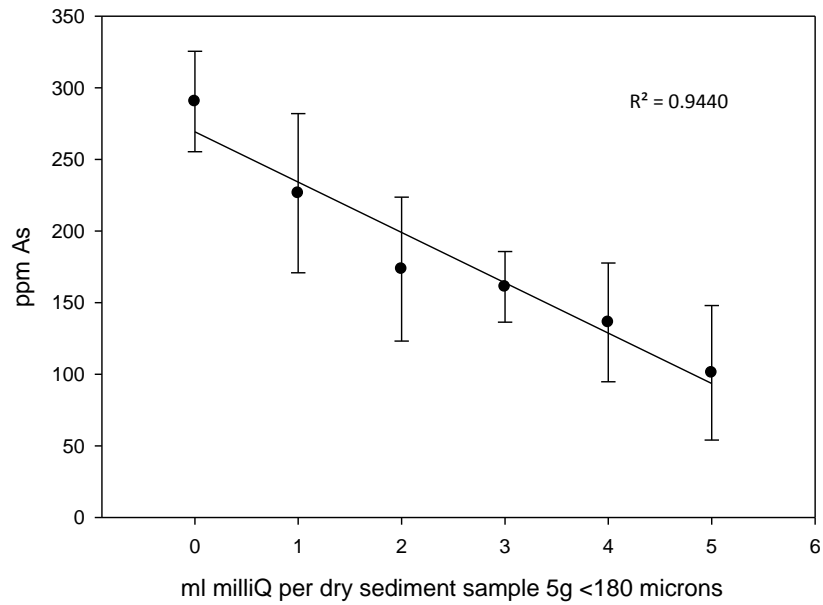


Figure 55. Water bias in As

Analytic bias of Ni due to moisture content with error bars of 2 standard deviation

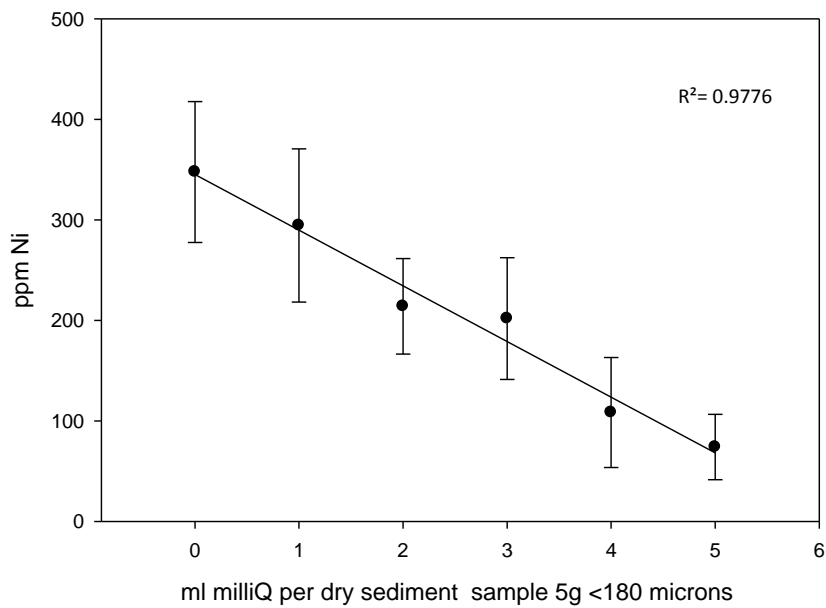


Figure 56. Water bias in Ni

Reduction of Pb, Zn, Cu, As and Ni concentration in 5 grams of sediment. values (ppm)															
sample	Pb	% reduction	5. reduction per 1 ml milliQ	% Zn	% reduction	6. reduction per 1 ml milliQ	% Cu	% reduction	% reduction per 1 ml milliQ	As	% reduction	% reduction per 1 ml milliQ	Ni	% reduction	% reduction per 1 ml milliQ
Dry sample	2723.8			5264.4			649.6			290.4			347.6		
1ml milliQ	2184.4	19.8	19.8	4192.4	20.4	20.4	529.6	18.5	18.5	226.4	22.0	22.0	294.4	15.3	15.3
2ml milliQ	1876.2	31.1	11.3	3524.6	33.0	12.7	450	30.7	12.3	173.4	40.3	18.3	214	38.4	23.1
3ml milliQ	1652.8	39.3	8.2	3162.8	39.9	6.9	412.2	36.5	5.8	161	44.6	4.3	201.8	41.9	3.5
4ml milliQ	1408.2	48.3	9.0	2747.2	47.8	7.9	362.4	44.2	7.7	136.2	53.1	8.5	108.4	68.8	26.9
5ml milliQ	1063.8	61.0	12.7	2002.2	62.0	14.2	273.8	57.9	13.6	101	65.2	12.1	74	78.7	9.9

**Table 9.** Summary of the % reduction.

Comparison of element % reduction at 20, 40, 60, 80 and 100% dilution									
milliQ per 5grams of sediment	Pb	Zn	Cu	As	Ni	total	mean	std	rsd %
1ml milliQ	19.8	20.4	18.5	22.0	15.3	95.98	19.80	2.52	12.74
2ml milliQ	31.1	33.0	30.7	40.3	38.4	173.62	33.05	4.37	13.24
3ml milliQ	39.3	39.9	36.5	44.6	41.9	202.30	39.92	3.00	7.50
4ml milliQ	48.3	47.8	44.2	53.1	68.8	262.24	48.30	9.68	20.04
5ml milliQ	61.0	62.0	57.9	65.2	78.7	324.75	61.97	8.13	13.12

**Table 10.** Comparison of % reduction at 20, 40, 60, 80 and 100 % dilution.

Correlation of water vs. element ratios for elements, copper, lead, zinc, arsenic and nickel as moisture to analyte increases produces a linear reduction in element concentration. There were only slight variations in the data from most elements, with only Ni showing any significant difference between the 80 % and 100 % dilutions.

Kalincky and Singhvi. (2001) suggest there may be a more severe effect to the x-ray lines with low energy level elements < 5 KeV as the moisture level increases, but less effect on high energy x-ray lines. They also suggested that the dilution levels may be counteracted by the reduced matrix absorption for the analyte x-ray lines as water replaces the high atomic number soils or sediments matrix.

Ge *et al.* (2004) also comment on two factors possibly responsible for the decrease in characteristic x-ray intensity of an analyte by the presence of pore water in the sample.

1. The intensity of characteristic x-rays of analytes decreases as the water content of the sample increases owing to the stronger x-ray absorption by water than by air in fractures and pores in samples.
2. The intensity of scattered primary x-rays from the source is increased as the water content of the sample increases. As a result, the net peak areas of characteristic x-rays from the analyte elements are reduced, which leads to lower precision, poorer detection limit and lower accuracy.

The results of this study's tests agree with Kalincky and Singhvi's. (2001) findings as the reduction in the element values for a range of the elements used are all above the < 5 KeV level. The reduced accuracy, precision and element detection also supports Ge *et al.* (2004) comments. However, the reduction of element concentrations at 1 ml / 5 gm sample dilution is *ca.* 20 % of the dry sample, which is more significant than the increased dilution at 40, 60 and 80 % inferring that the first 20 % dilution can have a greater impact on *in situ* testing, and under reporting element concentrations.

It may be possible to correct for this bias by calculating the percentage of moisture in a given sample, and correcting to a dry value, using a simple equation to account for the effect moisture has in diluting *in situ* samples:

$$C_c = \frac{C_f \cdot M_w}{M_d}$$

where  $C_c$  = Corrected concentration,  $C_f$  = the *in situ* field data,  $M_w$  = the wet mass of the sample and  $M_d$  = the dry mass of the sample.

Ge *et al.* (2004) consider the reduction is directly proportional to the increase in water content, similar to this study's findings. Bastos *et al.* (2012) show the effect caused in spectra acquired for the same sample with distinct water contents levels. They show that the characteristic X-ray peak areas diminish with the growing content of water. In the region of the spectrum where scattering dominates, it is interesting to observe that the scattering (coherent and incoherent) grows with the water content.

Simply evaluating and recording *in situ* conditions should be accounted for during field work. This will help in assessing the possibility of erroneous data leading to misinterpretation.

#### **4.16 Comparison of reported values of pXRF to AAS**

Though most users of pXRF may not question the fundamental parameters (FP) accuracy and precision, it is worth comparing the results by testing both certified reference materials and soil samples for the survey against AAS, this being a benchmark standard for testing concentrations for many elements. Comparing pXRF reported values for both *in situ* and prepared samples against AAS would highlight variations in the samples and results obtained by pXRF.

Preparation methods for sampling have been outlined in this. Statistical evaluation to assess agreement between the two methods used, AAS and pXRF, for the analysis of lead from  $n = 52$  samples, shows under-reporting of lead at higher levels  $> 1600$  ppm, but with overall good agreement between the AAS and pXRF returning  $R^2$  value of 0.9453. Removing the three outliers improved the  $R^2$  value to 0.9964, [see Figure 59].

AAS vs. pXRF (Pb ppm)

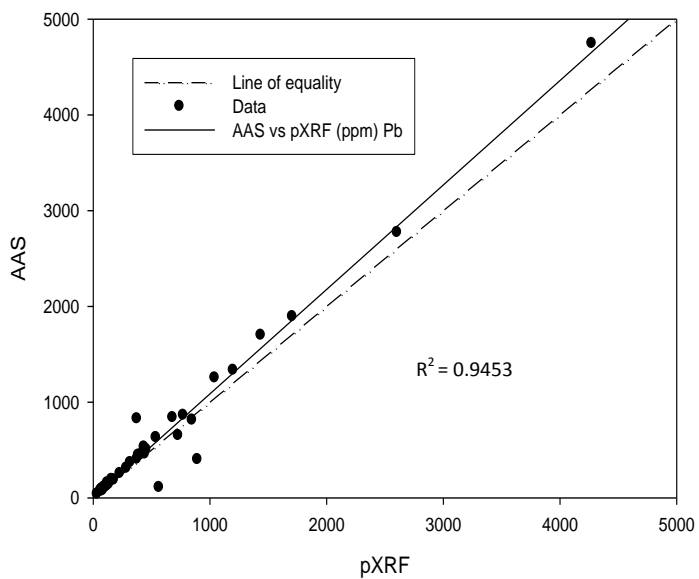


Figure 57. linear plot of Pb AAS vs. pXRF.

AAS vs. pXRF (Pb ppm) Log common with outliers

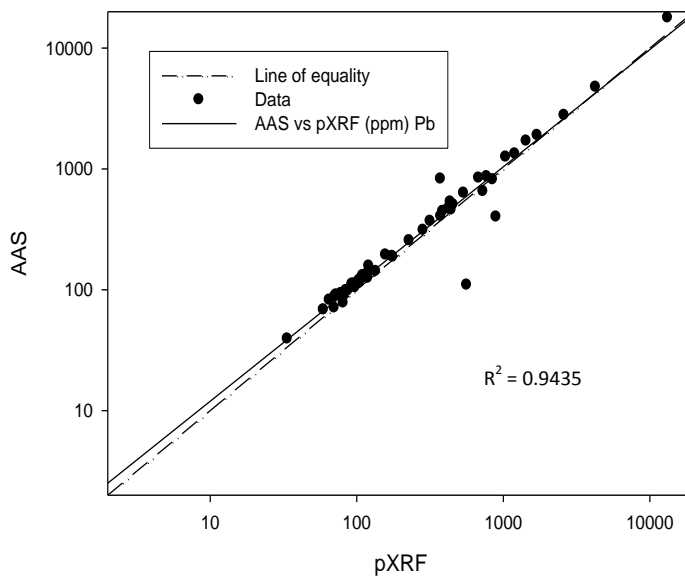


Figure 58. Log scale plot with outliers.

AAS vs. pXRF (Pb ppm) Log common without outliers

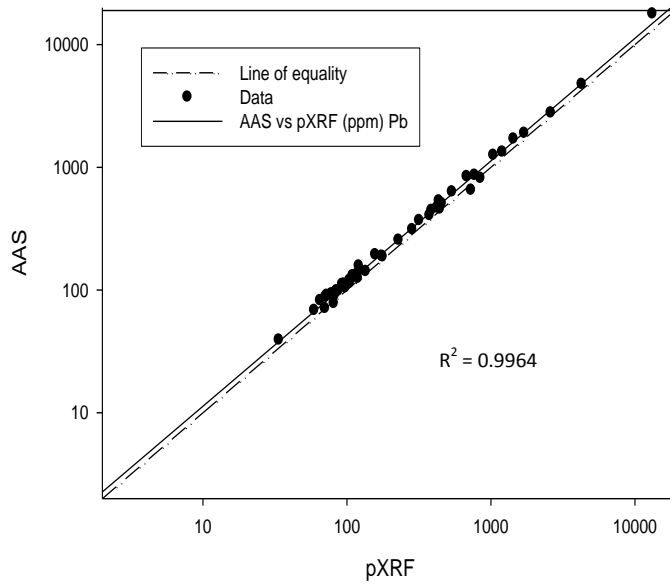


Figure 59. Log scale plot with and without outliers removed.

AAS vs. pXRF raw data (Pb ppm) Log common with outliers

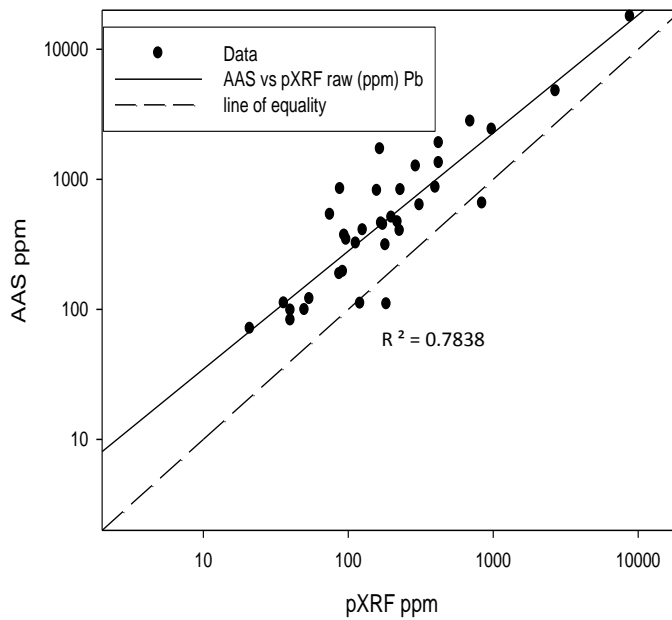


Figure 60. AAS vs. pXRF raw *in situ* sample.

Under reporting of lead, agrees with the methodology of Bland and Altman (1996), where the increase of lead in a sample is mirrored by the increase of variance as the

sample concentration increases. Statistical anomalies or errors in this type of measurement are common when measurements are taken across a large data range (Knowles, pers. Comm., 2013).

### **The non-parametric for two samples sets.**

In the statistical application of a Mann-Whitney test the null hypothesis asks 'is there a significant difference between 38 samples for the AAS vs. pXRF and 36 samples for the AAS and pXRF' for **lead, copper and zinc**.

#### **Mann-Whitney Test for ASS vs. PXRF (Pb)**

	N	Median
C1	38	429.0
C2	38	451.6

Point estimate for  $\eta_1 - \eta_2$  is -13.7  
95.1 Percent CI for  $\eta_1 - \eta_2$  is (-229.0,195.4)  
W = 1436.0  
Test of  $\eta_1 = \eta_2$  vs  $\eta_1 \neq \eta_2$  is significant at 0.7831

#### **Mann-Whitney Test for ASS vs. Raw pXRF (Pb)**

	N	Median
C1	36	462.3
C2	36	171.5

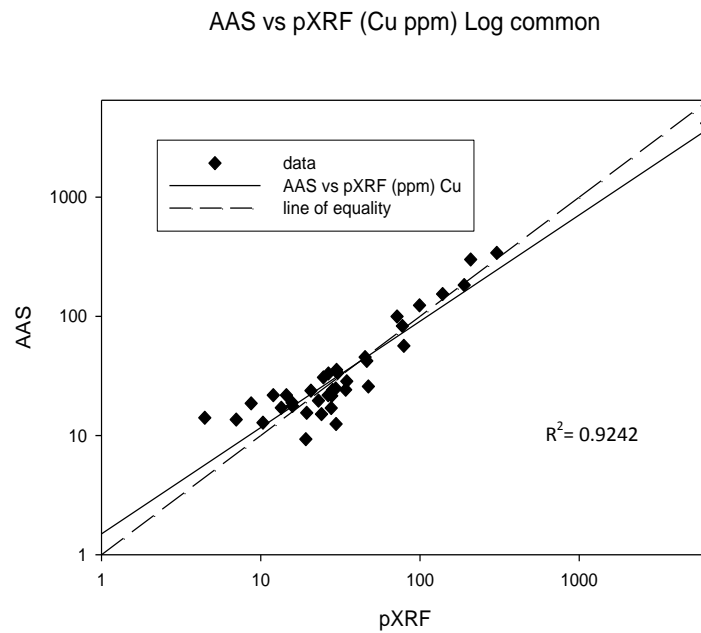
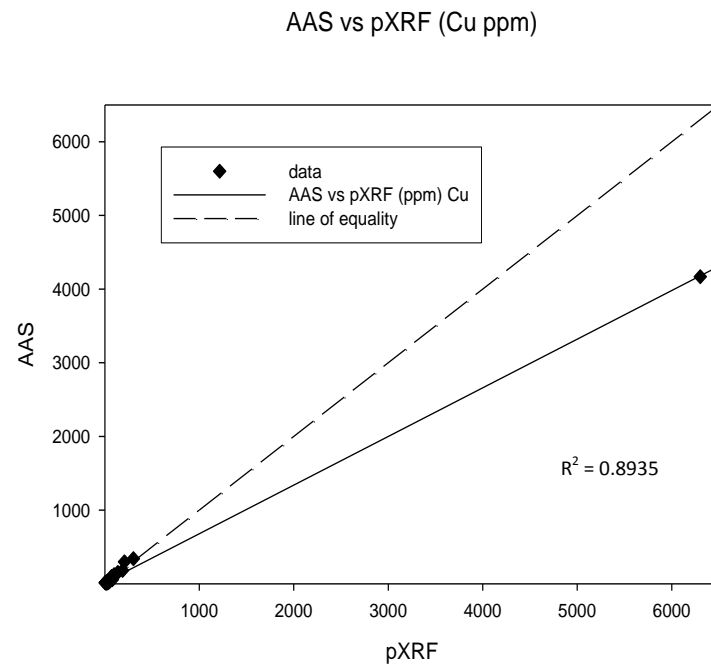
Point estimate for  $\eta_1 - \eta_2$  is 265.7  
95.1 Percent CI for  $\eta_1 - \eta_2$  is (72.6,436.2)  
W = 1596.0  
Test of  $\eta_1 = \eta_2$  vs  $\eta_1 \neq \eta_2$  is significant at 0.0015  
The test is significant at 0.0015 (adjusted for ties)

**Figure 61.** Statistical analysis of pXRF vs. AAS.

The results without outliers both suggest there is no significant difference between AAS and pXRF, as the test of  $\eta_1 = \eta_2$  vs  $\eta_1 \neq \eta_2$  being above ( $\alpha 0.05$ ). The raw *in situ* sample does suggest a difference with the test of  $\eta_1 = \eta_2$  vs  $\eta_1 \neq \eta_2$  being below the ( $\alpha 0.05$ ).

For **Cu**, 33 sets of normally paired distributed data were tested.

**Copper:**



**Figure 62.** Linear and log plot of Cu



The results for copper show the pXRF under-reporting at the higher range of concentration > 1000 ppm but over-reporting at the lower range. When outliers are removed, the  $R^2$  increases to 0.997.

**Mann-Whitney Test for AAS vs. pXRF (Cu)**

N Median

C1 32 29.74

C2 32 27.15

Point estimate for  $\eta_1 - \eta_2$  is 2.00

95.1 Percent CI for  $\eta_1 - \eta_2$  is (-7.86,10.86)

W = 1071.0

Test of  $\eta_1 = \eta_2$  vs  $\eta_1 \neq \eta_2$  is significant at 0.6822

The test is significant at 0.6821 (adjusted for ties)

There is no significant difference between the two sets of data

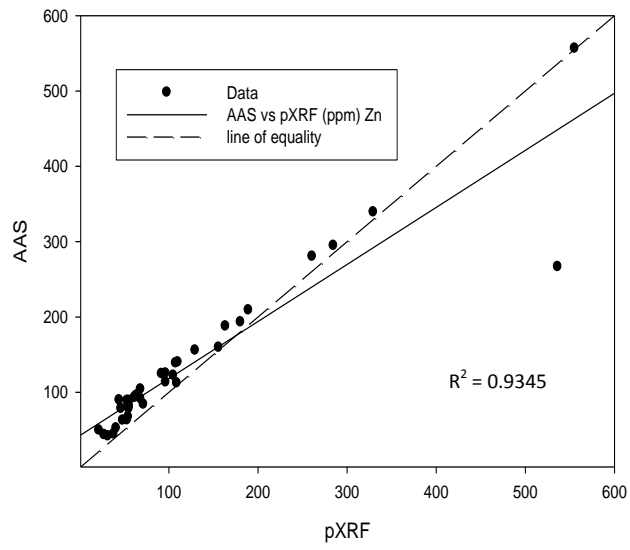
**Figure 63.** Statistical analysis of Cu.

Results concluded the  $\eta_1 = \eta_2$  vs  $\eta_1 \neq \eta_2$  was above  $\alpha$  0.05 (95% confidence) indicating the null hypothesis is not accepted.

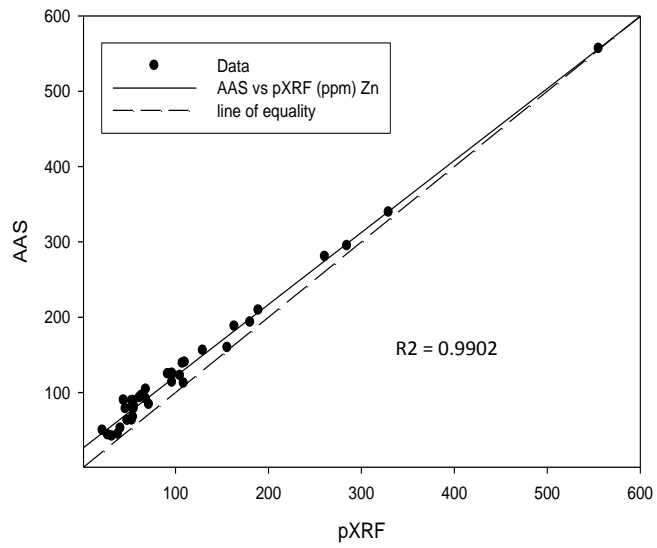
For zinc, thirty six pairs compared analysed by pXRF and AAS. The result gave an  $R^2$  value of 0.9345. When two outliers were removed this increased to 0.9902

**Zinc:**

AAS vs. pXRF (Zn ppm)



AAS vs. pXRF (Zn ppm) with outlier removed



**Figure 64.** Linear and log plot of Zn

### Mann-Whitney Test for AAS vs. pXRF (Zn)

N Median

C1 36 96.10

C2 36 68.42

Point estimate for  $\eta_1 - \eta_2$  is 24.97

95.1 Percent CI for  $\eta_1 - \eta_2$  is (-0.98,44.95)

W = 1481.0

Test of  $\eta_1 = \eta_2$  vs  $\eta_1 \neq \eta_2$  is significant at 0.0608

**Figure 65.** Statistical analysis of Zn.

In statistical analysis using the Mann-Whitney test the null hypothesis asks: Is there significant a difference between the results of the AAS and pXRF analysis of zinc. The  $\eta_1 = \eta_2$  vs  $\eta_1 \neq \eta_2$  p value was above  $\alpha$  0.05 (95% confidence) indicating the null hypothesis is not accepted.

Atomic absorption spectrometry and pXRF, when prepared up to the point where ASS needs to digest the prepared analyte into a aliquot, do not show a significant difference. However, the raw in situ sample vs. the ASS does, and is reflected in the Pearson correlation  $R^2$  value of 0.7838 for lead.

The results agree with work by Radu and Diamond. (2009), but with slight differences for zinc and copper. However, this may reflect the number of samples analysed, as 50 were used in this study compared to only 17 by Radu and Diamond. Also this study used sampling times of 90 seconds compared to the 45 seconds used by Radu and Diamond.

Element	Haylock @90 sec per sample analysis n=50	Radu and Diamond, 2009 @45 sec per sample analysis n=17
Zn	0.990	0.849
Cu	0.997 (without outliers) not shown)	0.959
Pb	0.996	0.995

**Table 11.** Comparison of this study's and Radu and Diamond's AAS vs. pXRF analyses R<sup>2</sup> value (with outliers removed).

Overall the data from the current study gave better R<sup>2</sup> values for all of the comparative elements than Radu and Diamond's (2009) study. What this suggests is the pXRF is reliable for the target elements of copper, lead and zinc on dried and milled samples, giving quantitative results.

#### 4.17 Time vs. error and comparison to reported element values

Increasing sampling times with pXRF can reduce the error on element concentration. These errors can be plotted against samples with known concentrations. Here, using three reference materials, till 4 (Canadian Natural Resources, 2013), GSS-7 and NIM-D (Gorvindaraju, 1989), a mix of low medium and high element concentrations were used to carry out comparative tests. These were integrated and displayed in Figure 66.

The method increased time of sampling by ten seconds on each analysis of Certified Reference Materials (CRMs) using pXRF, with the mean of five samples then calculated for precision and accuracy. Additionally, the maximum concentration of each CRM was plotted, and for **till 4**, it gives the maximum element value extractable by nitric acid (HNO<sub>3</sub>) digestion against the known values on chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, rubidium, strontium and lead were plotted. Ten elements for **GSS-7**: chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, rubidium, and lead, and seven elements for **NIM-D** chromium, manganese, cobalt, nickel, copper, zinc are also plotted.

Certified reference materials: Till 4 and HNO <sub>3</sub> . GSS-7 and NIM-D total content values (ppm unless stated)					
Reference material and analytic extraction technique	atomic number	till 4	Till 4 extractable by HNO <sub>3</sub>	GSS-7	NIM-D
Chromium (Cr)	24	53	26	410	2900
Manganese (Mn)	25	490	260	2300.00	2200.00
Iron (Fe <sub>2</sub> O <sub>3</sub> ) %	26	3.97%	3.3%	17.59%	14.63%
Cobalt (Co)	27	8	6	97	210
Nickel (Ni)	28	17	15	276	2050
Copper (Cu)	29	237	254	97	10
Zinc (Zn)	30	70	63	142	90
Arsenic (As)	33	111	103	4.8	n/a
Selenium (Se)	34	x	x	n/a	n/a
Rubidium (Rb)	37	161	n/a	15.8	n/a
Strontium (Sr)	38	109	n/a	n/a	3
Silver (Ag)	47	x	x	n/a	n/a
Cadmium	48	x	x	80	n/a
Tin (Sn)	50	x	x	3.6	2
Antimony (Sb)	51	x	x	0.42	n/a
Lead (Pb)	82	50	36	13.6	7
x = not used					
n/a =not available					

**Table 12.** Range of target elements with concentration values for both CRM and extractable values by HNO<sub>3</sub> [only for till 4].

The automated Niton software and bespoke bench-stand used to analysis CRM's ensured time and geometric repeatability. Reference materials were prepared with pXRF sample cells SC-4331 comprising double open ended 33 mm capsules and covered with Mylar x-ray film TF-160-255 gauge 0.00024 - 6 $\mu$ . This is the standard preparation for repeatability analysis. All results have being plotted to show all of the processes described above, and results are as follows:

Time vs. error till 4 (Cr)

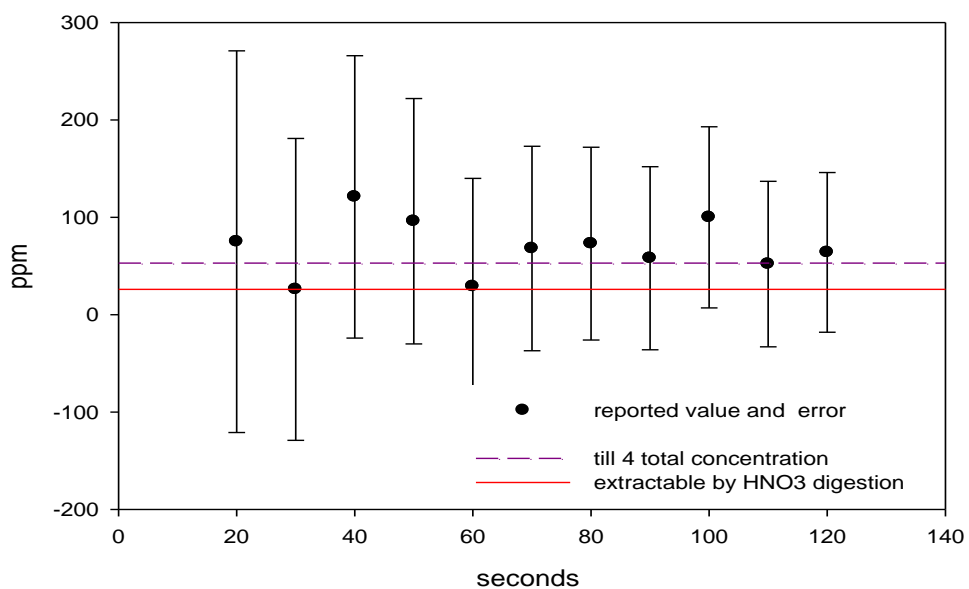


Figure 66. Time vs error for Cr

Time vs. error till 4 (Mn)

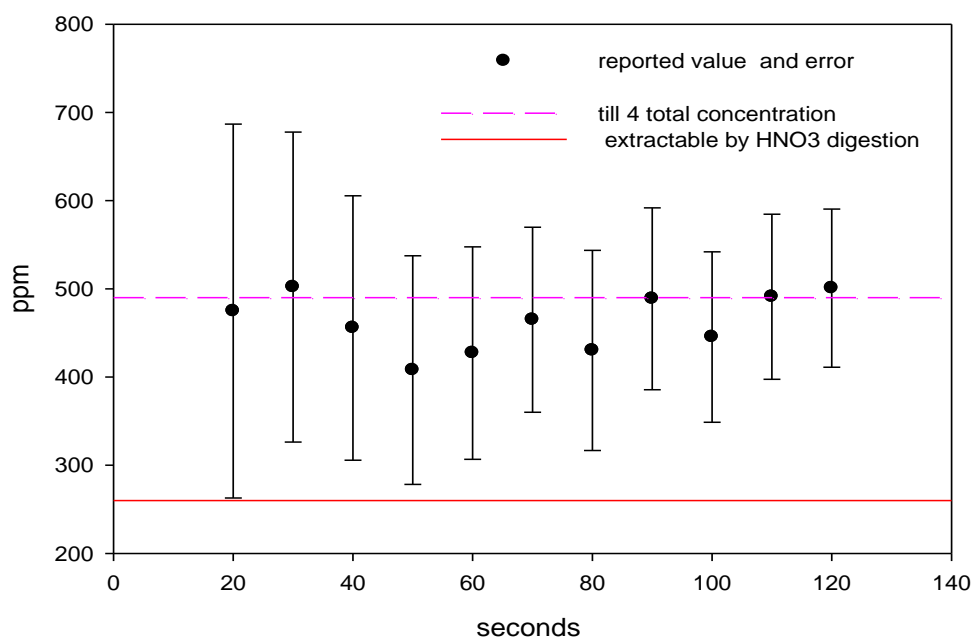


Figure 67. Time vs error for Mn

time vs.error till 4 (Fe)

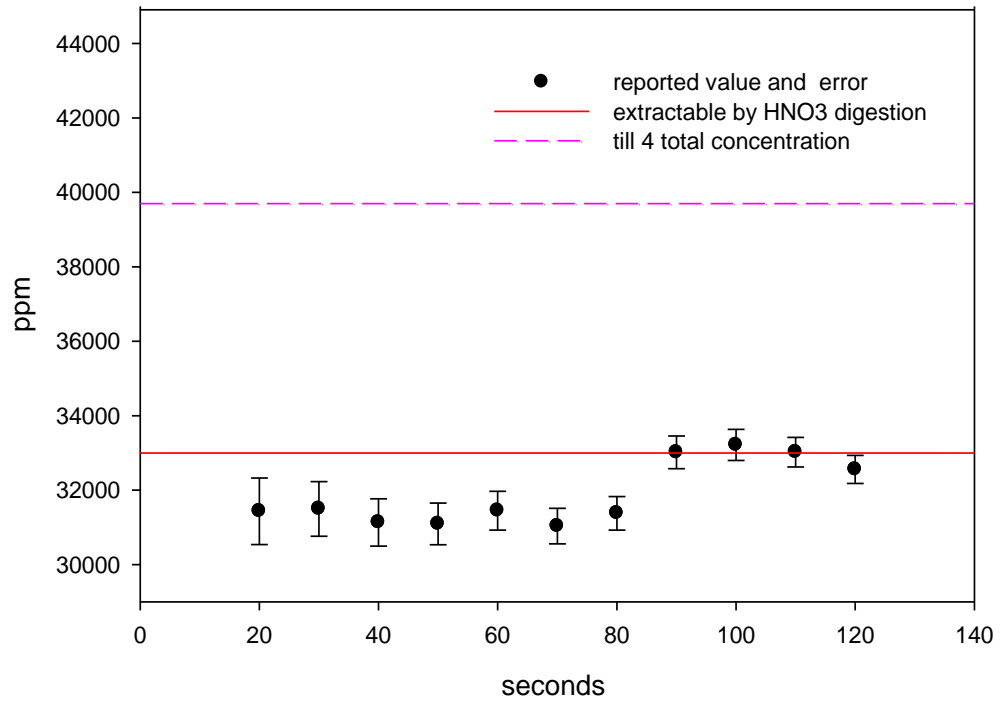


Figure 68. Time vs error for Fe.

time vs. error till 4 (Co) (log common)

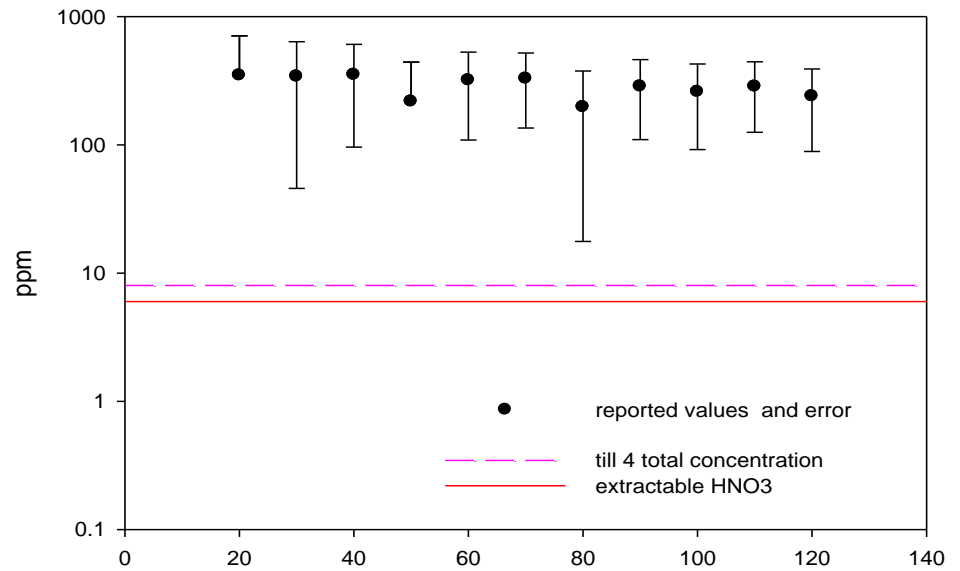


Figure 69. Time vs error for Co

time vs.error till 4 (Ni)

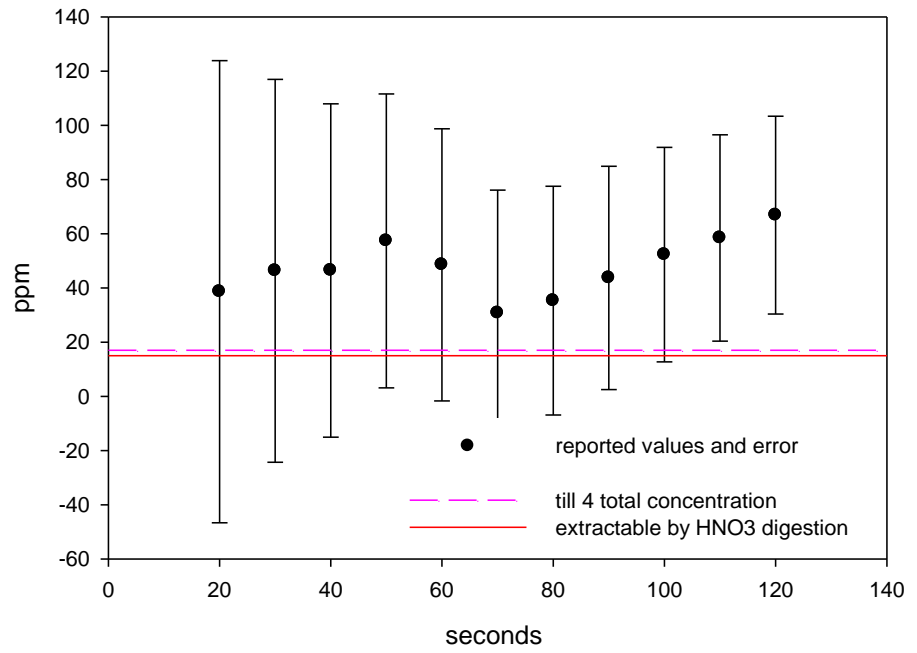


Figure 70. Time vs error for Ni

time vs.error till 4 (Cu)

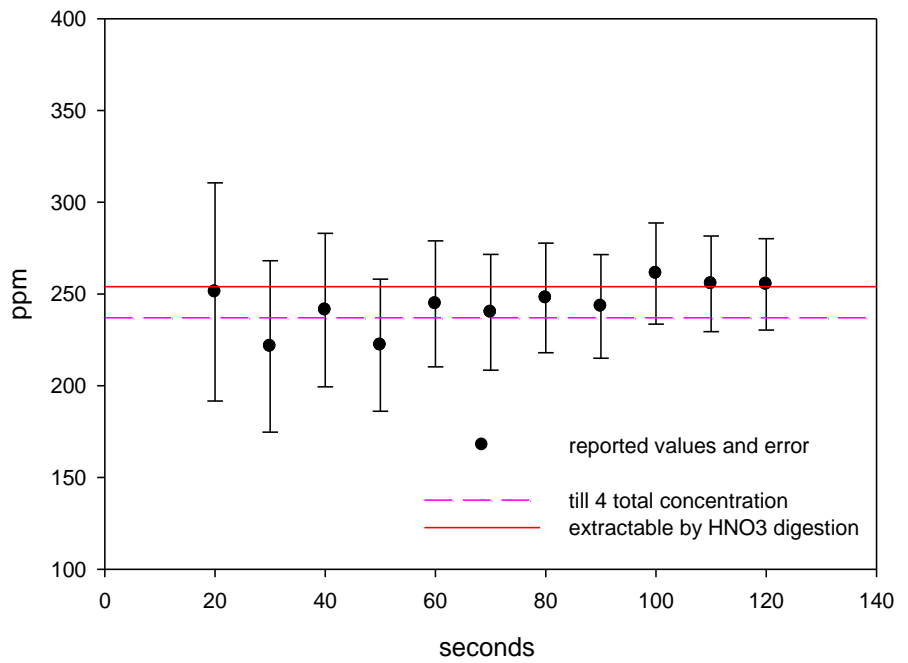


Figure 71. Time vs error for Cu



time vs. error till 4 (Zn)

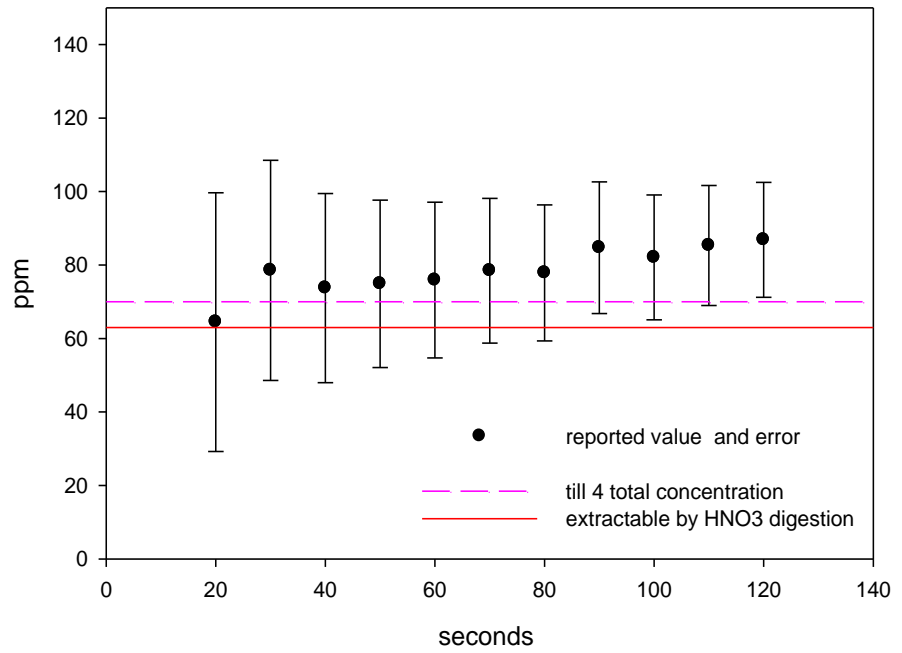


Figure 72. Time vs error for Zn

time vs. error till 4 (As)

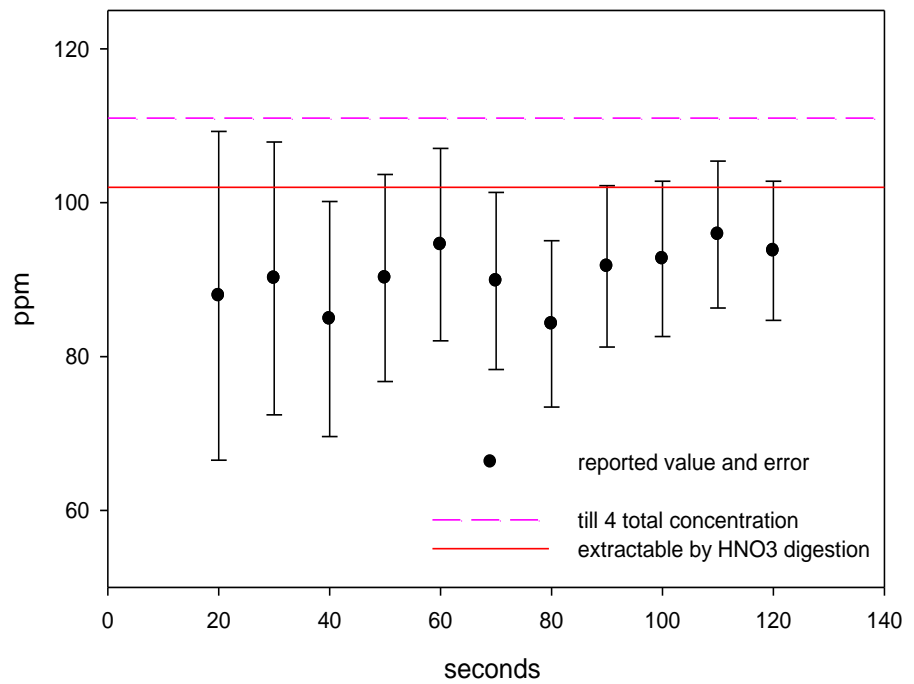


Figure 73. Time vs error for AS

time vs.error till 4 (Rb)

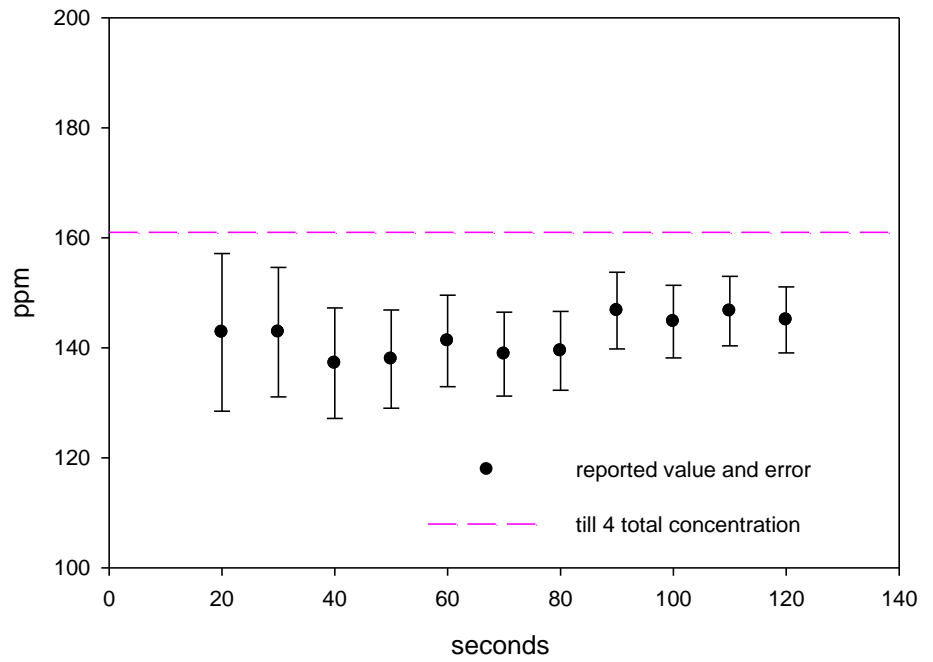


Figure 74. Time vs error for Rb

time vs. error till 4 (Sr)

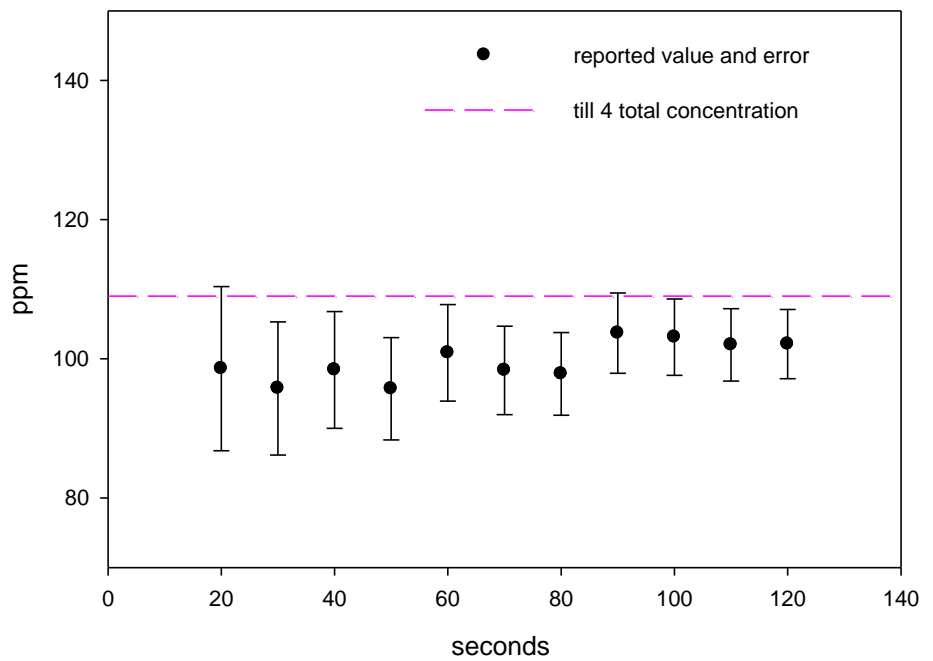


Figure 75. Time vs error for Sr

time vs. error till 4 (Pb)

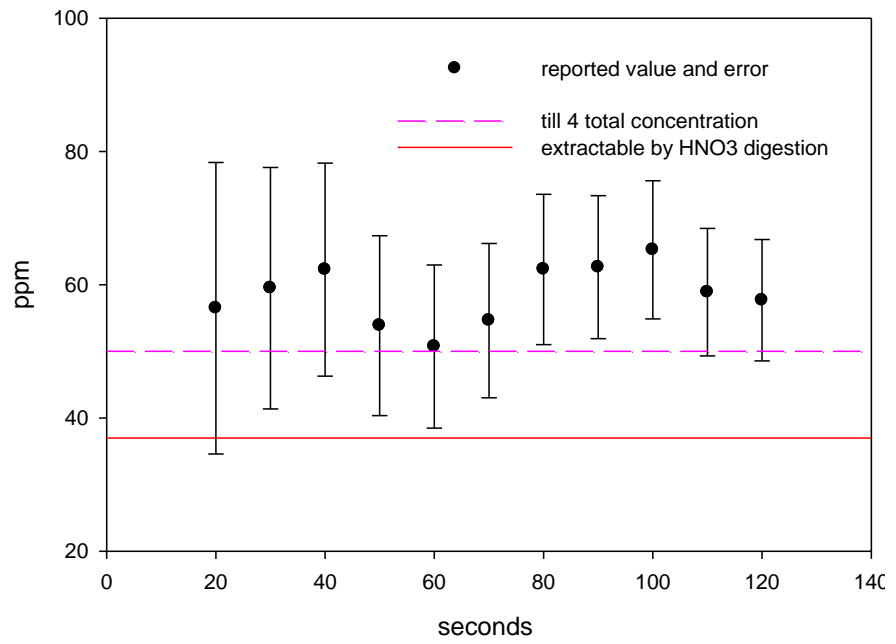


Figure 76. Time vs error for Pb

The following set of graphs relate to Certified Reference Material GSS-7:

time vs. error GSS-7 (Cd)

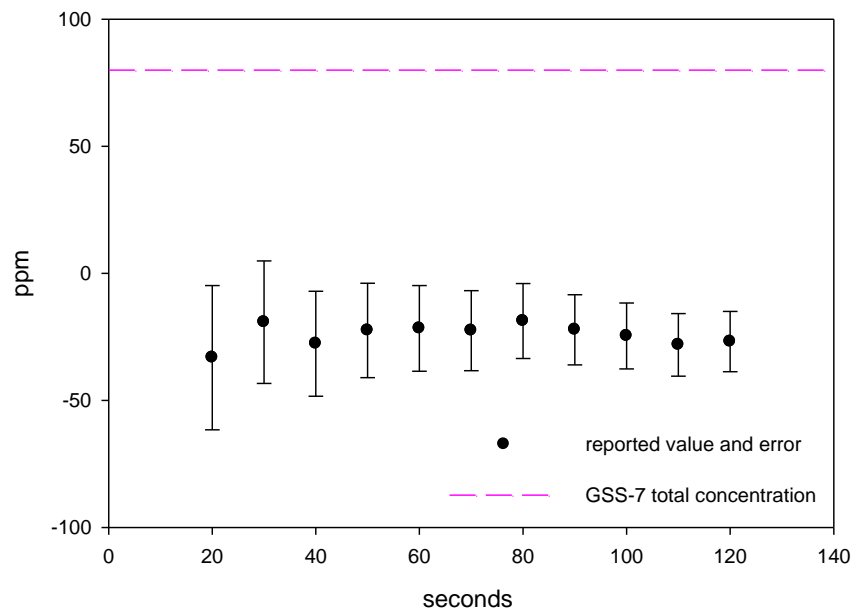


Figure 77. Time vs error for Cd

time vs. error GSS-7 (Rb)

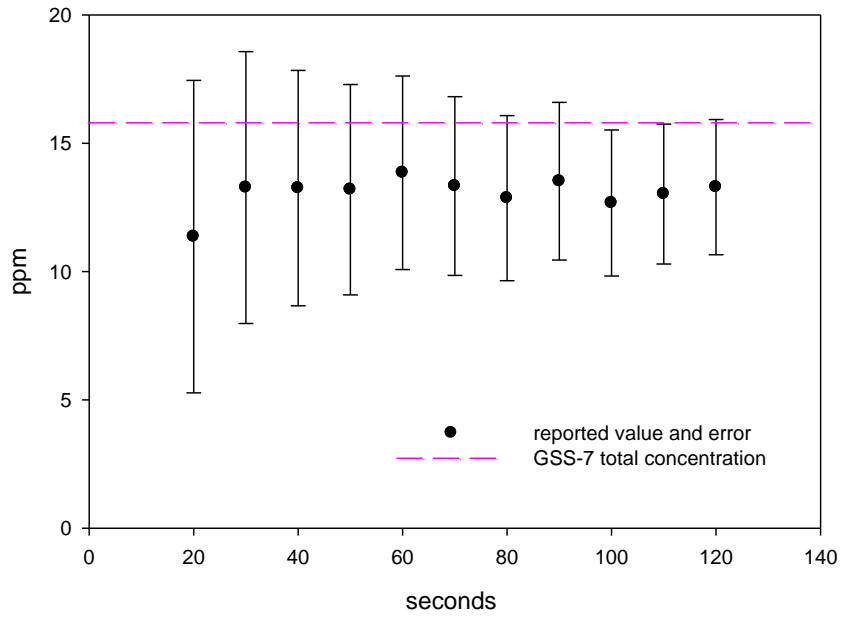


Figure 78. Time vs error for Rb

time vs. error GSS-7 (As)

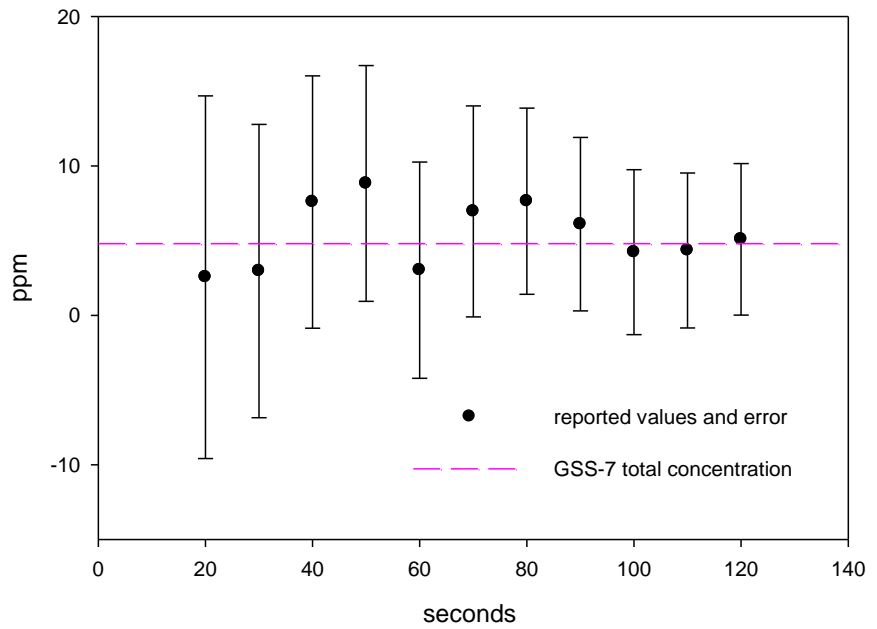


Figure 79. Time vs error for AS

time vs. error GSS-7 (Zn)

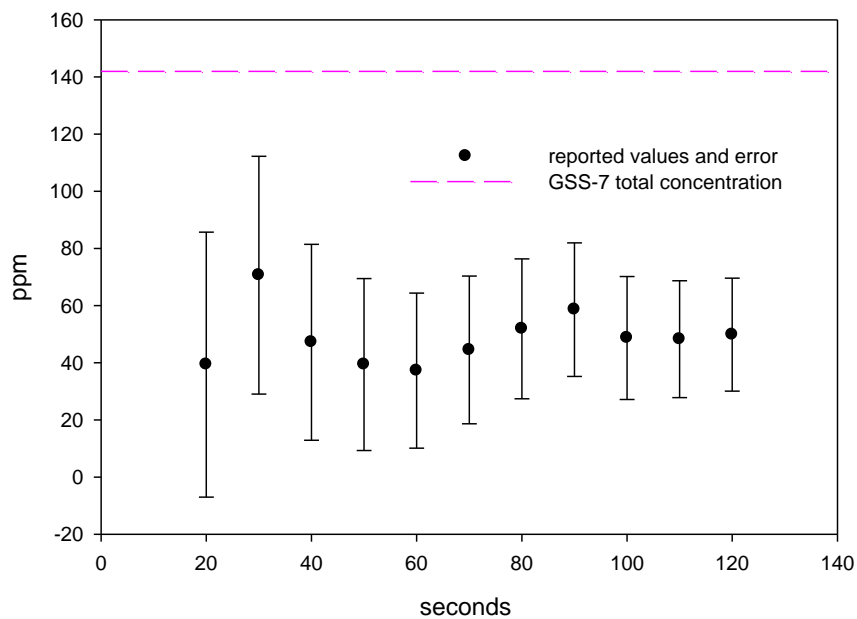


Figure 80. Time vs error for Zn

time vs. error GSS-7 (Cu)

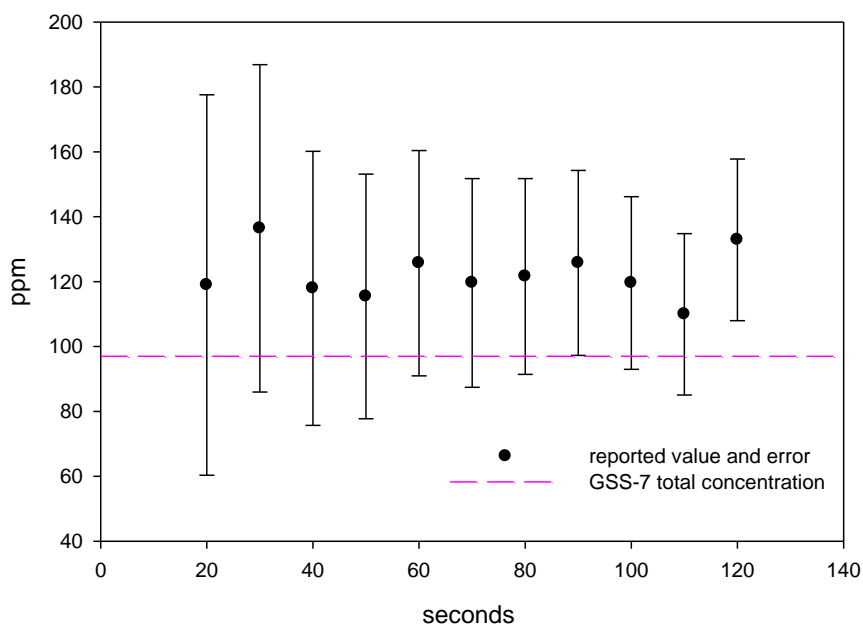


Figure 81. Time vs error for Cu

time vs. error GSS-7 (Ni)

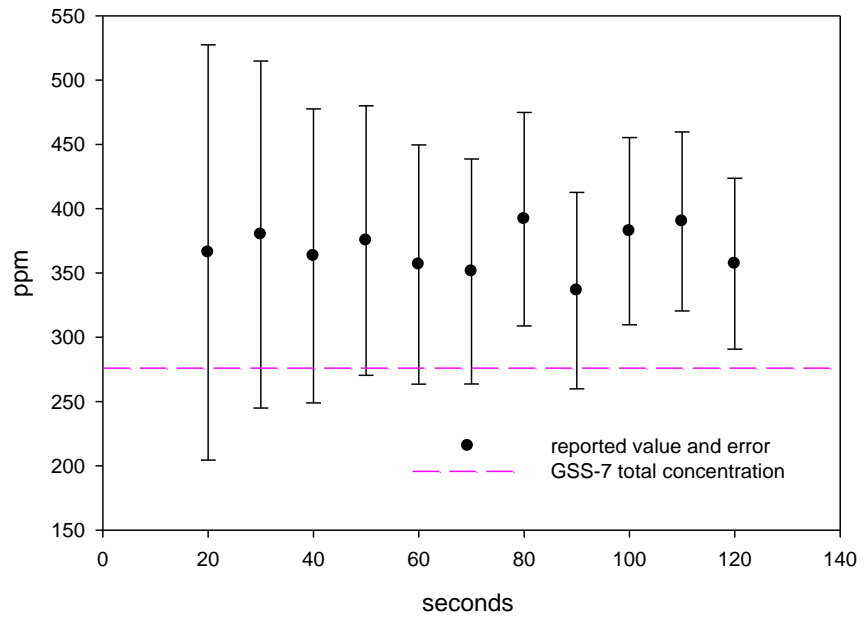


Figure 82. Time vs error for Ni

time vs.error GSS-7 (Co)

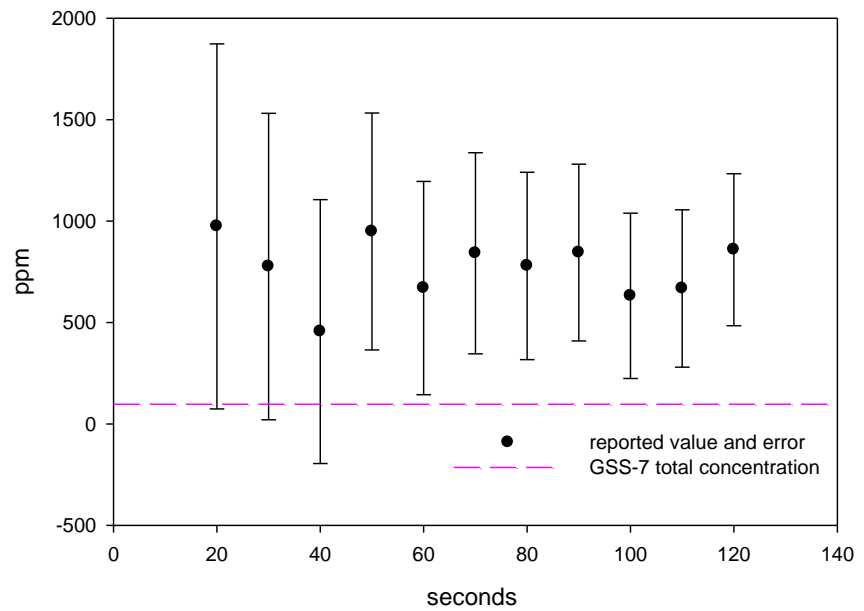


Figure 83. Time vs error for Co

time vs. error GSS-7 (Fe)

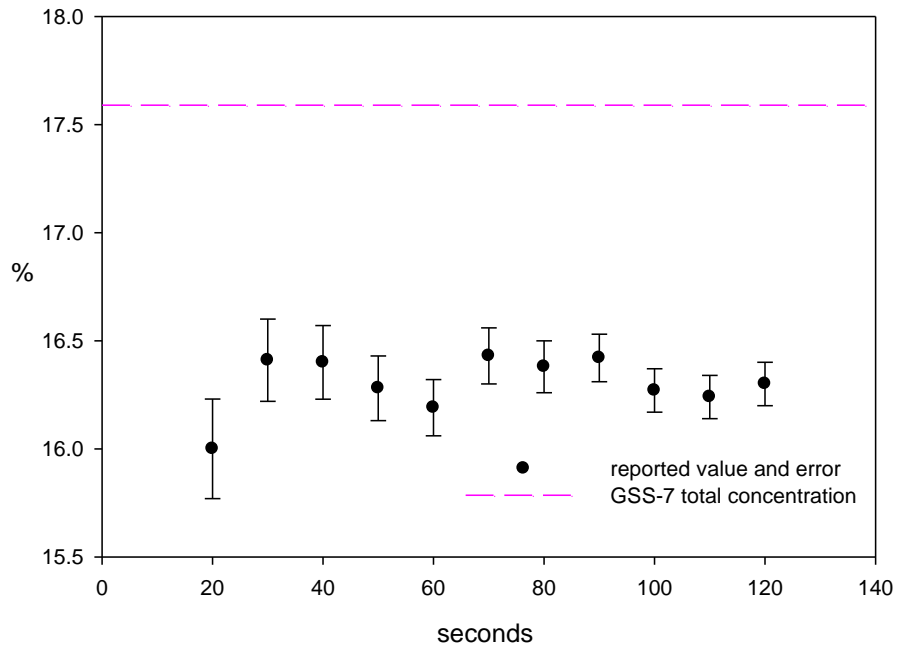


Figure 84. Time vs error for Fe

time vs. error GSS-7 (Mn)

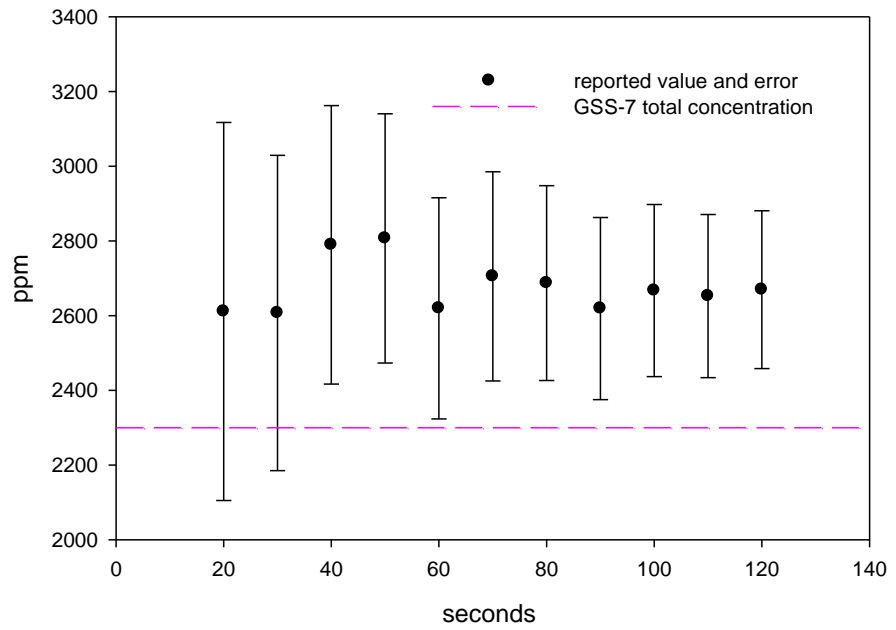


Figure 85. Time vs error for Mn

time vs. error GSS-7 (Cr)

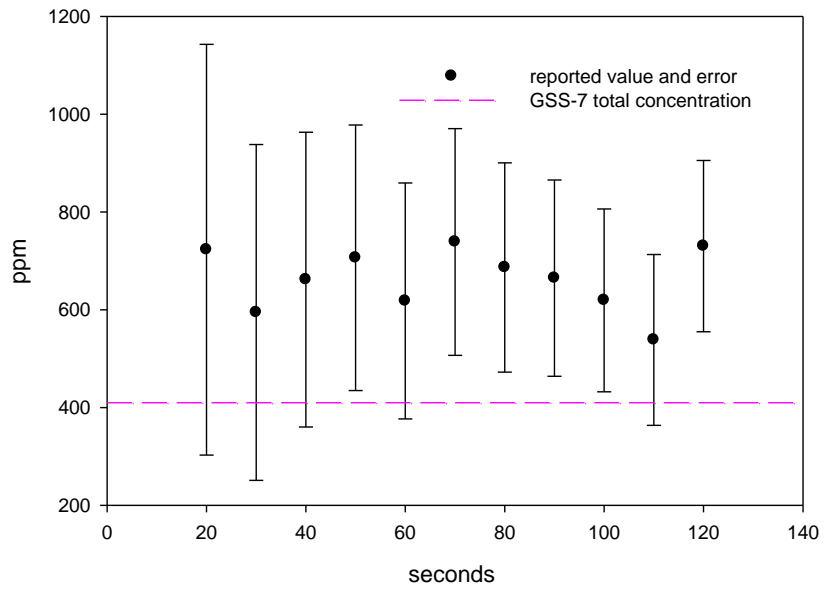
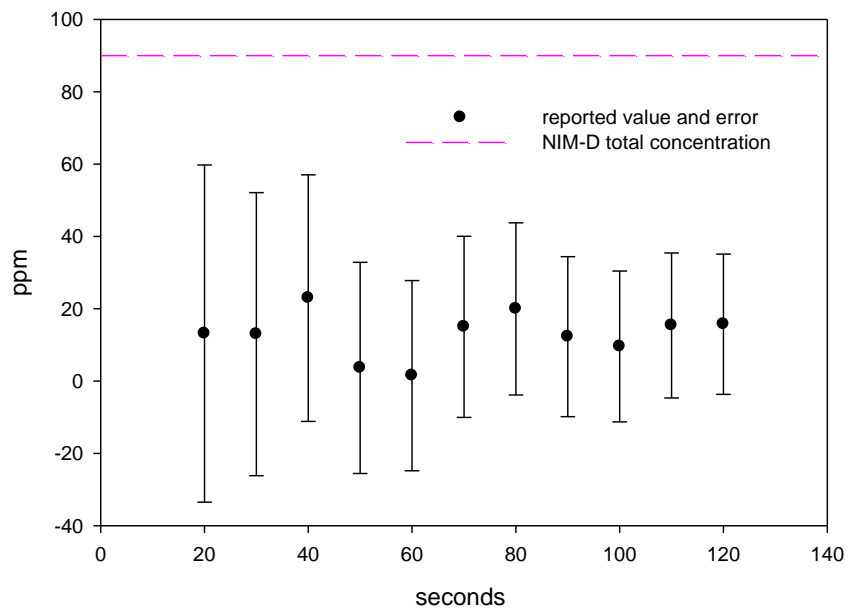


Figure 86. Time vs error for Cr

The following set of graphs relate to Certified Reference Material GSS-7

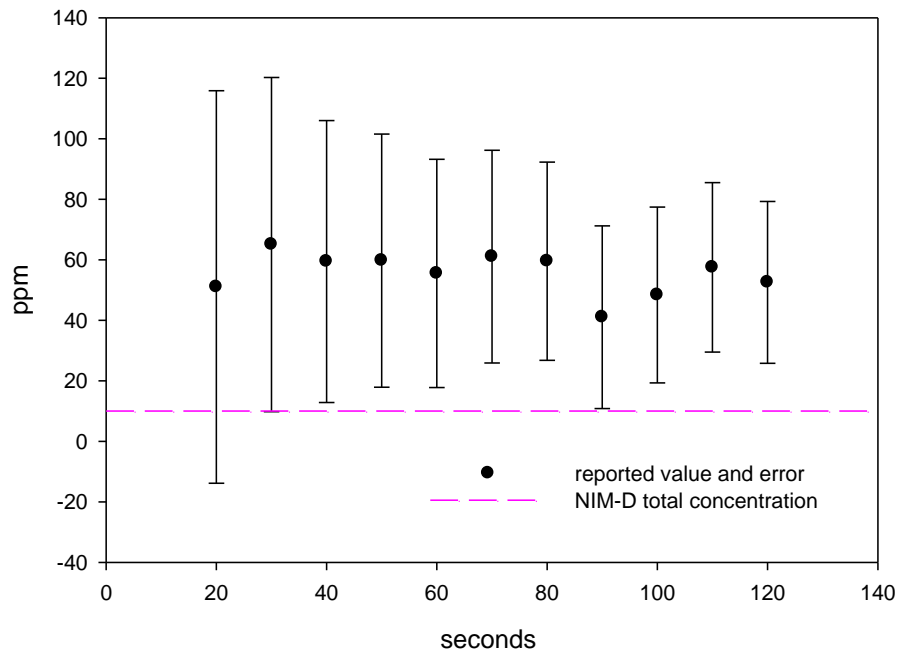
time vs. error NIM-D (Zn)





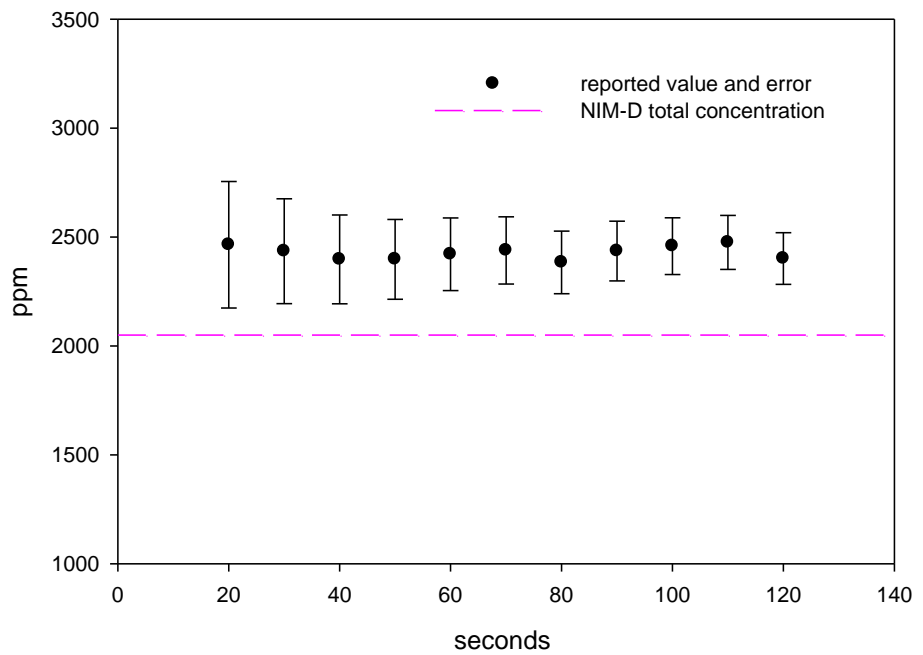
**Figure 87.** Time vs error for Zn

time vs.error NIM-D (Cu)



**Figure 88.** Time vs error for Cu

time vs. error NIM-D (Ni)



**Figure 89.** Time vs error for Ni

time v. error NIM-D (Co)

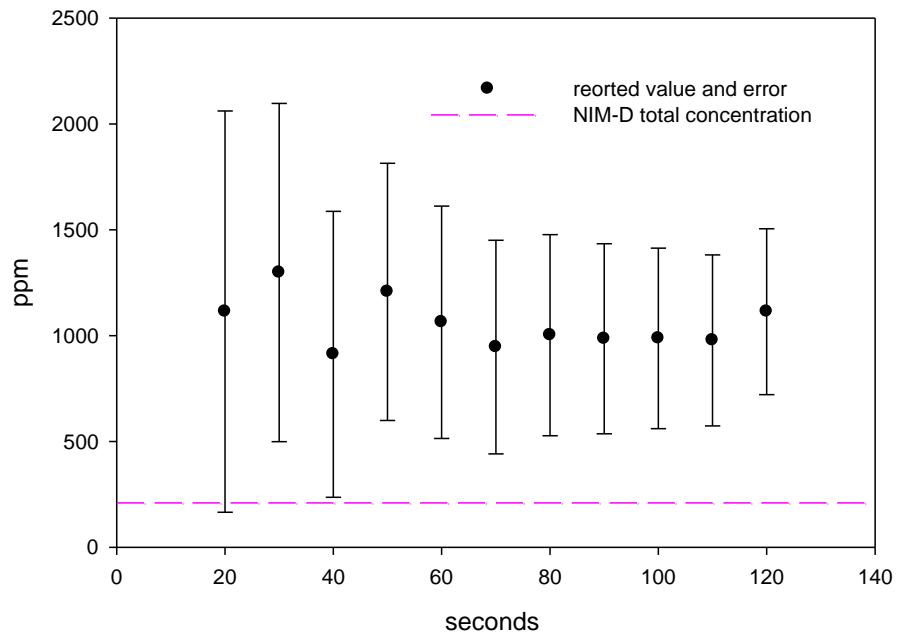


Figure 90. Time vs error for Co

time vs error NIM-D (Fe)

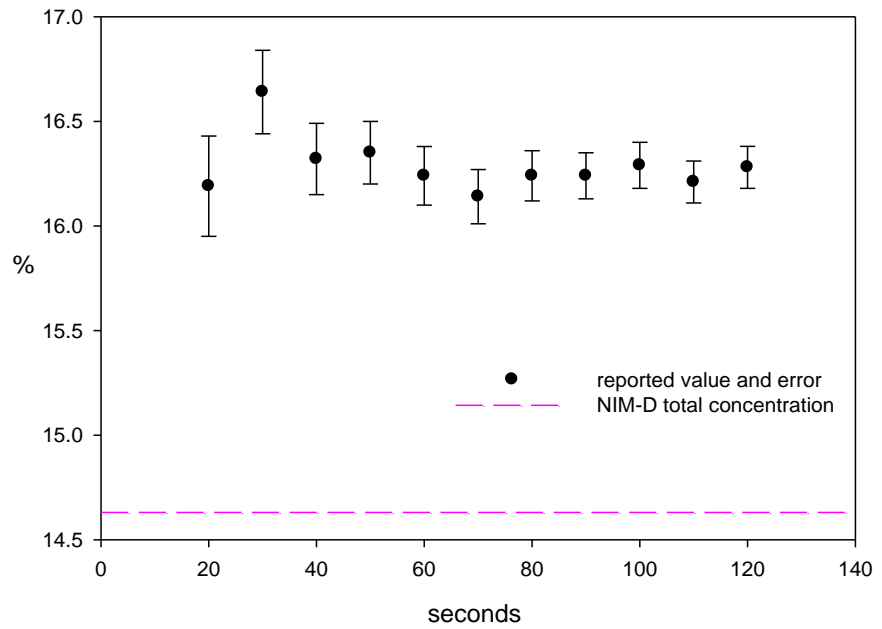


Figure 91. Time vs error for Fe

time vs. error NIM-D (Mn)

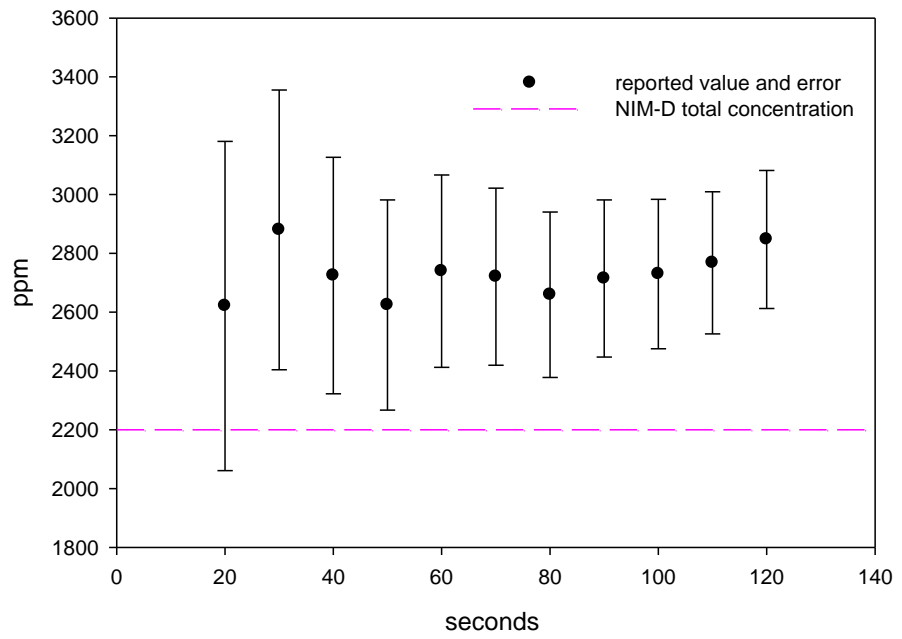


Figure 92. Time vs error for Mn

time vs. error NIM-D (Cr)

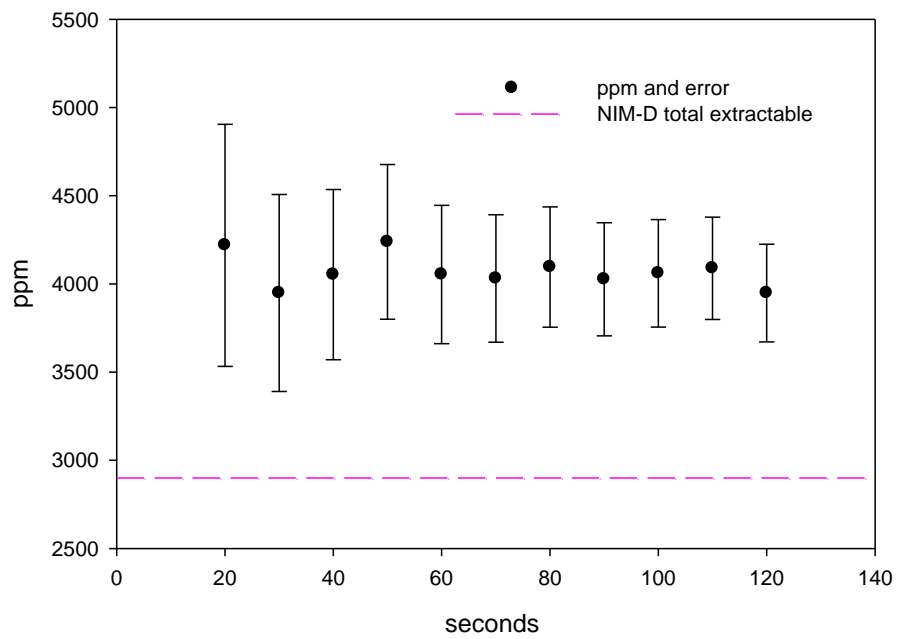


Figure 93. Time vs error for Cr

In general, the results obtained by comparing time against error show a linear reduction in error on all the elements sampled. However, each element gave differing results when compared to best fit for time of analysis and against comparisons with the total element content of: **till 4**, the total extractable content by HNO<sub>3</sub> and AAS, and total concentration of **GSS-7** and **NIM-D**.

**Precision** of the target elements involved calculating the standard deviation [std.] of the average and the relative standard deviation [rsd.] from the [std.]. The precision of the pXRF for each target element was then categorised based on the average rsd as either;

**Excellent (rsd < 5 %)**

**Good (rsd between 5 % and 10 %)**

**Fair (rsd between 10 % and 20 %)**

**Poor (rsd > 20 %)**

**Calculation for rsd :**

$$std = \frac{\sqrt{(x - \bar{x})^2}}{n - 1}$$

$$rsd = \frac{std}{mean} \times 100$$

Where:

rsd = relative standard deviation

std = average deviation of the pXRF data

*n* = number of samples

*x* = variance from the average

**Accuracy** of the target element was assessed and based on a comparison of the results obtained by the pXRF against the content of the CRM, giving a relative percentage difference [RPD] (modified from Billet 2006). The accuracy of pXRF for each element was then categorised based on the % RPD, as either:

**Excellent (RPD < 10 %)**

**Good (RPD between 10 % and 25 %),**

**Fair (RPD between 25 % and 50 %), or**

**Poor (RPD > 50 %)**

**Calculation for *RPD*:**

$$RPD = \frac{(Av - \bar{c})}{\bar{c}} \times 100$$

Where:

$Av$  = average of the pXRF target element data

$\bar{c}$  = concentration CRM certified reference material

RPD = relative percentage difference

CRM till 4	Using the criteria set out on pages 175 - 177				
Element	Overall pXRF % error reduction against actual value	Best fit time (seconds)	Precision	Accuracy	Comments
Cr	Did not reduce below actual	90 - 110	Fair	poor	Overall very poor; no internal filters for this element in the pXRF (Niton UK)
Mn	18 %	90	Excellent	Excellent	Within 10 % of the CRM. Very good, compares well with AAS and has excellent precision and accuracy
Fe	1.1 %	100	Excellent	Excellent	Comparable with HN03 digestion and ASS. Can be used as a target reference element (Billet, 2006)
Cu	10 %	90	Good	Excellent	Within 3 % of CRM and 4 % of NH <sub>3</sub> . Some evidence of spectral interference with Zn (Billet, 2006)
Zn	18 %	60	Excellent	Good	Over-reported values compared to HN03 and the CRM; some evidence of spectral interference with Cu (Billet, 2006)
As	< 10 %	90 - 100	Good	Good	Under-reporting by 15 % and ca.8 % CRM and the extractable amounts by HNO <sub>3</sub> respectively. Arsenic was successfully analysed with pXRF but can be subject to spectral interference if Pb to Arsenic ratio is > 10 to 1 (Billet, 2006).
Rb	< 5 %	90	Excellent	Excellent	Under-reported actual values by 9 % compared to the CRM.
Sr	< 5 %	90	Excellent	Excellent	Under-reported actual values by 8 % compared to the CRM.
Pb	16 %	70 - 90	Good	Good	Over-reported the CRM value by 16 %. Spectral interference between peaks Pb and As can affect the pXRF reported values when the As to Pb ratio is 10 – 1 or more, also with close atomic numbers may skew the recorded values (Billet, 2006).
Co	50 %	n/a	Good	Poor	Over-estimated by x 123 – 220; higher than actual spectral interference by Fe causing high bias, unreliable at low levels
Ni	50 %	90	Poor	Poor	In excess of the actual reported values of the CRM suggesting it was below level of detection. Unreliable as quantitative data, and only applicable for trends at higher levels

**Table 13.** Results from testing CRM till 4 for error reduction accuracy and precision and best fit sampling time.

CRM GSS-7		Using the criteria set out on pages 175 - 177				
Element		Overall pXRF % error reduction against actual value	Best fit time (seconds)	Precision	Accuracy	Comments
Cr		35 %	110	fair	poor	Better results with higher content compared to <b>till 4</b> , but still poor accuracy (no filters)
Mn		7.9 %	120	Excellent	Good	Within 10 % of CRM good target element with excellent precision and good accuracy
Fe		1 %	90 - 100	Excellent	Excellent	Target reference element
Cu		18 %	110	Good	Good	Lower CRM than <b>till 4</b> gave poorer results but this may be due to high Fe causing some spectral overlaps with Zn. Still within 20 %
Zn		39 %	60	Fair	Poor	Zinc reports higher content than CRM than <b>till 4</b> but poor results may be due to high Fe and spectral overlaps with Cu
As		99 %	90	Poor	fair	Poor; error exceeded CRM on all but one sample
Rb		20 %	100	Excellent	Good	Under reported values by 20 % but the CRM contained only 10 % compared to <b>till 4</b>
Pb		44 %	90	Poor	Good	As with other elements with lower content in the CRM compared to <b>till 4</b> , Pb was poor
Co		63 %	n/a	poor	poor	Spectral interference by Fe creating high bias; unreliable at lower levels
Ni		18.5 %	110	Fair/good	Fair	Higher content in the CRM gave better results than <b>till 4</b>

**Table 14.** Results from testing GSS-7 for error reduction accuracy and precision and best fit sampling time.

CRM NIM-D		Using the criteria set out on pages 175 - 177				
Element		Overall or best pXRF % error reduction against actual value	Best fit time (seconds)	Precision (rsd)	Accuracy (RPD)	Comments
Cr		7%	30 - 120	<b>excellent</b>	<b>fair</b>	With higher levels of Cr in the CRM pXRF works well with Cr. But in situ Cr can often be presented as small heterogeneous flakes (Pearce pers. comm., 2013); and needs to be homogeneous to assess averages.
Mn		8.25%	<b>20 - 120</b>	<b>excellent</b>	<b>good</b>	Within 10 % of CRM good target element with excellent precision and good accuracy
Fe		< 1%	20 - 120	<b>excellent</b>	<b>excellent</b>	Target reference element
Cu		Reduced to ~50% of actual	120	<b>fair</b>	<b>poor</b>	The low level of Cu in the CRM is below LOD
Zn		Did not reduce below actual	120	<b>poor</b>	<b>poor</b>	Unlike till 4, which gave reasonable accuracy and precision this CRM may have been affected by high spectral overlap with Fe
Pb		Generally, the error did not reduce below actual	110-120	<b>poor</b>	<b>excellent</b>	Even though the CRM was just below the LOD, it gave good accuracy but poor precision
Co		Over-estimated the concentration by a 400%		<b>Fair</b>	<b>Poor</b>	Affected but the high Fe and due to lack of filters for Co means it may have confused Fe with Co
Ni		~5%	30 - 120	<b>excellent</b>	<b>good</b>	When higher levels of Ni are present in a CRM the pXRF performs well with Ni

**Table 15.** Results from testing CRM NIM-D for error reduction accuracy and precision and best fit sampling time.



Validation against three standards used with a mixture of low, medium and high extractable values suggested there may be some matrix effect. Raw sample and prepared sample values may also be affected by total organic content (TOC), sediment size and pH balance. All of these issues have implications for the outcome of the testing but how a multiplicity of these can be gauged is difficult.

Fundamental parameters or algorithms can interpret and correct many issues of attenuation or spectral interference (Mahuteau, 2008). Slight error in these may account for variation in over and under-estimating reported values in mid and high range CRMs. High Iron content > 4 % can cause high bias with chromium and low bias with copper, also affecting values given with some other elements. Overall the pXRF was comparable with AAS and ICP-MS with excellent/good accuracy and precision for manganese, iron, copper, zinc, arsenic rubidium, strontium and lead. However, nickel, chromium and cobalt are poor in both accuracy and precision against **till 4**. Outcomes differed with **GSS-7** and **NIM-D**, as either the element concentration changed or, higher iron content in the CRM affecting nickel, cobalt, and copper (Billet, 2006).

Testing determined that certain elements were consistent with precision and accuracy at both the lower and higher range of iron, rubidium and manganese. With high levels, > LOD pXRF analysis most elements was effective. What is clear is the need to understand what affects both attenuation and spectral overlap when analysing sediment, soil, ores or artefacts.

The pXRF parameters on how the lower level of detection [LLOD] and the level of quantification [LOQ] are calculated are indicated in [Table 16]. However, these can vary but the standard methods are set out below:

LOQ = 10 x the standard deviation of the background

LLOD = standard deviation of the background x 3 standard deviation of the background

LLOD by pXRF are presented in lower limits of detection, [see Table 16] [LOD]

Filter 1	Sand Matrix	SRM Matrix
Ba	500	1000
Sb	54	72
Sn	50	70
Ag	30	50
Cd	30	40
Sr	10	10
Rb	4	10
Pb	11	18
As	9	18
Zn	24	48
Cu	50	80
Ni	80	160
Co	150	500
Fe	120	500
Mn	90	300

**Table 16.** LLOD of detection for sand and standard reference material. Source: Niton UK 2014.

Shefsky, (1997) considered the level of detection [LOD] where the lower limit of detection is normally less than other laboratory based techniques of AAS and ICP-MS, and suggested the operating parameter is ideally suited for field work application which looks for hot spots [discrete anomalies]. This is within the scope of the pXRF, especially when gauging contamination that may have implication to human health or land use. This assessment and the general application of pXRF may have merit, but recent research into *in situ* analysis by pXRF and other field instruments attaches considerable value to this type of *in situ* analysis (Ramsey and Boon, 2012).

It must be acknowledged that there are other environmental biases that may affect pXRF accuracy and precision, and its comparison with other analytic processes to validate pXRF for *in situ* and laboratory base analysis. Some of these tests have given good agreement for some elements, but what is also evident is the susceptibility to a matrix effect on moisture bulking, reducing concentration values for copper, zinc, lead, arsenic and nickel by 58 – 79 %. It is therefore important to assess *in situ* samples for

this bias and correct for it by either extrapolating percentage moisture to dry samples by drying and correcting, or further laboratory based AAS or pXRF sampling.

Even though testing informs the study that moisture content of soils affects the reported values taken by pXRF, it demonstrates that pXRF is a valuable addition to *in situ* analysis. Even with soils containing high moisture content it still returns qualitative data, conversely when used in laboratory conditions the data is comparable with AAS or ICP-MS quantitative data.

The application of pXRF to the study has complied with the initial license requirements set out by CADW and obviated the need for lengthy and expensive laboratory analysis as the combined samples analysed by pXRF amount to > 2500, but its real value has been its speed and mobility when applied to *in situ* sampling, which can be modified as and when required to interpret soil archives.

#### **4.18 Summary**

This chapter has outlined all of the methods used throughout this study with reference to many of the authors who have tested and used these for environmental enquiry. It has described how and why these methods have been applied in a stepwise process. What these methods have identified are outlined and interpreted in Chapter 5 and 6.

## Chapter 5: Survey results and interpretation

### 5.1 Introduction and overview of background, method application and aims

Over 1200 hill forts constructed during the Late Bronze and Iron Age and many Roman forts and settlements are widely distributed throughout Wales. The cataloguing, surveys and excavations of these settlements have yielded evidence which has developed theories on how the occupants have modified the surrounding environment over millennia. These include how they may have organised their societies, architecture, developed trade, farming and husbandry, and how hierarchical systems may have controlled many of these aspects.

However, this study is concerned with pyro-metallurgy and the relationship with Ceredigion's prehistoric and Classical period forts and settlements built and occupied through the Iron Age and Roman period. The governing bodies, CADW and the RCAHMW, who manage these sites, granted licences for non-destructive surveys to assess the sites selected for evidence of pyro-metallurgy. This chapter presents and interprets results from each site as individual case studies.

The sampling strategy used *in situ* pXRF and laboratory analysis of soil and supplementary samples collected from all of the hill forts. These included platforms, which had been created by the natural topography and developed by further construction of ramparts and earthworks. Subsequent re-surveys used increased sampling resolution when areas were identified with iron, and the heavy metals lead, copper and zinc, consistently higher than the expected levels for their location. Samples from control points were also taken for background levels near to each site. All of the surveys were conducted during late November 2011, December – June 2013 and March 2014.

Further visits to all of the sites collated and plotted all the sample points using DGPS. With annotated plans re-drawn in CAD, these were geo-referenced alongside the survey *in situ* geochemical data from pXRF analysis, and compared with results from the corresponding supplementary soil samples taken for wet analysis by AAS and ICP-

MS. These data populated distribution maps for the target elements copper, lead, zinc and iron.

## 5.2 Odyn Fach grid reference SN6466 8769

### 5.2.1 Site description

See Chapter 3 for full description.

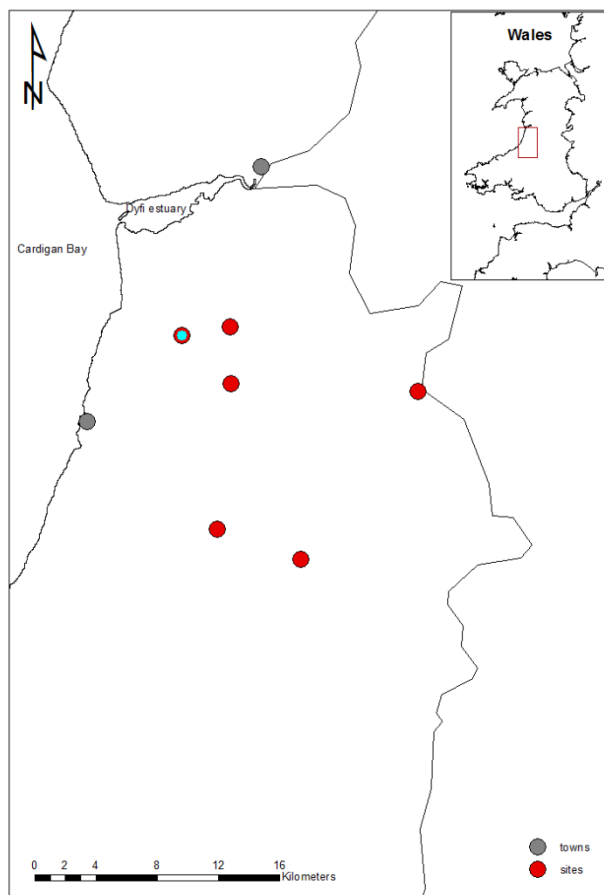


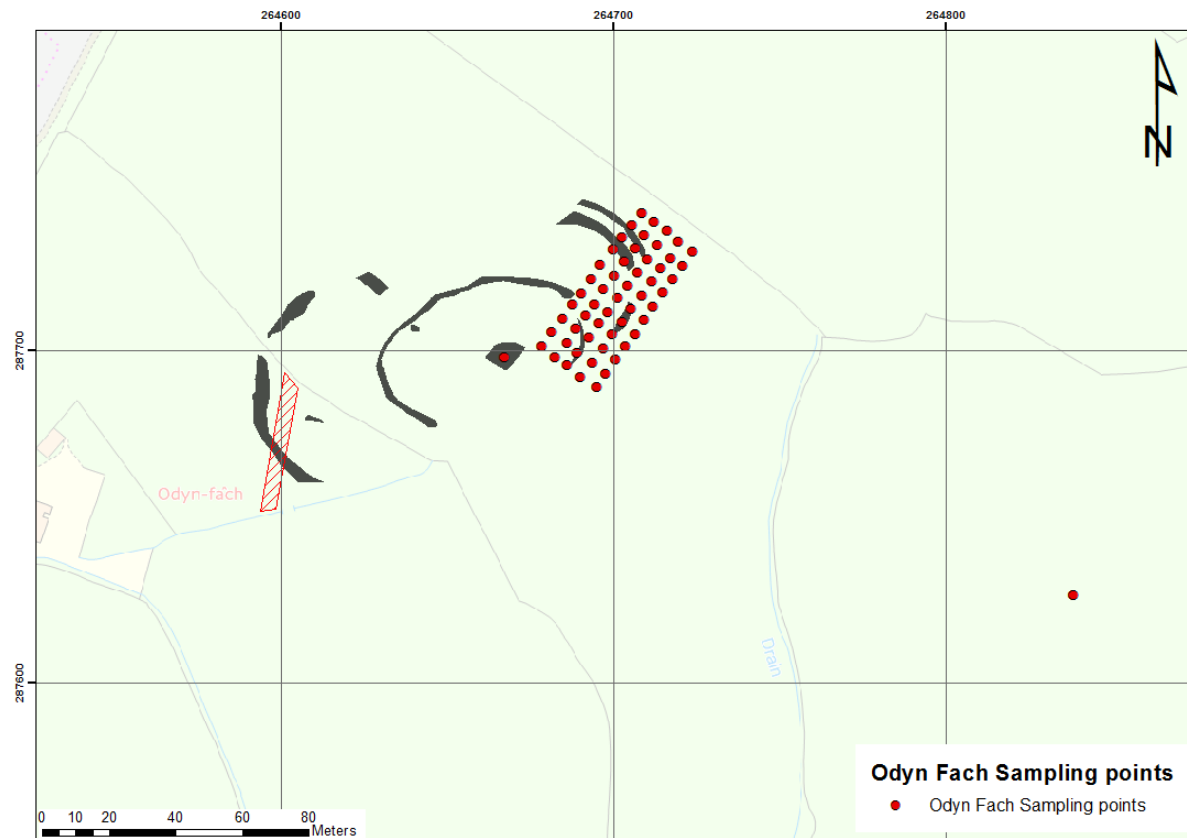
Figure 94. Odyn Fach hill fort highlighted in blue.



**Figure 95.** Odyn Fach with the outline of earthworks just visible within the red circle. Source: RCAHMW (2013).

### 5.2.2 Survey method

One hundred and twelve samples were analysed *in situ* with a further control point sample taken 150 m to the south west. These data were geo-referenced and imported into ArcMap to assess if any of the target elements copper, lead, zinc and iron were elevated above background levels, or if control points created any clustering or hot spots. The level topographic nature of this site allowed for a gridded sampling strategy, while avoiding the previous excavation carried out by Murphy. (1988). Here, a gridded section with a 5 m resolution was marked out to the north-east section of the site, covering a 50 x 20 m section from the outer perimeter to the centre of the enclosure.



**Figure 96.** Odyn Fach sampling points. Note the previous excavation in hatched red.

### 5.2.3 Soil geochemistry

<b>Odyn Fach. Iron Age</b>	<b>pH 4.5 – 5.6</b>		
<b>Element (ppm)</b>	<b>Regional Geochemistry Stream sediment and soil values for Wales</b>	<b>Site control</b>	<b>Site survey average n=114</b>
<b>Cu</b>	23 - 30	24.5	34.4
<b>Pb</b>	110 -1100	58.3	74.23
<b>Zn</b>	180 - 300	57.2	84.5
<b>Fe</b>	64000 - 98000	13048.7	25693.5

**Table 17.** Site survey element average compared to the Regional Geochemistry Steam sediment and soil values Wales.

<b>Geochemical survey (Odyn Fach) Iron Age</b>	<b>All values in ppm</b>			
<b>Element</b>	<b>Cu</b>	<b>Pb</b>	<b>Zn</b>	<b>Fe</b>
<b>Median</b>	33	72.3	84.7	24792
<b>Max</b>	74.9	129.7	134.9	40706.3
<b>Min</b>	6.4	41.1	41.9	9813.8

**Table 18.** Main geochemical findings from Odyn Fach.

The geochemical analysis of the top soil 10 cm below the turfed surface is outlined in the following geochemical concentration maps. Table 17 outlines the Regional Geochemistry Stream sediment and soil values for Wales, the site control, and the average of the total survey analyses.



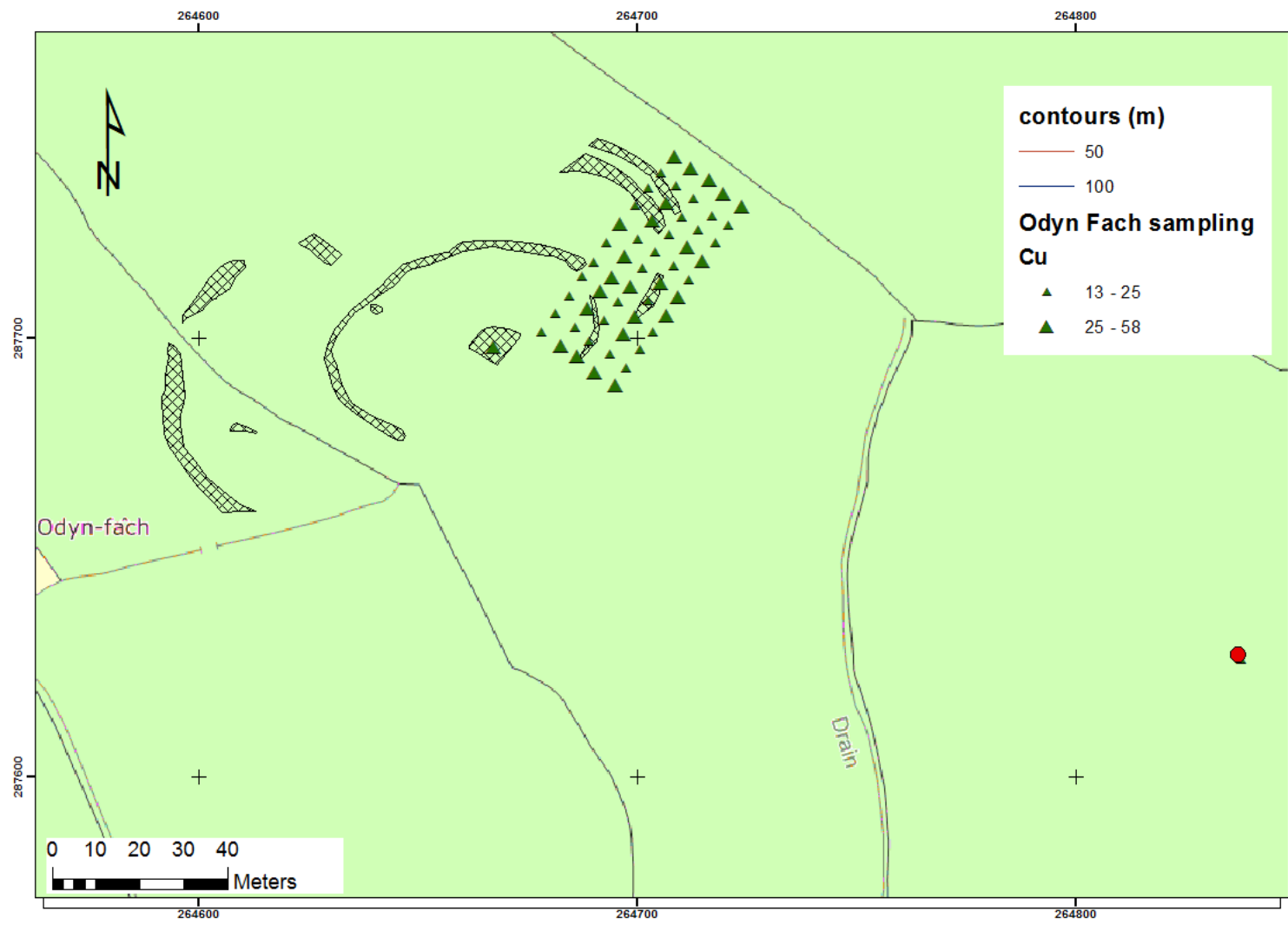


Figure 97. Surface analysis of Cu at Odyn Fach (all values in ppm).

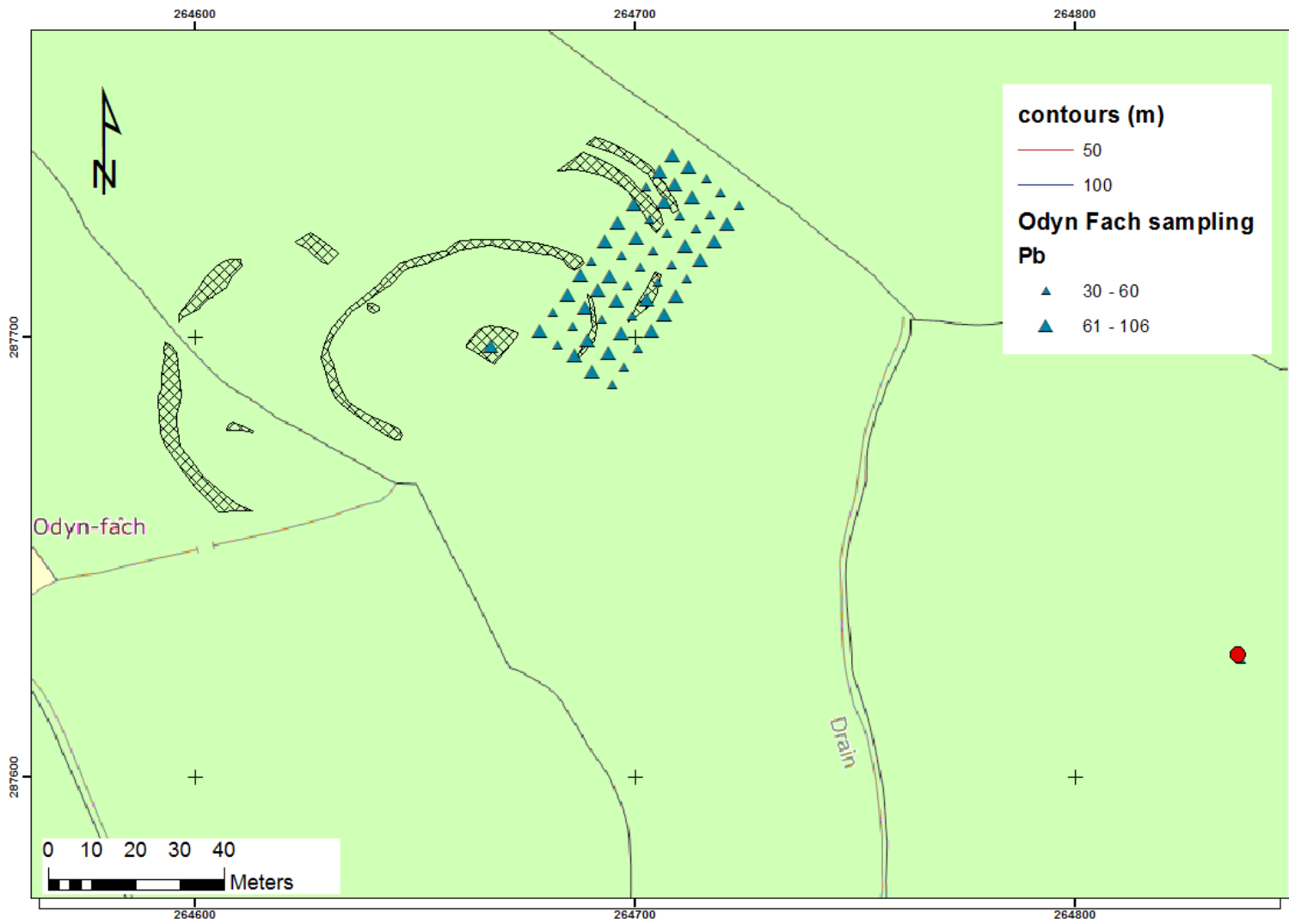


Figure 98. Surface analysis of Pb at Odyn Fach (all values in ppm).

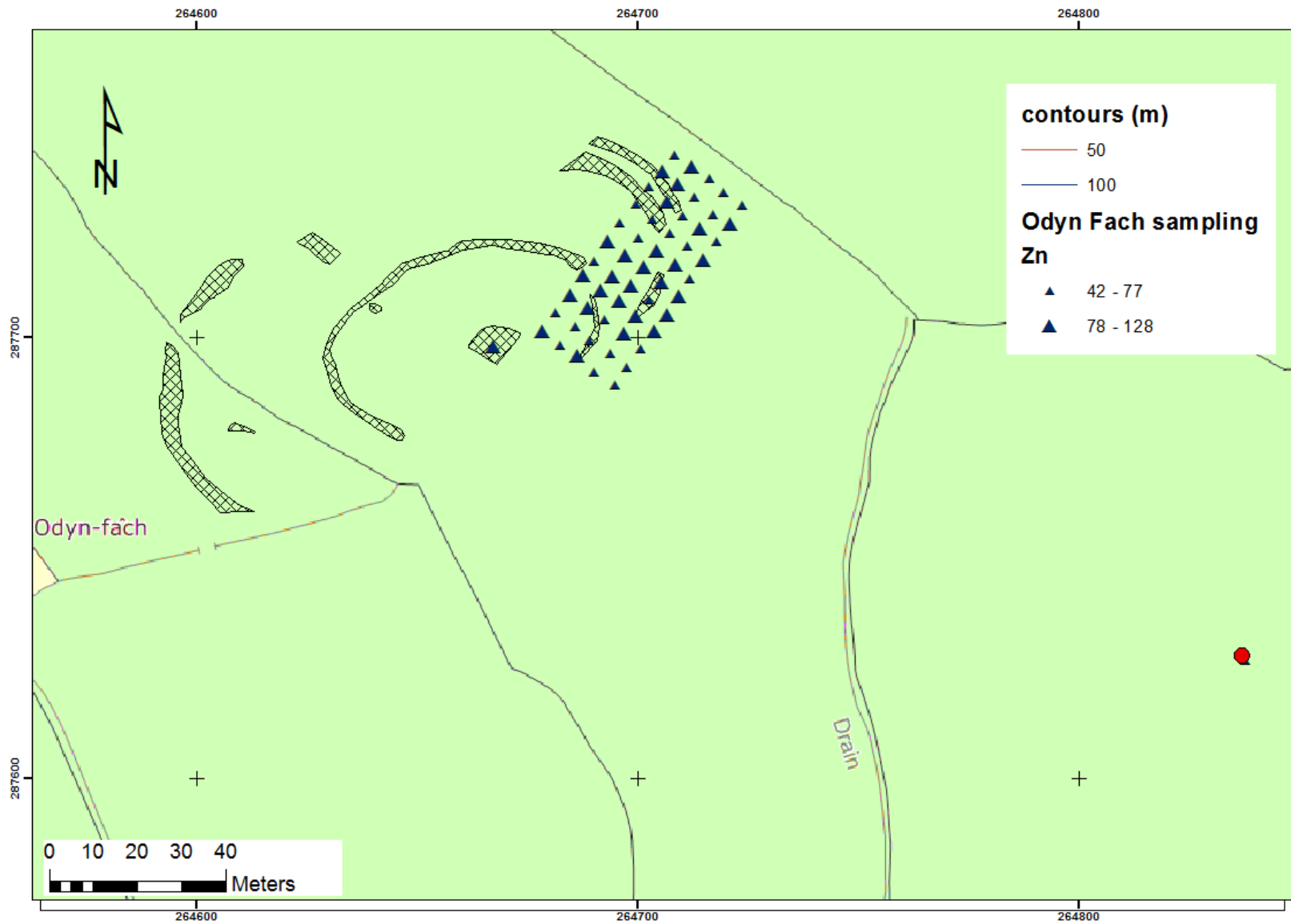


Figure 99. Surface analysis of Zn at Odyn Fach (all values in ppm).

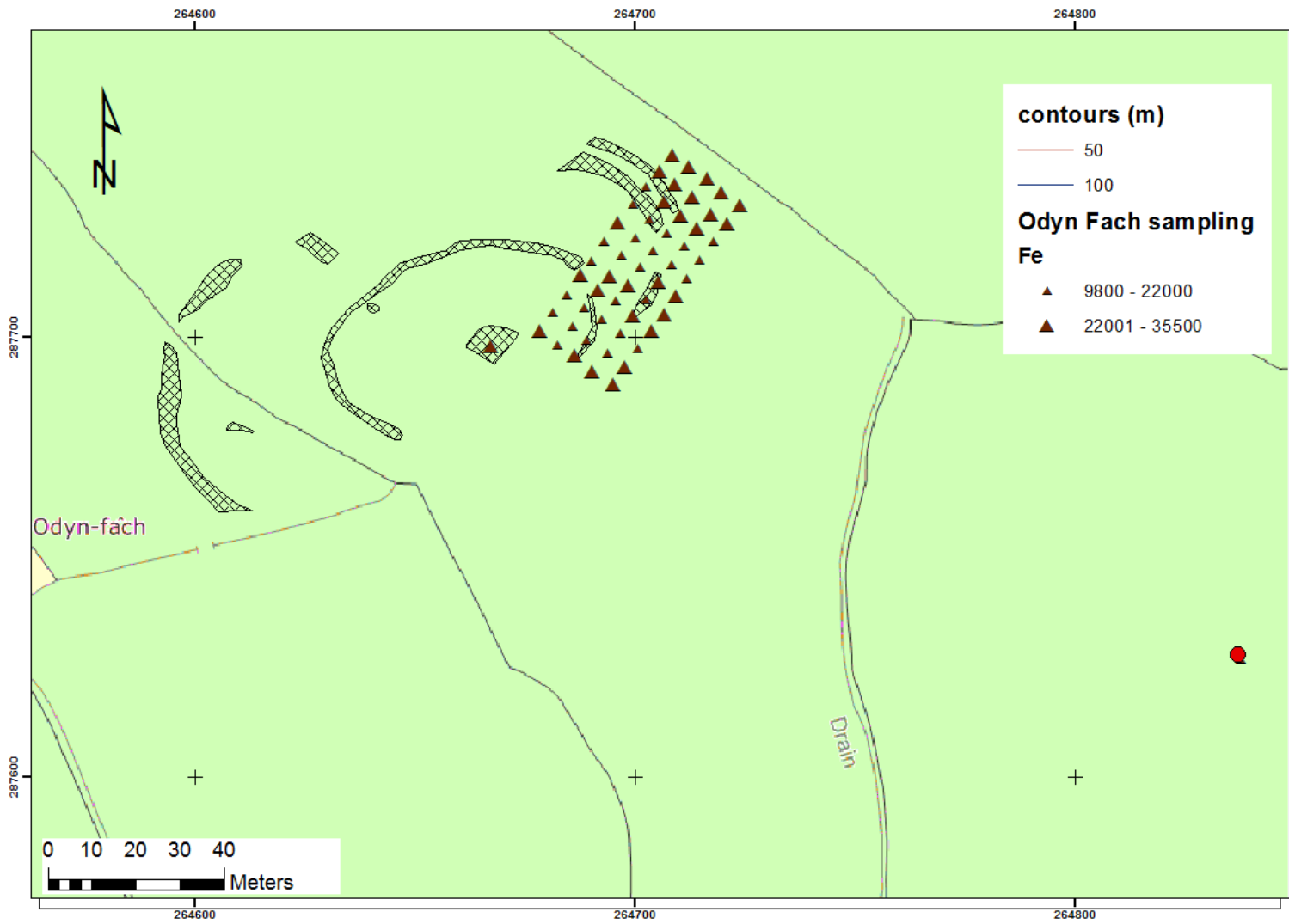


Figure 100. Surface analysis of Fe at Odyn Fach (all values in ppm).

#### 5.2.4 Interpretation

The site survey identified only slight increases in copper to a maximum of 74.9 ppm on one of the analyses, but overall the majority of the analyses were near to or within the expected range for this area, being between 23 - 30 ppm. Even extrapolating the results to account for the moisture matrix effect the maximum expected median would only increase to *ca.* 66 ppm. Lead was below the expected range with a median of 72.3 ppm and a maximum of 123.7 ppm in the lower expected range for this area. This was also reflected in the values for zinc where all of the analyses were below the values for the area at 180 - 300 ppm. Iron, iron is ubiquitous within the landscape, but again did not show any elevated values above the expected minimum of 64000 ppm. The ratios of Pb/Cu, Pb/Zn and Zn/Cu even though they do not reflect the average for the areas soil values for Wales are also within the expected range.

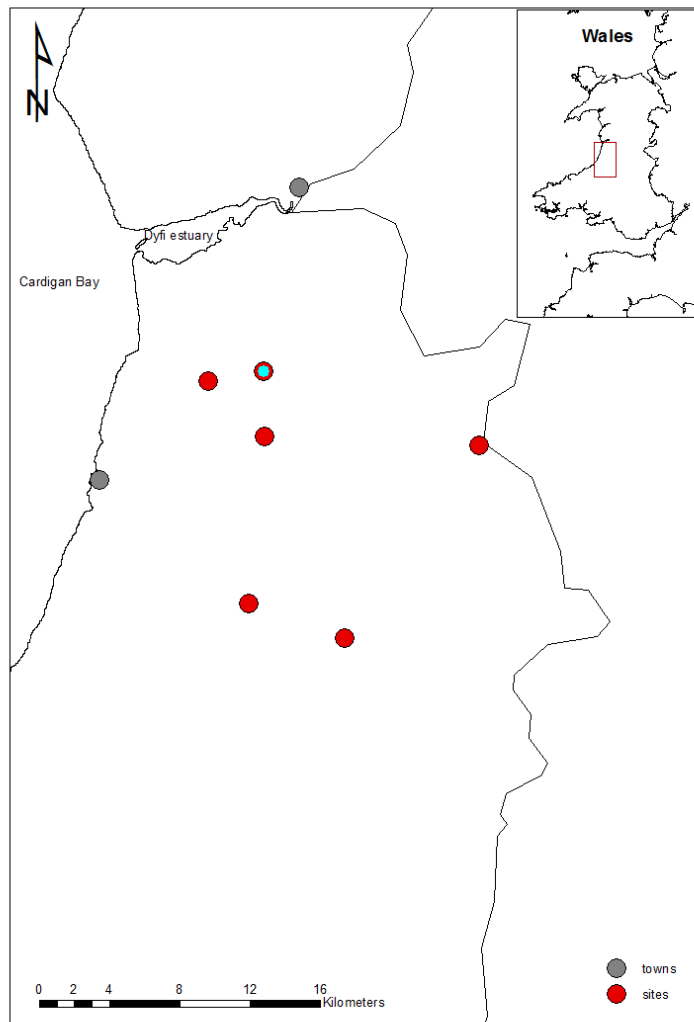
Lack of geochemical evidence pointing to increased metalliferous hotspots at Odyn Fach for pyro-metallurgy suggests that no smelting or smithy work has been undertaken here. However, the recent addition to the sites surface soil may possibly have masked some underlying metalliferous evidence, but for now this is unclear. Some questions remain as to the origin of the earlier slag find within the excavated ditch at this site (Murphy, 1988), and whether these finds are related to hill fort's initial construction and occupation.

Recent work at Glanfred, within 1 km of this site, uncovered iron slag that was radiocarbon dated: UBA-24080 723-739; 767-780; 788-874 Cal AD 68.3% 1 sigma, 688-889 Cal AD 95.4% 2 sigma, placing it in the early Medieval Period (Jones, 2013 unpublished). This suggests possible re-occupation or re-use of Iron Age hill forts in Ceredigion, and may suggest some metallurgical relationship. But to explain the iron slag finds from both, Odyn Fach and Pen Dinas (Elerch) would require geochemical evidence and the micro-structure of these samples. It is possible that this small hill fort was used for transhumant and agricultural practices. It is similar in size to the other small hill forts and enclosures of Glanfred, Caer Gety Llwyd enclosure, Caer Allt-Goch and Cunnill Mawr enclosures which are all within 900 m.

## 5.3 Pen Dinas (Elerch) grid reference SN 6772 8767

### 5.3.1 Site description

See Chapter 3 for full description.



**Figure 101.** Pen Dinas (Elerch) hill fort highlighted in blue.



**Figure 102** Looking east at the western elevation of Pen Dinas (Elerch) with the Plynlimon massif in the background and peatland in the foreground. On the right hand shoulder are the south bastions, which would have formed part of the gated entrance.



**Figure 103.** Looking north-east, note the two bastions and the recent track that cuts through and continues to the left of the rock outcrop near the summit.

### 5.3.2 Survey method

One hundred and twenty seven samples were analysed *in situ* by pXRF, and samples from two control points 50 m to the east at SN 6730 8718, and 15 m to the west adjacent to the track with runs alongside the western revetment SN 6735 8725. These

data were geo-referenced and imported into ArcMap to assess if any of the target elements, copper, lead, zinc and iron were elevated above background levels or control points creating clustering or hot spots.

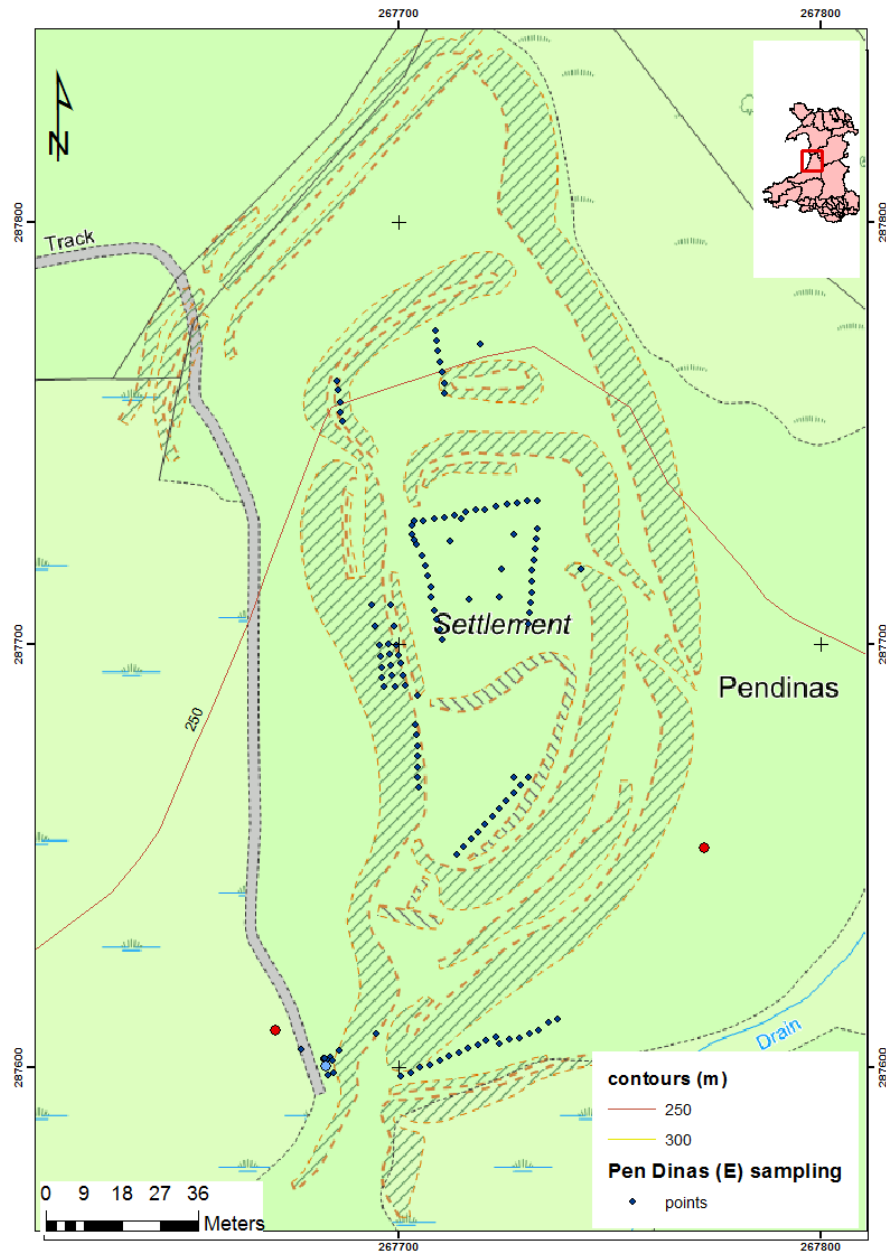


Figure 104. Pen Dinas (Elerch) sampling points.

#### 5.3.4 Soil geochemistry



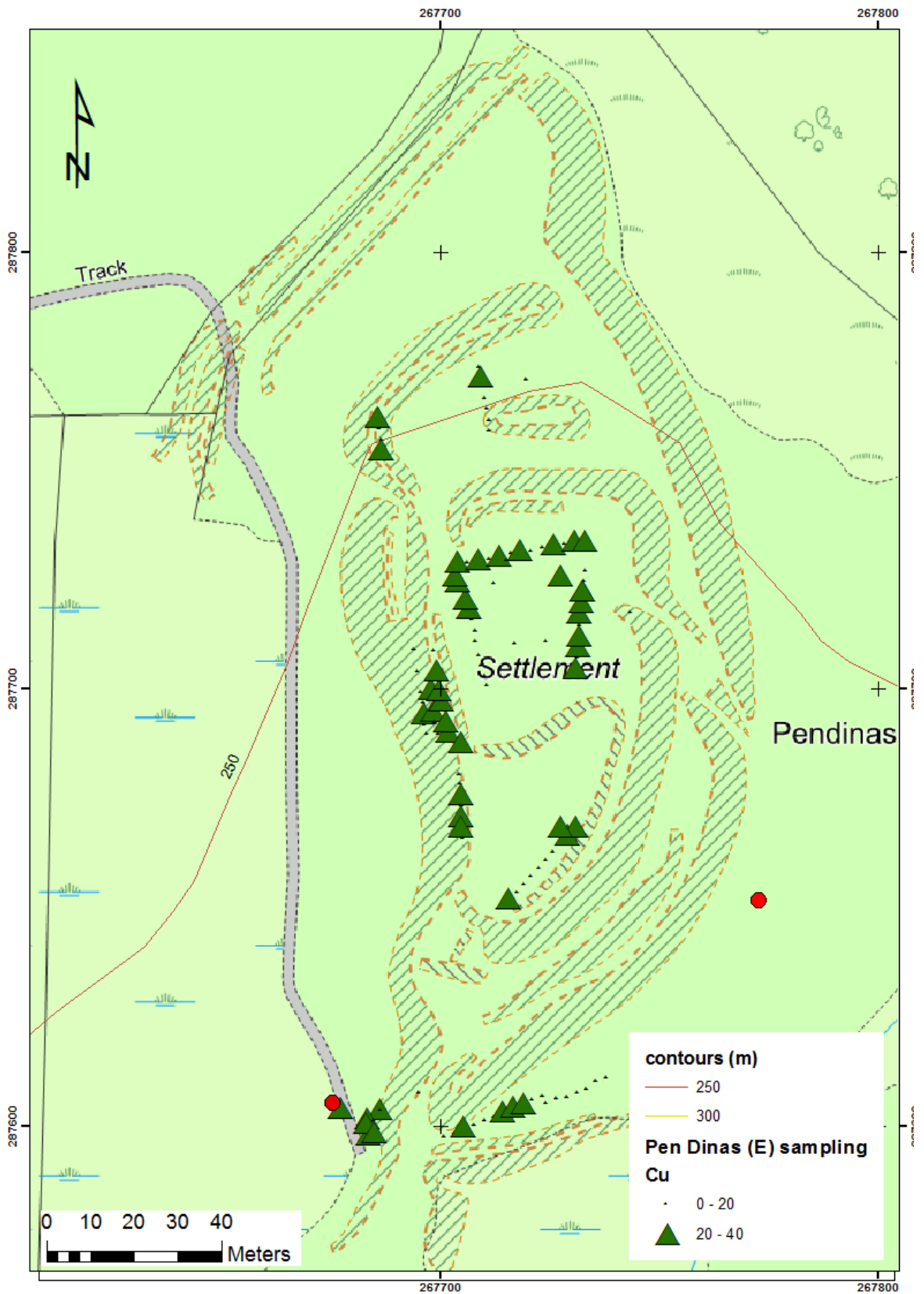
The geochemical analysis of the top soil 10 cm below the turfed surface is outlined in the following geochemical concentration maps.

<b>Pen Dinas (Elerch) Iron Age</b>	<b>pH 4.5 – 5.6</b>		
<b>Element (ppm)</b>	<b>Regional Geochemistry Stream sediment and soil values for Wales</b>	<b>Site control</b>	<b>Site survey average n = 127</b>
<b>Cu</b>	23 - 30	< LOD	11.2
<b>Pb</b>	110 - 1100	26.3	70.25
<b>Zn</b>	180 - 300	23.7	89.1
<b>Fe</b>	64000 - 98000	9698.2	16747.62

**Table 19.** Outline of the regional stream sediment and soil values for Wales, the site control, and the average of the total survey analyses.

<b>Geochemical survey (Pen Dinas (Elerch) Iron Age)</b>	<b>All values in ppm</b>			
<b>Element</b>	<b>Cu</b>	<b>Pb</b>	<b>Zn</b>	<b>Fe</b>
<b>Median</b>	8.9	42.2	36.4	15212
<b>Max</b>	36.9	121.9	76.11	53650.8
<b>Min</b>	<LOD	14	10.23	1932.9

**Table 20.** The main geochemical findings from Pen Dinas (Elerch).



**Figure 105.** Surface analysis of Cu at Pen Dinas (Elerch) (all values in ppm), red markers indicate the control points.

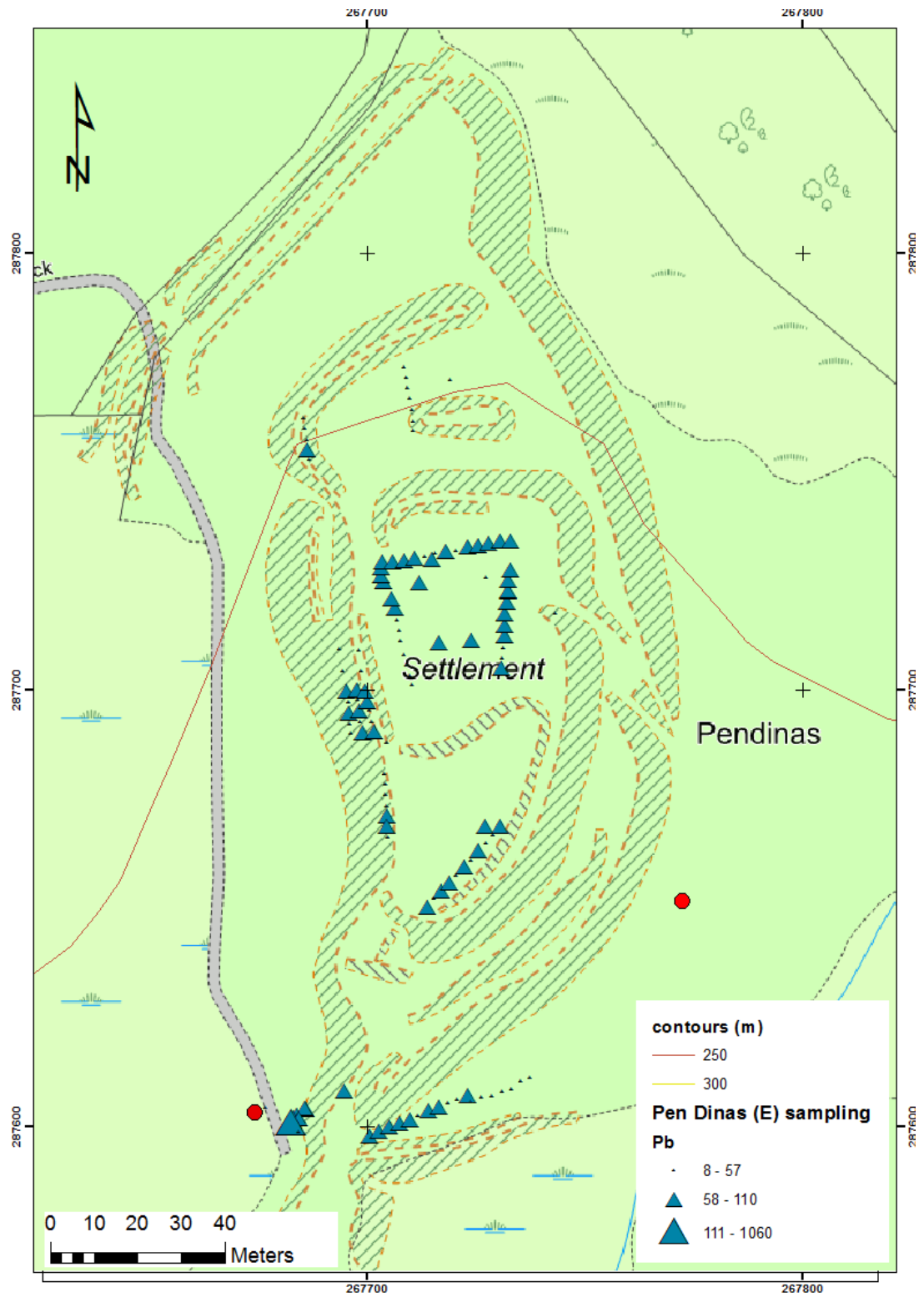


Figure 106. Surface analysis of Pb at Pen Dinas (Elerch) (all values in ppm).

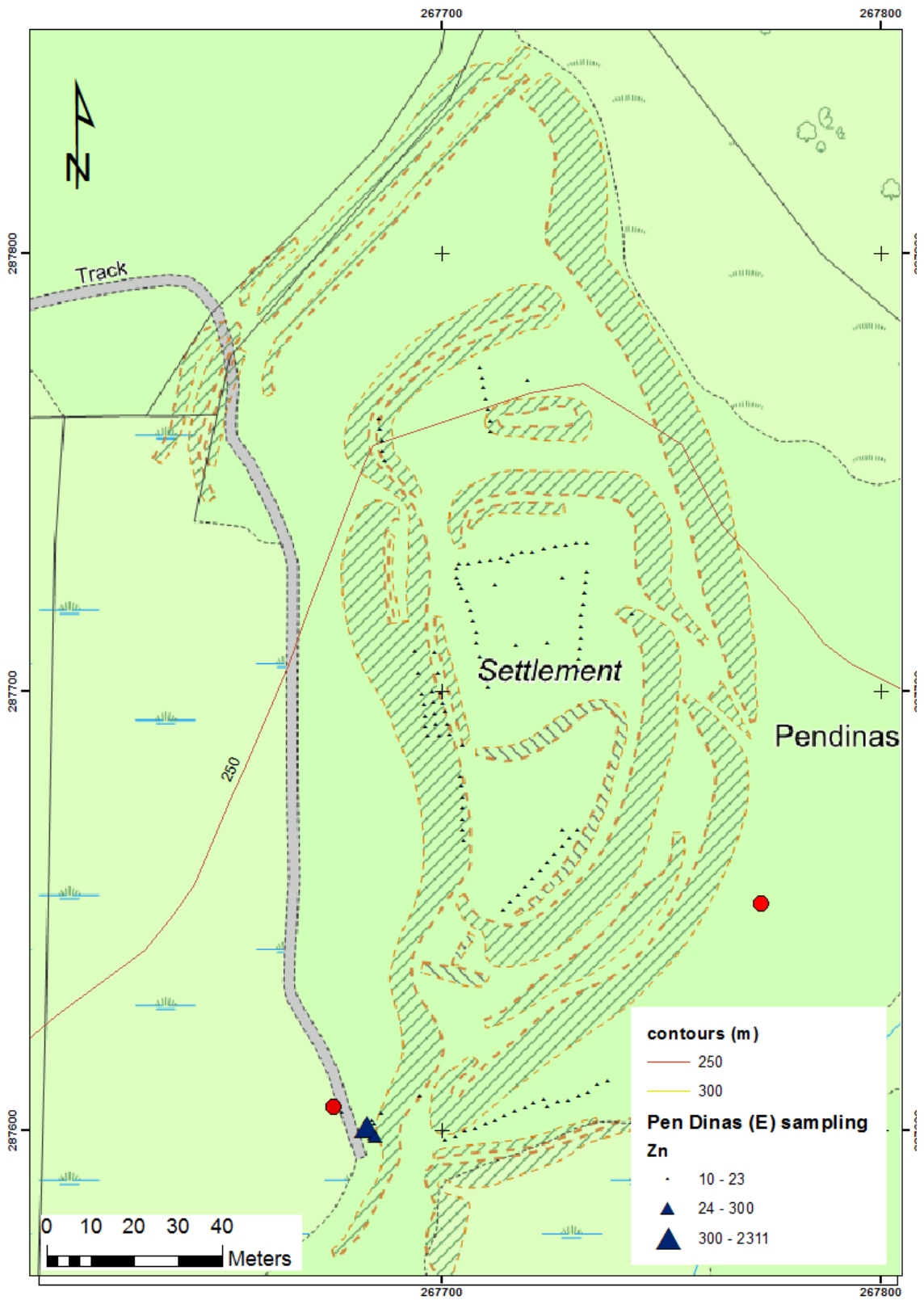


Figure 107. Surface analysis of Zn at Pen Dinas (Elerch) (all values in ppm).

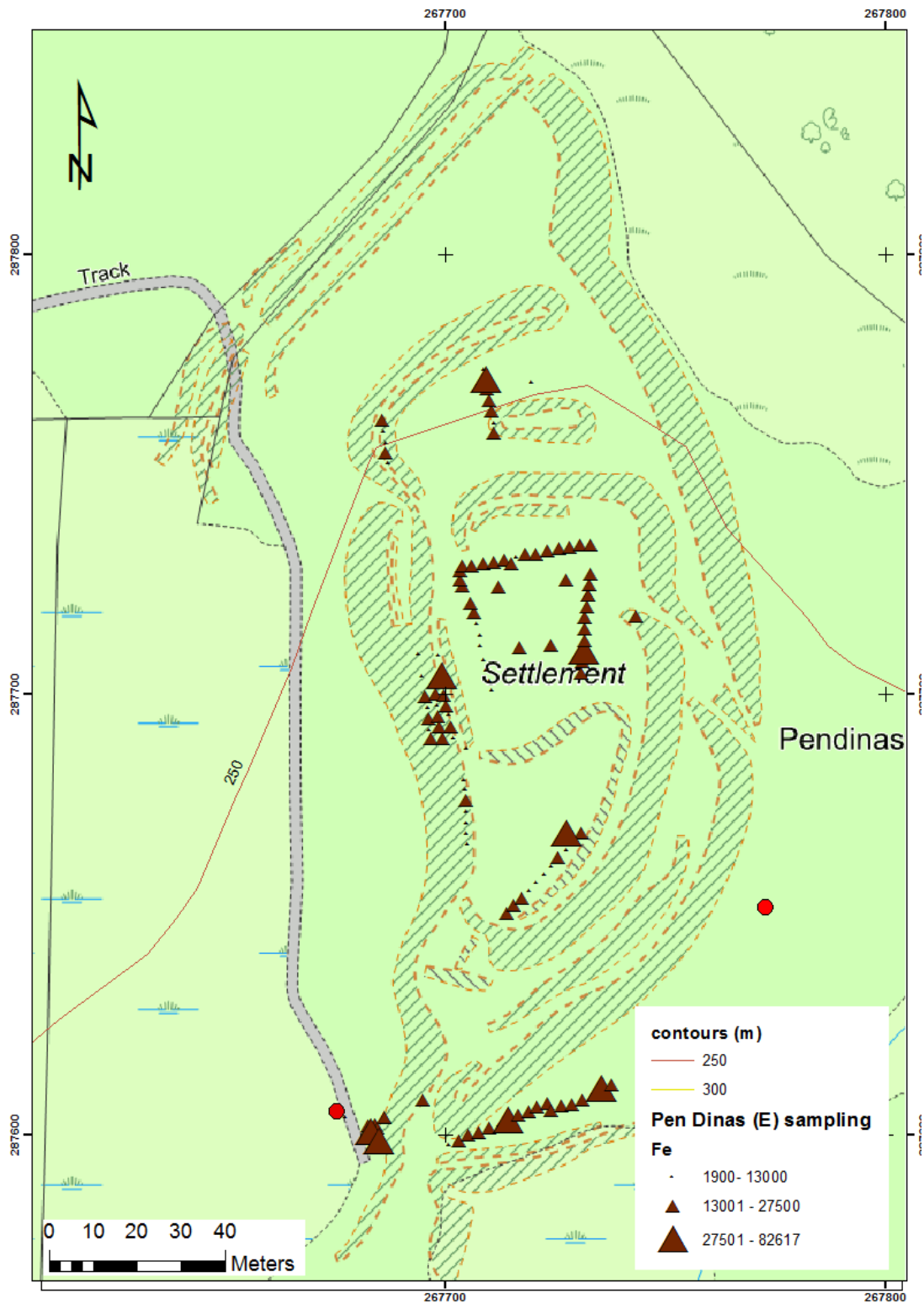


Figure 108. Surface analysis of Fe at Pen Dinas (Elerch) (all values in ppm).

Sampling analysis suggested that the hill fort platforms are within expected ranges for copper, lead, zinc and iron. Copper [see Figure 105]. There is some clustering, but none exceeded the expected range for this location. This suggests that no evidence of pyrometallurgy exists within the fort's interior.

The previous 2005 survey of this site uncovered one artefact resembling iron slag on the upper edge of the western rampart (Davies and Driver, 2012). This area was sampled using pXRF during this survey but did not reveal any increased iron values or smelting or smithy evidence.



**Figure 109.** Slag remnant found at Pen Dinas (Elerch) By Dr T Driver in 2005. Source: RCAHM (2012).

Samples taken near the South entrance bastion, within a sheep scrape, which had been further eroded by a water pipe trench and revealing a breccia inclusion during the pXRF *in situ* analysis, returned levels of lead 1059 ppm, zinc 2311 ppm and copper 36 ppm. These elements are typical of this area's mineral lode suggesting both galena and sphalerite deposits with high lead and zinc content. Subsequent analyses of exposed soils around the southern gateway also recorded increased values of lead, zinc and iron to 83,000 ppm, which is higher than any other sample taken in or around

the hill fort. Importantly, iron can have a matrix effect on pXRF analysis [see Chapter 4].



**Figure 110.** Cross section of the breccia.



**Figure 111.** The location of sling stones and breccia to the left of large glacial erratic used in the gateway construction.

#### **5.3.4 Interpretation**

The site survey identified high levels of copper, lead, zinc and iron by the southern gateway, [see Figure 111], with values of lead 1059.6 ppm, zinc 2311.2 ppm and copper 36.9 ppm. Iron was also elevated but within the expected range for this site. These high values are possibly explained by the breccia inclusion found here. This type of breccia is not uncommon in this geological setting where folding and fracturing have sheared or been opened by mineralising fluids. If these gateways used random

material like breccia as back fill, this may be the source that has increased the levels of iron possibly leaching around the inclusion into the soil. The high iron content is derived from the brecciated mud stone being coated with these fluids. Within mid Wales these can be either iron rich carbonates or iron rich silicates. In the context of where the material was uncovered, it is more likely to be the latter (Perkins, pers. comm., 2014). It is therefore unlikely this is evidence of iron working or smelting within the hill fort.

The survey did not produce any further data on the earlier find of slag material found by Driver, (2005) on the western revetment (Davies and Diver, 2012).

Overall, the pXRF analyses, even if extrapolated to adjust for high moisture, which is on average around double for copper, lead and zinc the raw data values still do not present any evidence of elevated metalliferous values. Even though this hill fort is situated close to the Allt y Crib lode where lead and copper have possibly been extracted since the Bronze Age, there is, for now, no evidence that any pyrometallurgy has been carried out within this settlement.

#### **5.2.5 Other finds**

Further finds included a cache of two smooth pebbles (exotics) possibly sling stones found near to the south gate during the initial pXRF survey. The lithology of both differs, one being igneous and the other sandstone. These would have most likely been collected from the nearby beaches, as their form and shape are consistent with turbid swash created by continuous wave action, and are similar to other finds associated with the Iron Age period both in Wales and England with similar assemblages found in Danebury, Maiden Castle and Castell Grogwynion (Cunliffe, 1991; Timberlake *et al.*, 2013).





**Figure 112.** Sling stones found near to the south gate. Typology is in context with other known finds. Both are typical of beach pebbles possibly transported by ice flow during the last glacial maximum.

Source: RCAHMW (2012).

The only other item found within the inner platform was a whetstone, often used as a sharpening stone.

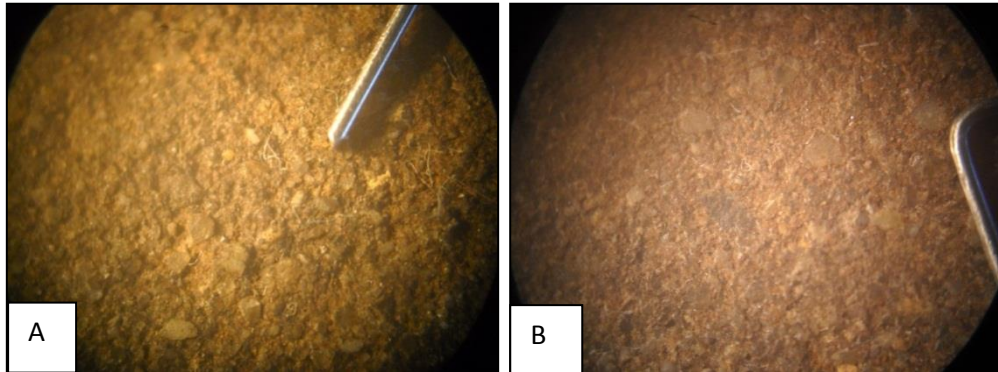


**Figure 113.** Whetstone of siliceous cemented sandstone found in the central platform of Pen Dinas (Elerch) hill fort. Origin is possibly local Pencerrigewion member (PTM) situated 3 km north-east.

Source: Image T Driver RCAHMW (2012).

Using the XRF Itrax scanner to map both the upper and lower surfaces for metalliferous residue proved inconclusive. The whetstone's geochemistry showed a decrease of chromium and tin (on the top polished facet indicating some wear

Polishing of the surface is also seen in high resolution images of the surface, showing the smoothing of quartz inclusions.



**Figure 114.** Comparison of the left and right hand surfaces of the whetstone the scale is indicated by the staples width 0.25 mm to the right of both images.

Further appraisal by Cardiff museum's curator of small finds suggested it was medieval or even earlier (Ludwick pers. comm., 2012)

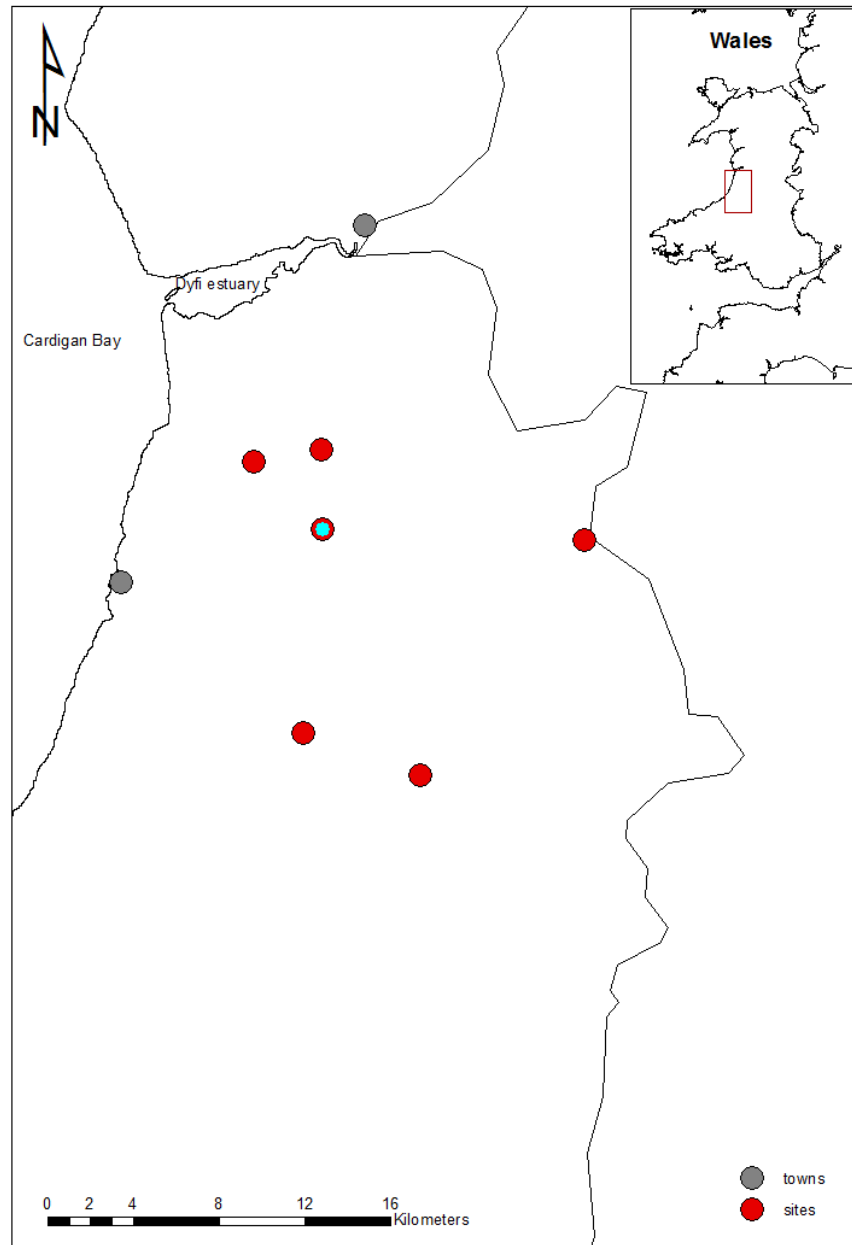
#### **5.2.6 Interpretation**

Sling stones are synonymous with Iron Age hill forts, as these are often unearthed around the gateways of many Iron Age settlements in Britain. However the whetstone, if dated correctly, poses the further question to whether Pen Dinas (Elerch) was used in post Roman or medieval periods for upland transhumant practice or agriculture.

## 5.4 Banc y Darren Grid reference SN 67908302

### 5.4.1 Site description

See Chapter 3 for full description.



**Figure 115.** Banc y Darren hill fort location highlighted in blue.



**Figure 116.** View to Pen Dinas hill fort at Aberystwyth.



**Figure 117.** East to Clarach bay.



**Figure 118.** View looking north to Pen Dinas (Elerch) (to the right of the wind farm) with the Cader Idris range in the back ground.

#### 5.4.2 Survey method

One hundred and eighty one samples were analysed *in situ* by pXRF, with one sample from the control points 80 m to the north-west indicated in red [see Figure 119]. These data were geo-referenced and imported into ArcMap to assess if any of the target elements copper, lead, zinc and iron were elevated above background levels and control points, creating clustering or hot spots.

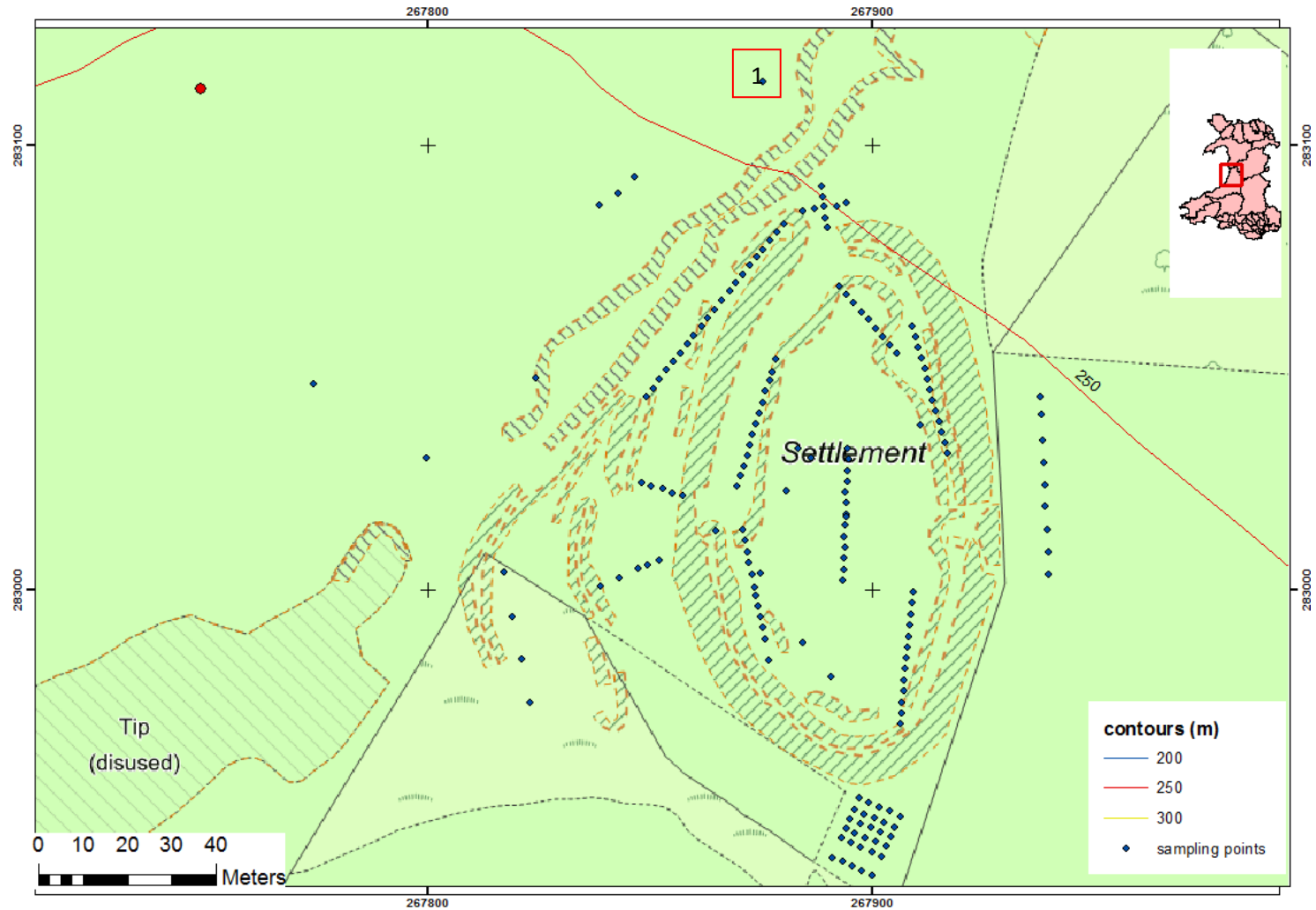


Figure 119. Banc y Darren pXRF sampling points.

### 5.4.3 Soil geochemistry

The geochemical analysis of the top soil ca.10 cm below the turfed surface is outlined in the following geochemical concentration maps. Table 21 outlines the regional geochemistry, stream sediment and soil values for Wales, the site control, and the average of the total survey analyses.

<b>Banc y Darren (Iron Age)</b>	<b>pH 4.5 – 5.6</b>		
<b>Element (ppm)</b>	<b>Regional Geochemistry Stream sediment and soil values for Wales</b>	<b>Site control</b>	<b>Site survey average n= 181</b>
<b>Cu</b>	18 - 19	12.5	27.0
<b>Pb</b>	59 - 110	154	371.5
<b>Zn</b>	85 - 90	26.8	18.4
<b>Fe</b>	82000 - 110000	21940.3	13190.6

**Table 21.** Site survey element average compared to the Welsh stream sediment/soil Atlas and site control.

<b>Geochemical survey (Banc y Darren) Iron Age</b>	<b>All values in ppm</b>			
<b>Element</b>	<b>Cu</b>	<b>Pb</b>	<b>Zn</b>	<b>Fe</b>
<b>Median</b>	11.08	189.2	15.5	13728.3
<b>Max</b>	2510.7	26162.9	274	34460.5
<b>Min</b>	< LOD	30.6	< LOD	901.8

**Table 22.** Main geochemical findings from Banc y Darren.

The Banc y Darren survey found that the spatial distribution of metal elements lack homogeneity, with the higher levels of lead 26500 ppm, copper 2500 ppm, and zinc 274 ppm detected near the north-west edge of the earthworks, which are dissected by the open cut mine. This is in contrast to the lower levels over the rest of the internal platforms and outer annexes. It must also be noted these are *in situ* pXRF analyses which have been affected by matrix effect of high moisture content within the soil. However, these platform and outer annex values still do not exceed the local averages for, copper 19 ppm and zinc 90 ppm, and the control point of lead at 154 ppm 80 m west of the site.

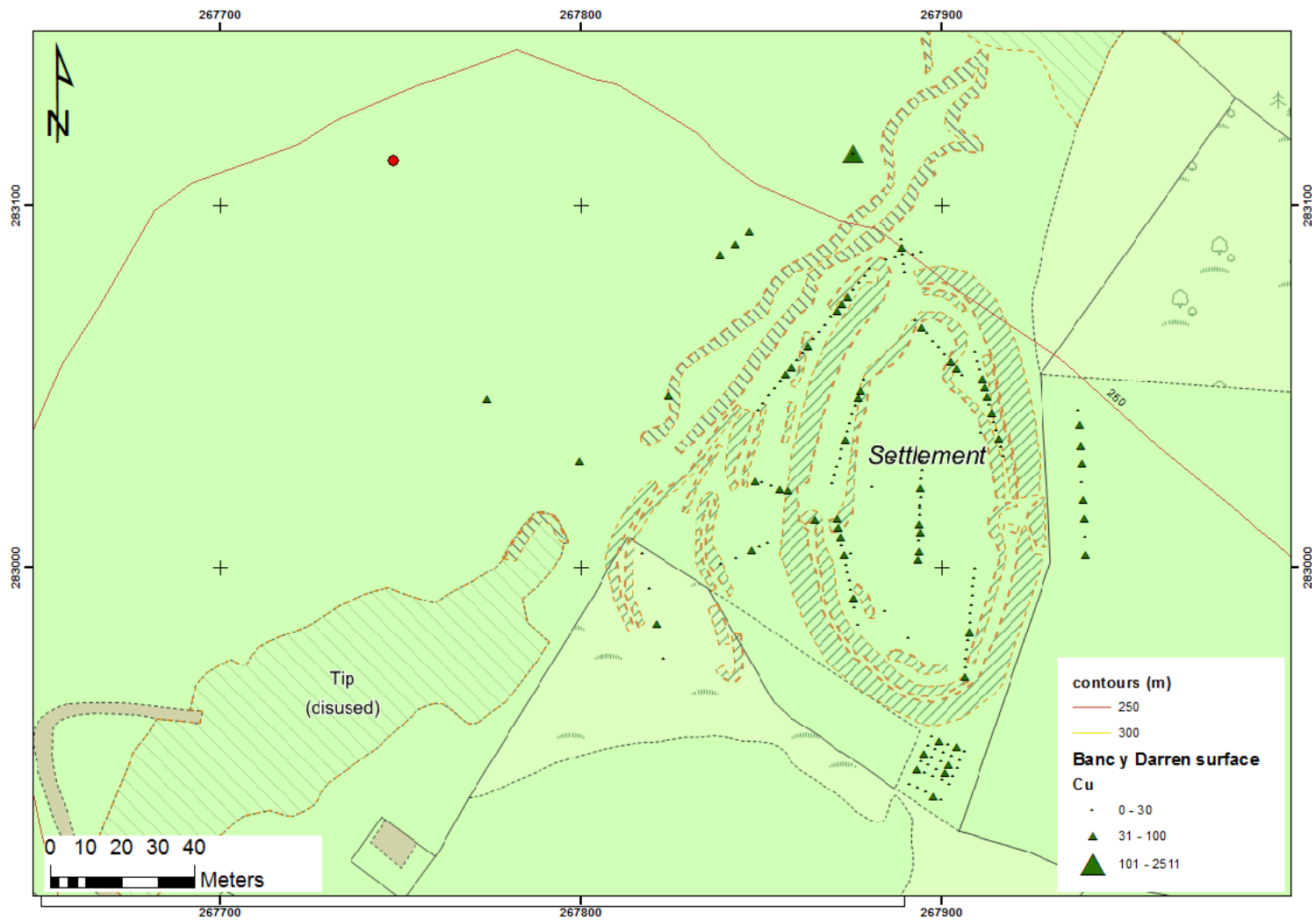
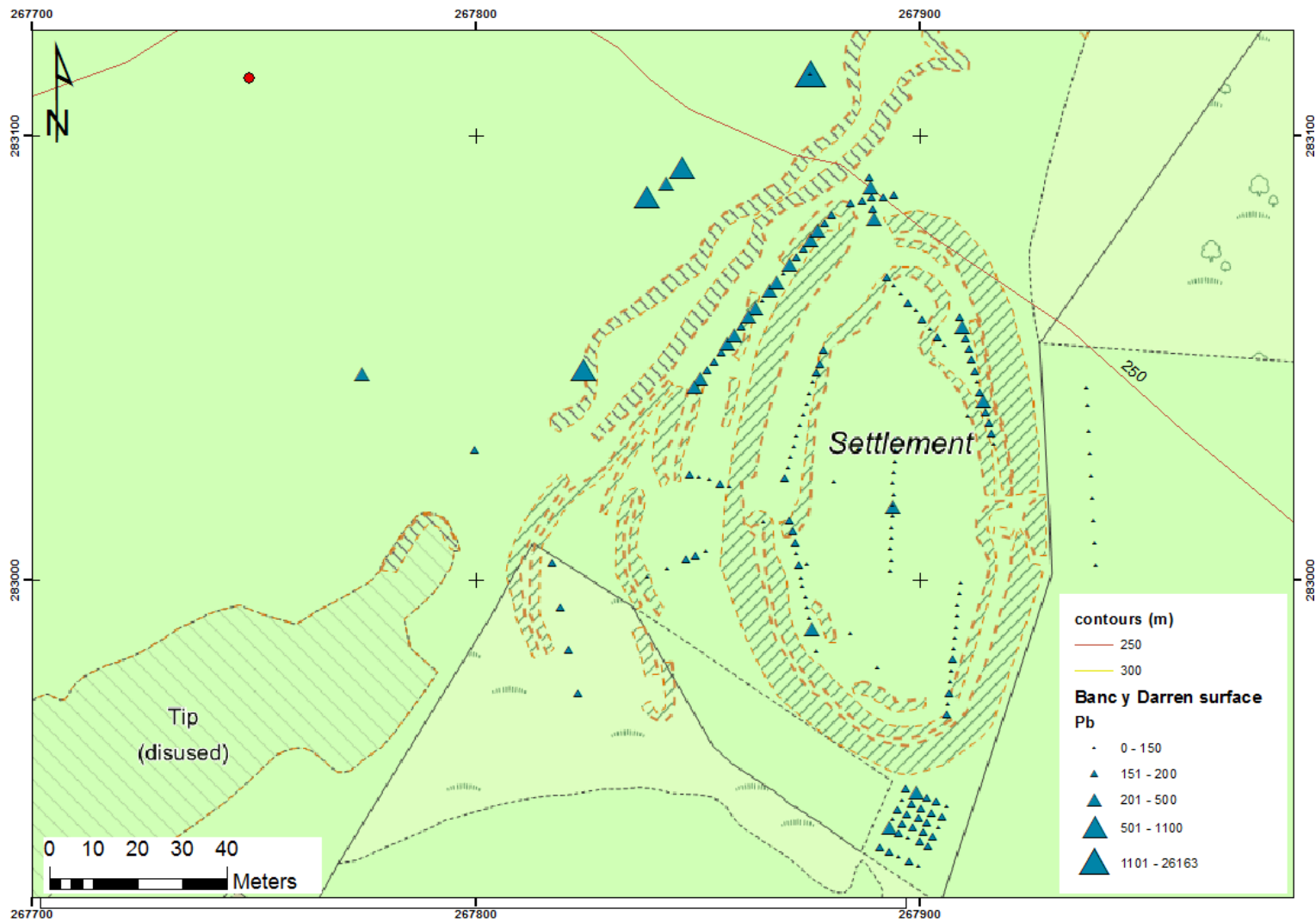


Figure 120. Surface analysis of Cu at Banc y Darren (all values in ppm).





**Figure 121.** Surface analysis of Pb at Banc y Darren (all values in ppm).

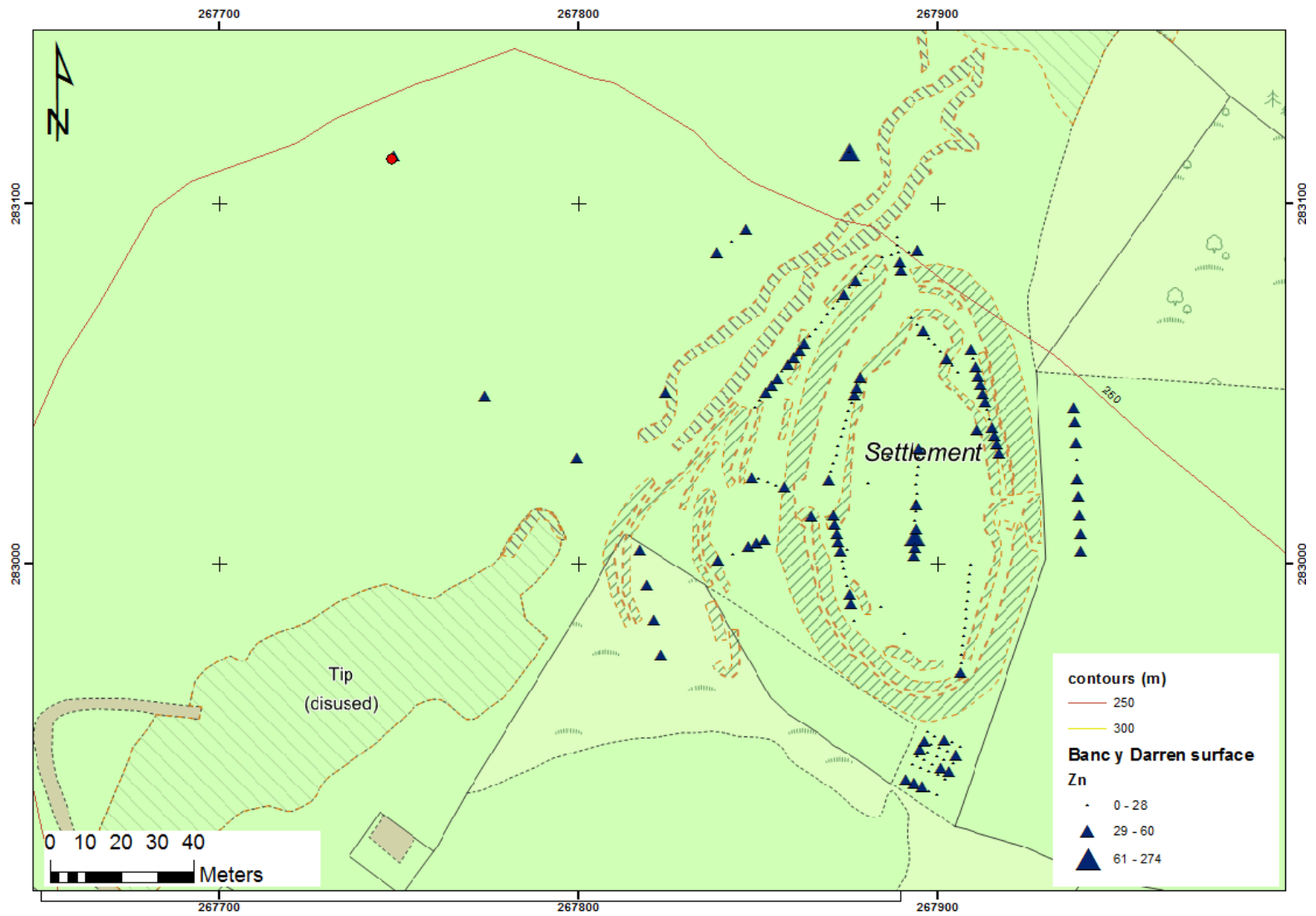


Figure 122. Surface analysis of Zn at Banc y Darren (all values in ppm).

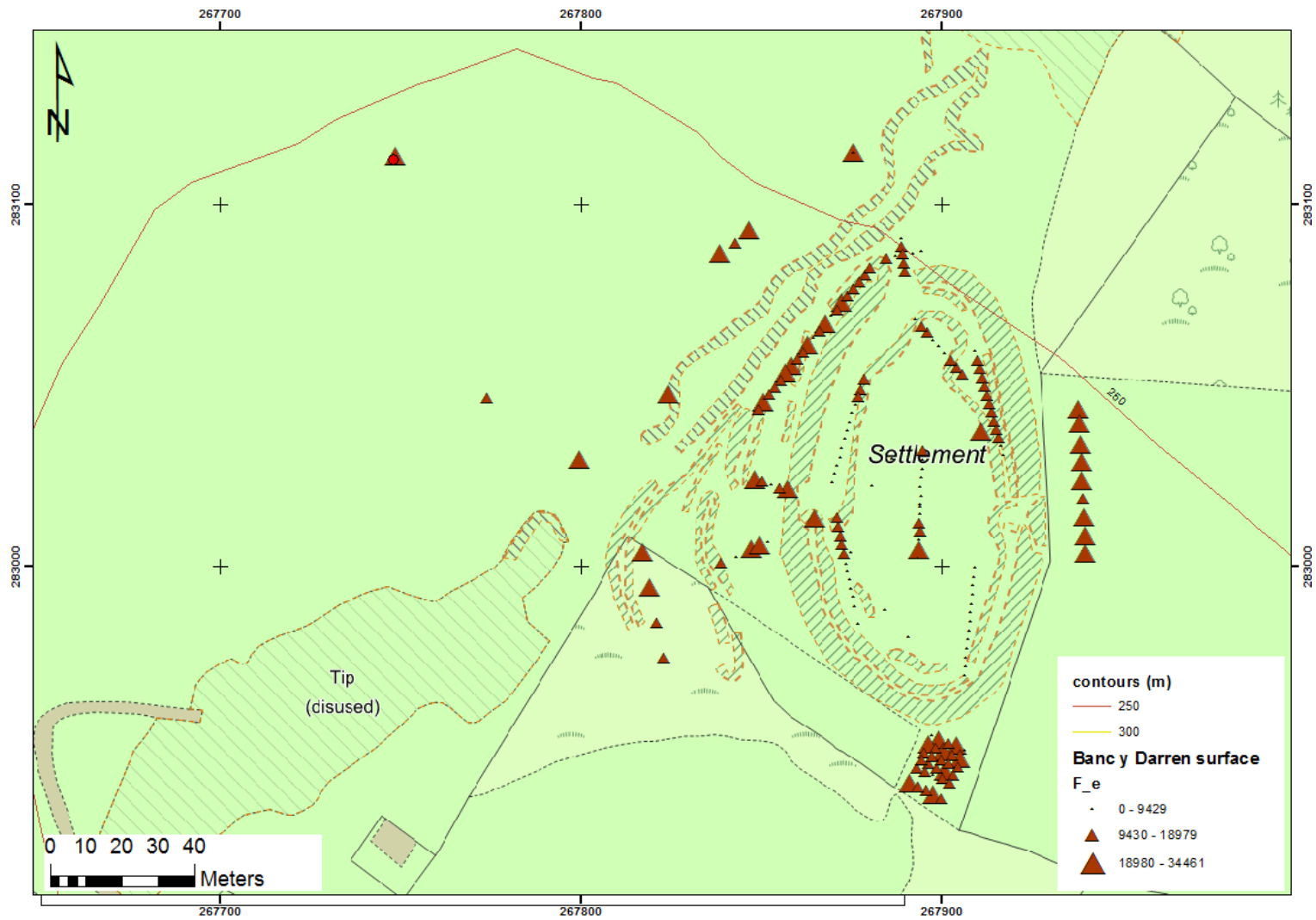


Figure 123. Surface analysis of Fe at Banc y Darren (all values in ppm).

#### **5.4.4 Interpretation**

Average levels for lead are 371.5 ppm, which are well above the back-ground 110 ppm and control points' 154 ppm. One theory considers that prior to the vegetation of the spoil tips, that dust and weathered spoil < 2m $\mu$  may have been carried by prevailing wind over the site (Davies and White, 1981; Johnson *et al.*, 1978). The maximum lead level of 26162.9 ppm was found at the northern edge of one of the outer earthworks with copper levels of 2510.7 ppm, and further high levels distributed either side of the open cut mine. Within the interior, distribution was more randomised possibly due to the matrix effect (moisture) reducing some of the values by two thirds.

Copper is within the expected level for this area over the hill fort, except at one point near the open cut mine which shows a level of 2510.7 ppm. This also reflected in the value of lead at 26162.9 ppm suggesting that both chalcopyrite and galena are present. However, this isolated find is associated with a small piece of metal rich material.

#### **5.4.5 Metal rich slag find**

One inclusion found within the upper lithofacies of an exposed sheep scrape to the north-west of the open cut mine (see sample point 1 [see Figure 119]), shares comparable surface properties to vesicular slag, with additional surface vitrification. Further analyses by both pXRF and ASS were carried out to assess geochemical properties and returned high levels of copper, lead, arsenic and zinc. Further analysis of surrounding soil revealed comparable high levels of these elements [see Table 22].



**Figure 124.** Vitrified material collected during the Banc y Darren survey.

Analysis results from pXRF and AAS			
	pXRF Ore	pXRF soil	AAS soil <180µm
<b>Pb</b>	440000	26162	83769
<b>As</b>	10000	2006	Nd
<b>Zn</b>	150000	273	266
<b>Cu</b>	16000	2510	4168
<b>Fe</b>	100000	30322	Nd

**Table 23.** Metal concentration in the vitrified slag/smelting detritus and surrounding soil samples.

This find was uncovered 50 cm down the face of a sheep scrape.



**Figure 125.** Sheep scrape in spoil or earthwork on the north-west sampling point. The ore was found in the soil profile at 50cm depth in line with the top of the field note book, which is *ca.*23 cm in length.

#### 5.4.6 Interpretation

With all the analysis of the metal rich slag like sample and surrounding soil there is limited agreement between pXRF and AAS for data on lead and copper, surrounding the slag like inclusion, [see Table 23], even taking into consideration the matrix effect where values may be increased when samples are dried, milled and re-sampled with pXRF or wet analysis by AAS.

High temperature may have created vesicular and vitrified characteristics in the sample, and a number of reasons that may explain how these occurred are outlined here;

- Fire setting and increased oxygen pressure.
- Later experimental work may have been carried out nearby and this slag like sample may have been discarded.

- Furnace smelting debris, as the sample resembles results obtained from a crude smelting process, which may have been unearthed and re-distributed in a later spoil tip.
- It may also be evidence of early smelting.

Further examination would require intrusive sampling to survey for any smelting evidence. Further sampling may reveal concomitant charcoal assemblages, which could possibly radio carbon date this or other stratigraphic layers if further inclusions were uncovered. But given there is evidence of Bronze Age copper smelting locally at Cwmystwyth 15 km to the south-east, and that further evidence of a cache of hammer stones synonymous with both Iron Age and Bronze Age mining (Timberlake, 1988) have been located within 1 km of Banc y Darren, it would seem reasonable to postulate some association with early smelting processes, but for now, this remains unproven.

Overall, Banc y Darren hill fort poses questions as to whether the open cut mining preceded or post-dated the fort development, or if they were developed in tandem. It is highly likely the stone work above the yellow field note book [see Figure 125] is part of the Iron Age earthworks and is likely to be anthropogenic in construction. If the vitrified sample was found below this, does it imply it was included in the earthwork construction, and if so, it is possible that it predates construction of these earthworks.

Unlike Pen Dinas and Odyn Fach where the study's aims were to further evaluate sites where previous finds of iron slag may be contemporaneous with pre-historic smelting, here, evidence is circumstantial and only suggests smelting finds may be pre-historic. But there is still need for further hypothesis testing to strengthen these arguments. For now, the evidence only suggests some metalliferous relationship within the hill fort and prehistoric exploitation of the local mineral lodes. But further geophysical analysis may detect dipoles associated with smelting and deep burning.

## 5.5 Llys Arthur grid reference SN7865882505

### 5.5.1 Site description

See Chapter 3 for full site description.

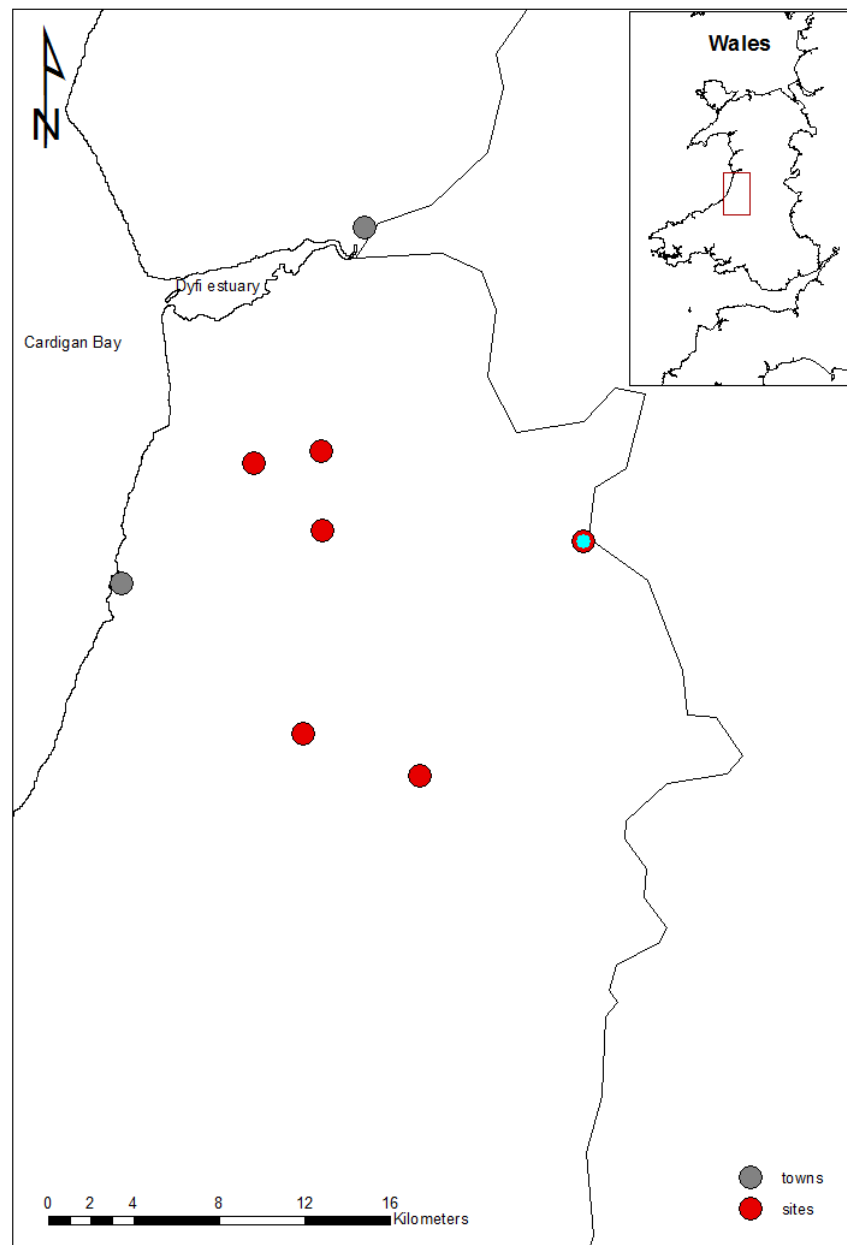


Figure 126. Llys Arthur Roman fort highlighted in blue.





**Figure 127.** Llys Arthur rectangular shaped enclosure with the open end orientated to the east.

### 5.5.2 Survey method

Two Hundred and fifty nine samples were analysed *in situ* with a further control point sample being taken 100 m to the north-east. These data were geo-referenced and imported into ArcMap to assess if any of the target elements copper, lead, zinc and iron were elevated above background levels or those of the control points, creating clustering or hot spots. Here, the level topographic nature of this site allowed for a gridded sampling strategy, set out a with 5 m<sup>2</sup> resolution covering a 75 x 75 m area incorporating the complete earthworks. Additional samples were taken from a small tump 15 m to the west of the site.



**Figure 128.** Llys Arthur, survey covered internal and the external perimeter of the earthworks, Esgair Lle mine and a small mound 60 m west of the enclosure.

### 5.5.3 Soil geochemistry

Geochemical analysis of the top soil 10 cm below the turfed surface is outlined in the following geochemical concentration maps.

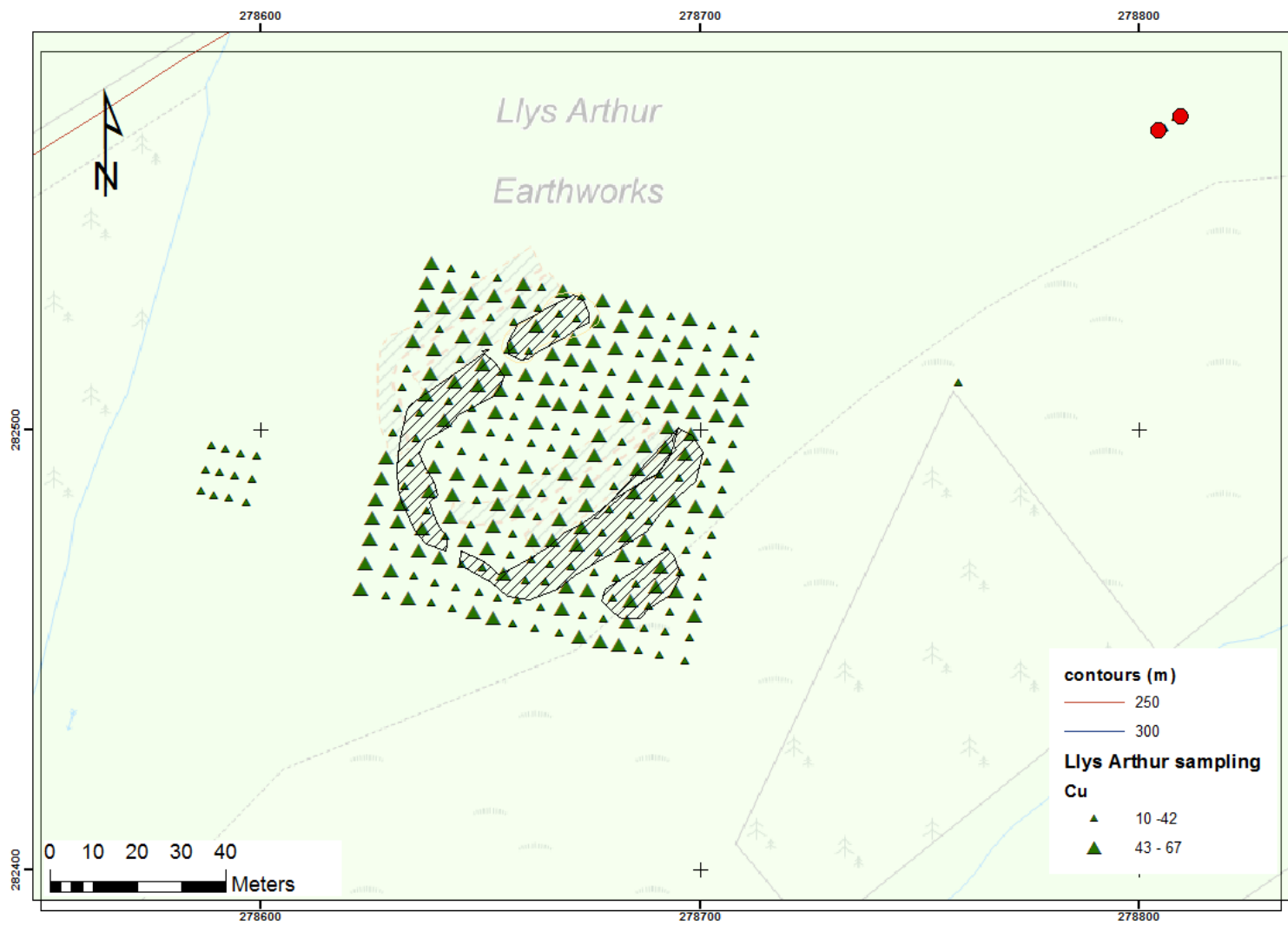
Table 24, outlines the regional geochemistry, stream sediment and soil values for Wales, the site control, and the average of the total survey analyses.

<b>Llys Arthur (Roman)</b>	<b>pH 4.5 – 5.6</b>		
<b>Element (ppm)</b>	<b>Regional Geochemistry Stream sediment and soil values for Wales</b>	<b>Site control</b>	<b>Site survey average n=259</b>
<b>Cu</b>	42	30	14.8
<b>Pb</b>	110	44.9	46.9
<b>Zn</b>	300	38	25.78
<b>Fe</b>	98000	19563.9	16884.75

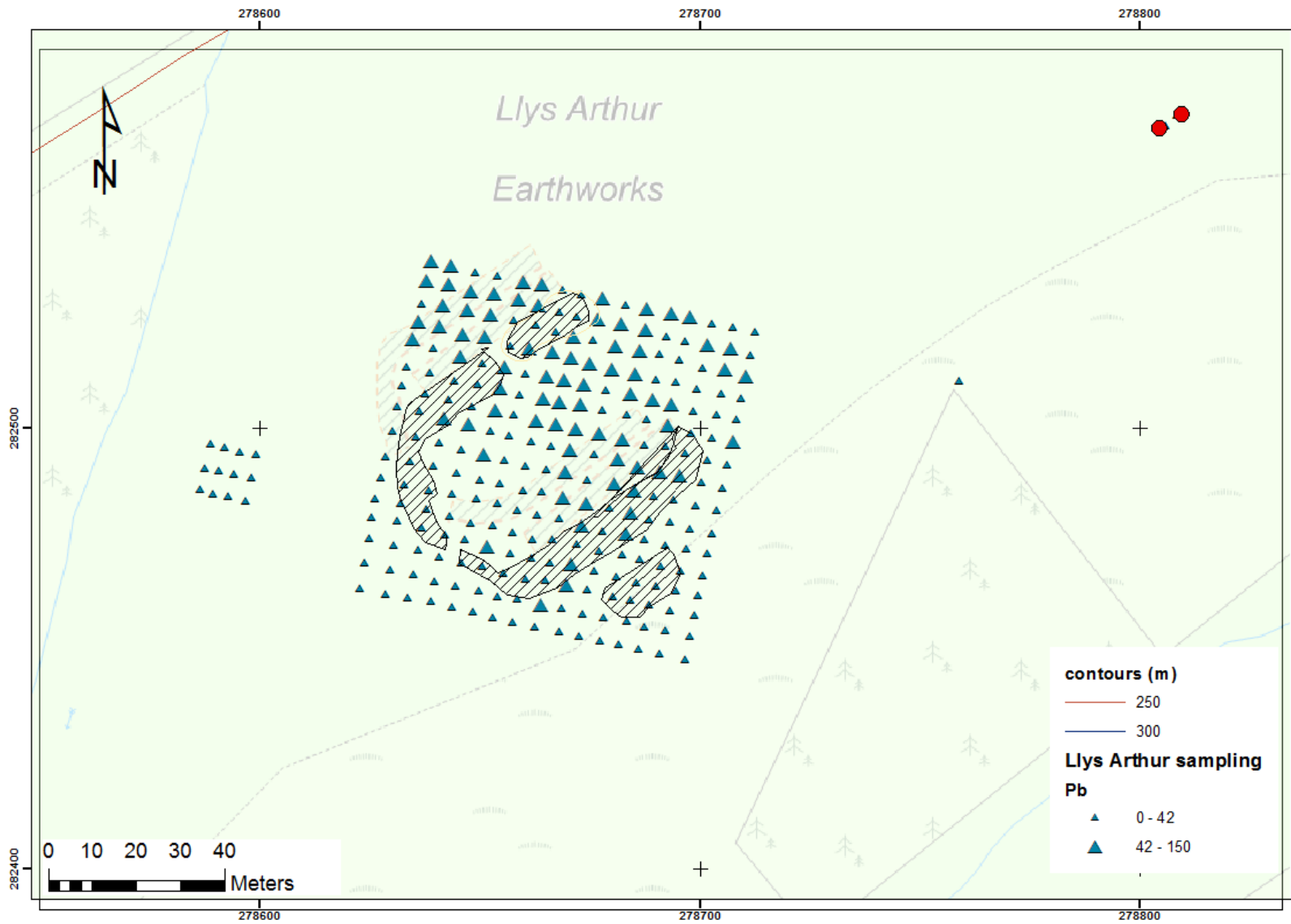
**Table 24.** Site survey element average compared to the Welsh stream sediment/soil Atlas and site control.

<b>Geochemical survey (Llys Arthur)</b>	<b>All values in ppm</b>			
<b>Element</b>	<b>Cu</b>	<b>Pb</b>	<b>Zn</b>	<b>Fe</b>
<b>Median</b>	14.31	44.9	25.2	15820.9
<b>Max</b>	66.5	147.9	103.4	43225.1
<b>Min</b>	< LOD	6.9	< LOD	2226.7

**Table 25** Main geochemical findings from Llys Arthur.



**Figure 129.** Surface analysis for Cu at Llys Arthur (all values in ppm).



**Figure 130.** Surface analysis for Pb at Llys Arthur (all values in ppm).

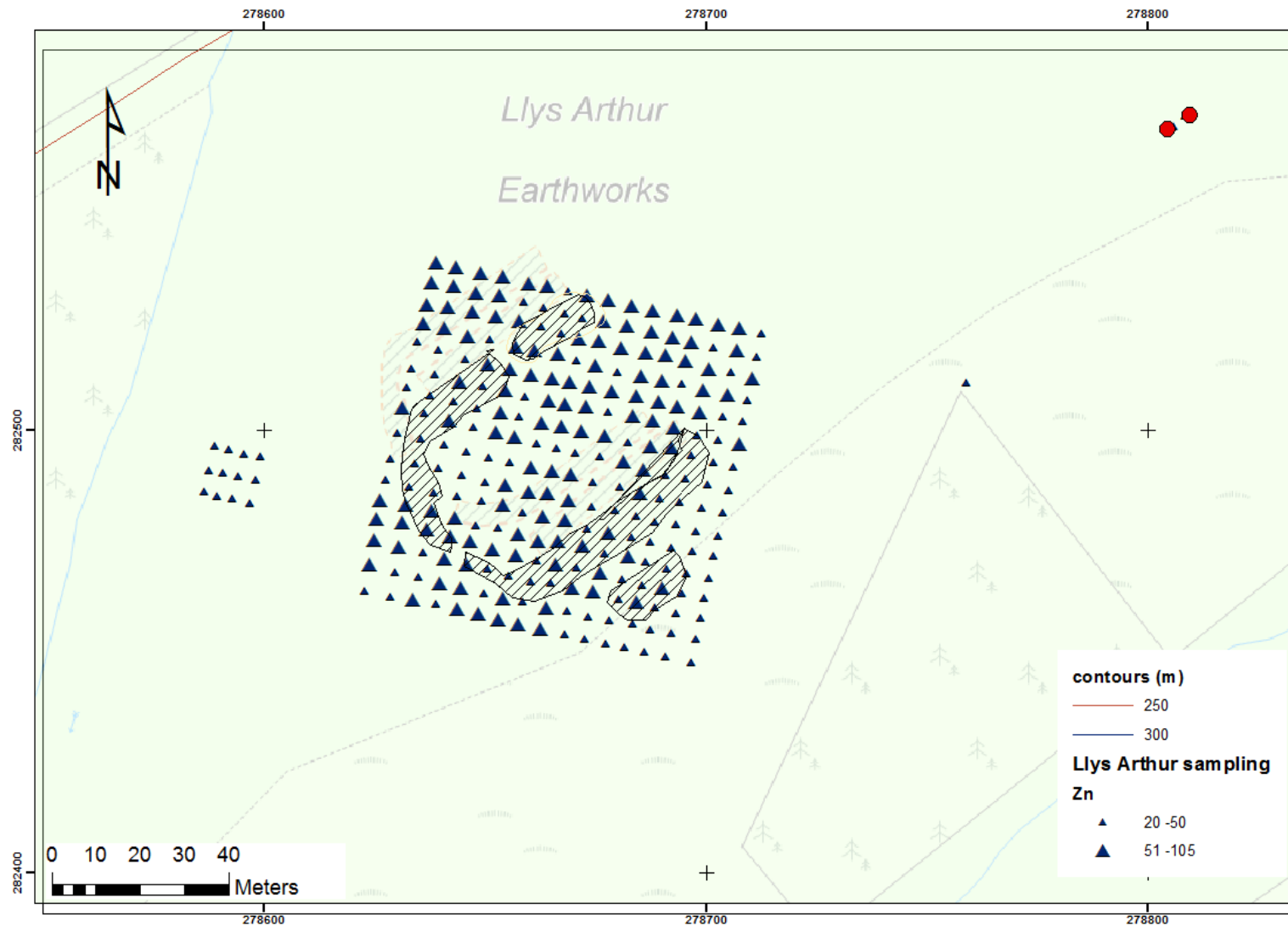


Figure 131. Surface analysis for Zn at Llys Arthur(all values in ppm).

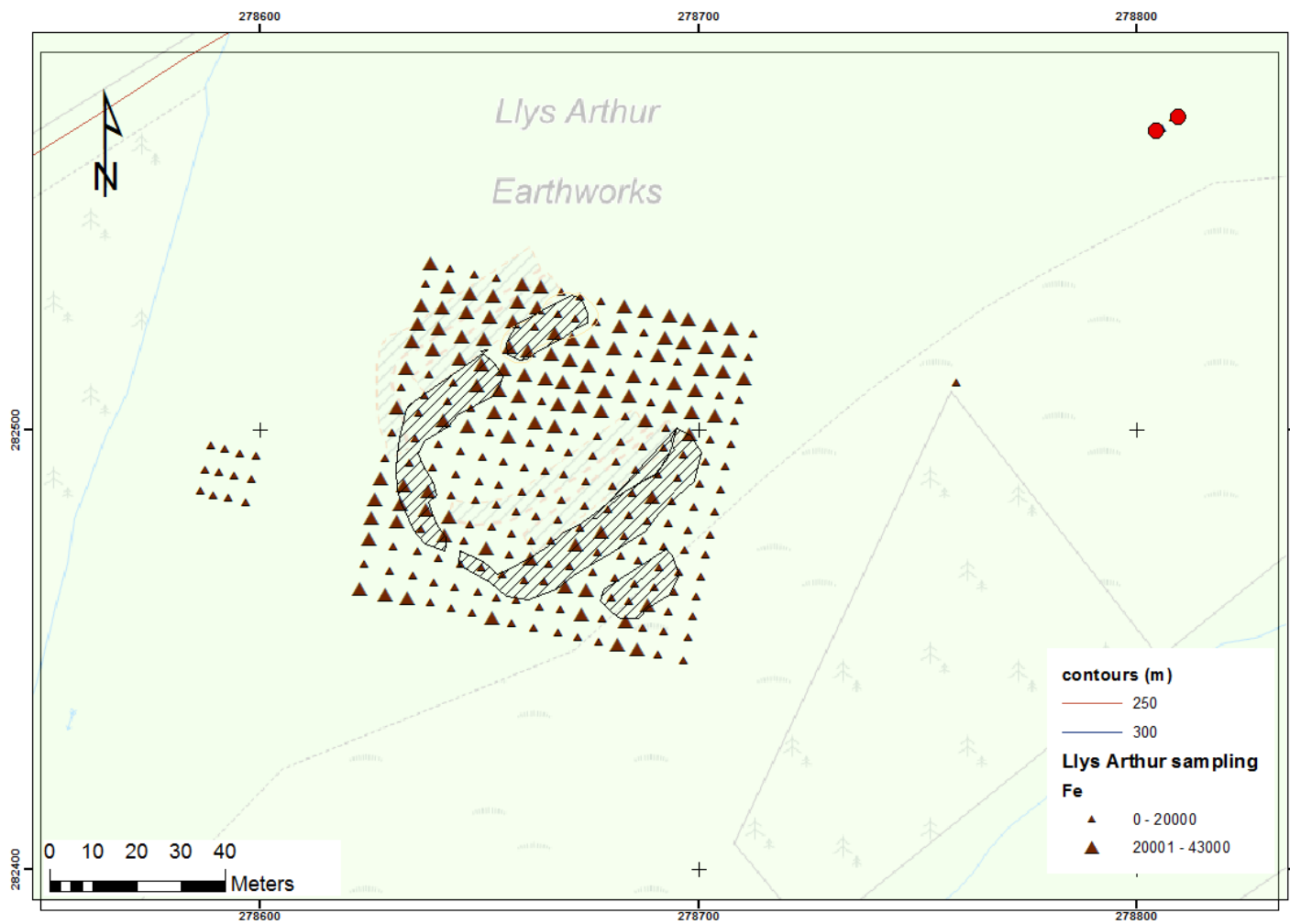


Figure 132. Surface analysis for Fe at Llys Arthur (all values in ppm).

The proximity of the site to Esgair Lle, situated 500 m to the east, raised the question of re-mobilised spoil. On a reconnaissance survey, only background levels of metalliferous elements were detected between the spoil tips and Llys Arthur earthworks. The survey's results show a defined decrease in lead concentrations to the south and south-west sections of the earthworks, with only three points raised above the background levels. The spatial distribution of zinc is homogenous ca. 25 ppm which is below the crustal average of 300 ppm for this area. Only three plots show slightly elevated values in comparison to the northern earthworks, but still are within the expected range for a site with nearby historic mining evidence.

Iron follows a similar pattern to lead, where a noticeable reduction in iron is seen on the southern section of the site. The average level of iron is lower than expected levels for this area of 98,000 ppm.

#### **5.5.4 Interpretation**

An explanation for the decrease in concentration at the southern and western perimeters must consider the possibility that three water features, two to the west side and one to the south of the existing earthworks, may have re-mobilised iron and zinc metal contamination from the soil. Firstly, by the original Nant Coch Mawr, which, initially flowed to the north-western edge of the earthworks, or secondly by overland flooding prior to the stream being diverted during the late 1960s. This included installation of new drainage ditches [see site description Chapter 3]. Here, one ditch runs south from the south-western corner with a further drainage ditch following the old Nant Coch Mawr stream course to the south-west [Edina 2013]. Secondly, works carried out on these engineering projects or land improvements may have removed evidence of elevated zinc and iron or any artefacts that may have been *in situ*. There is also evidence of a depression water feature possibly post medieval in period, directly to the south of the earthworks, but within the area sampled. This may have also



contributed to the reduction in heavy metal concentrations as both zinc and iron are mobile in water.

Even though current lead values recorded show values above the local average, for evidence of any metal smelting or smithy work these values would need to be in high hundreds to thousands of ppm. This survey, has not detected any evidence of metal working within or near this site.

## 5.6 Abermagwr Grid reference SN 66887418

### 5.6.1 Site description

See Chapter 3 for full site description.

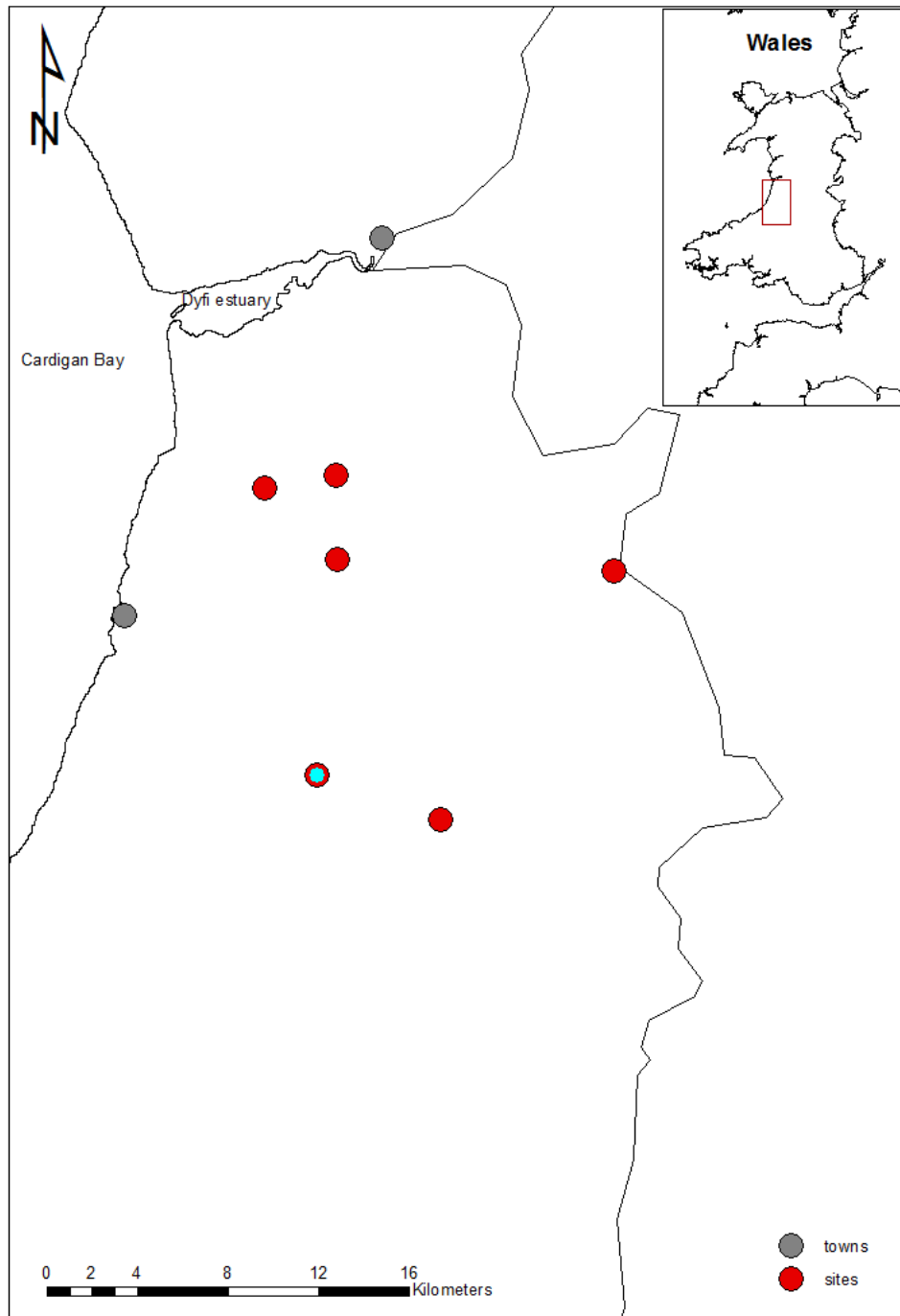
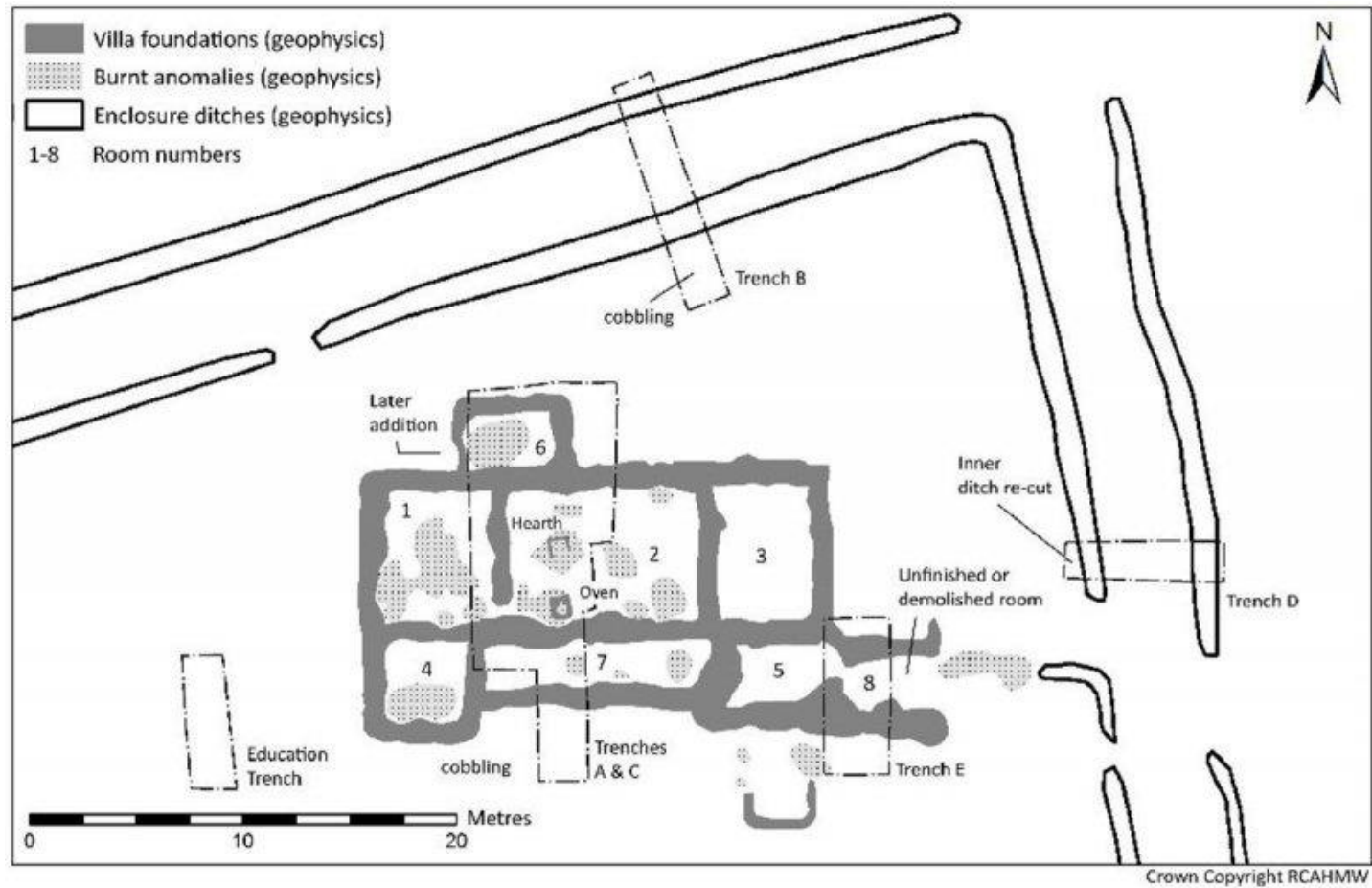


Figure 133. Abermagwr villa highlighted in blue.



**Figure 134.** Note: trenches A and C outline the 2011 excavation, which incorporated a series of fire pits. Source: RCAHMW (2012).



**Figure 135.** Romano-British villa situated at Abermagwr. Aerial view of the foundation base circled in red with the double ditch perimeter clearly visible. Source: RCAHMW 2006.

### 5.6.2 Survey method

This survey considers if the villas construction incorporated any metals sourced and produced from local metal lodes, specifically lead. In total, 50 analyses of a series of fire pits and ovens within two of the excavated rooms were analysed *in situ* with pXRF. Supplementary soil samples were taken for later laboratory analyses for both comparison of *in situ* analyses and lead isotope provenance to local ores. Furthermore, lead isotope signatures from the fire pits were used to ascertain if these were exotic (not from a local ore source).



**Figure 136.** Partial excavation of rooms 1.2.6 and 7, note the scorch marks highlighted in red, and the rear room's fire pit in blue. Source; RCAHMW (2012).

### 5.6.3 Soil geochemistry

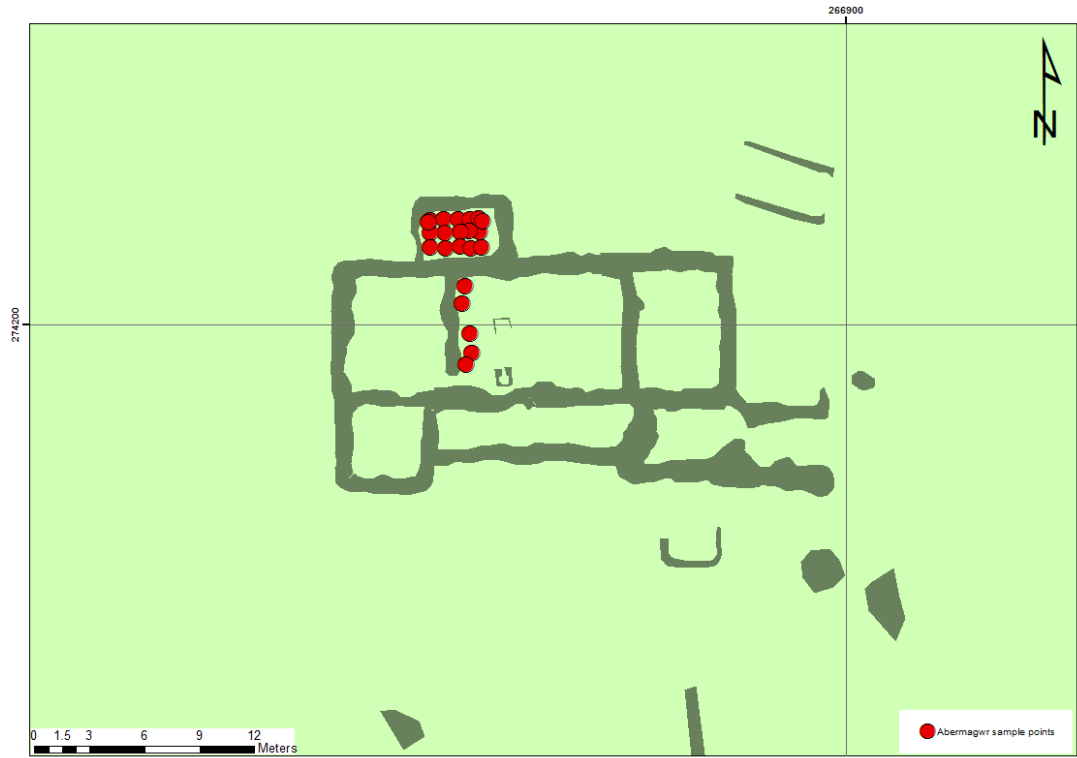
The geochemical analysis of the floor surface of the excavation is outlined in the following geochemical concentration maps. Table 26, outlines the regional geochemistry, stream sediment and soil values for Wales, the site control, and the average of the total survey analyses.

<b>Abermagwr Roman – British villa</b>	<b>pH 4.5 – 5.6</b>		
<b>Element. (ppm)</b>	<b>Regional Geochemistry Stream sediment and soil values for Wales</b>	<b>Site control</b>	<b>Site survey average n=50</b>
<b>Cu</b>	19 - 30	38.6	77.0
<b>Pb</b>	39 - 110	37.2	194.9
<b>Zn</b>	130 - 180	68.0	146.92
<b>Fe</b>	82000 - 98000	50525.3	30030.2

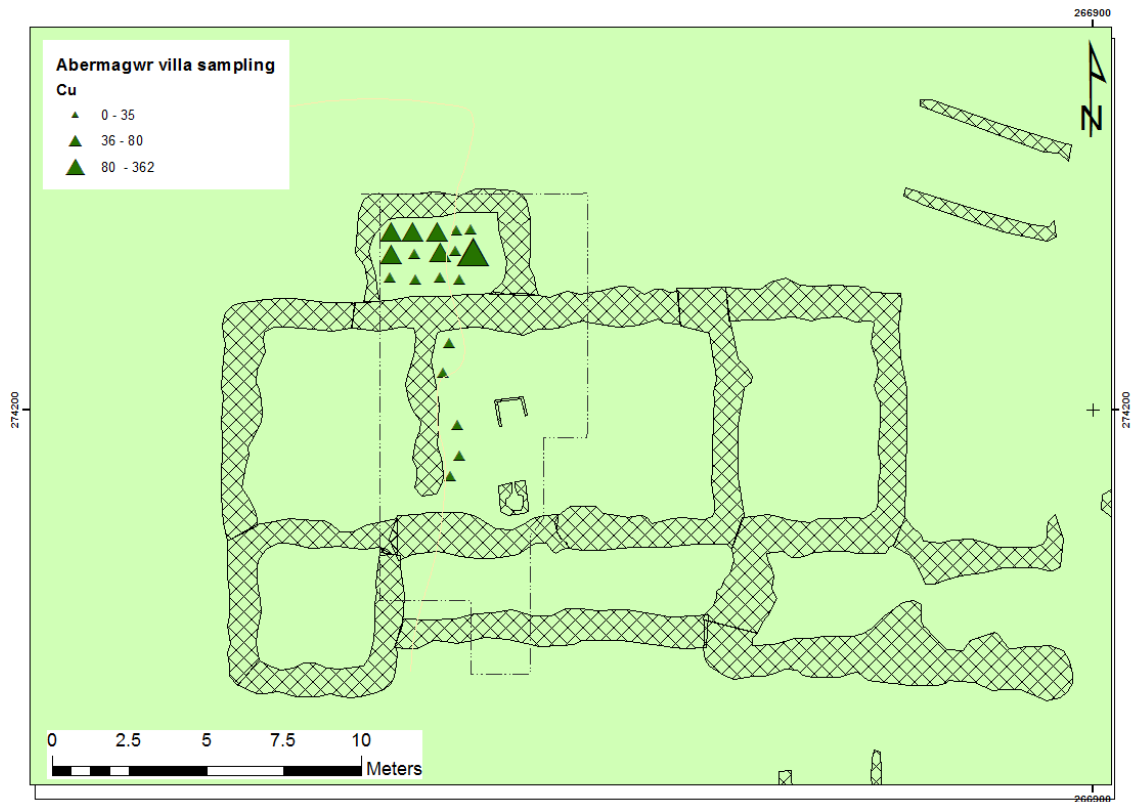
**Table 26.** Site survey element average compared to the Welsh stream sediment/soil Atlas and site control.

<b>Geochemical survey (Abermagwr)</b>	<b>All values in ppm</b>			
<b>Element</b>	<b>Cu</b>	<b>Pb</b>	<b>Zn</b>	<b>Fe</b>
<b>Median</b>	66.7	131.8	146.9	31546.0
<b>Max</b>	362.0	1491.3	361.9	50525.3
<b>Min</b>	25.2	37.2	67.9	21808.9

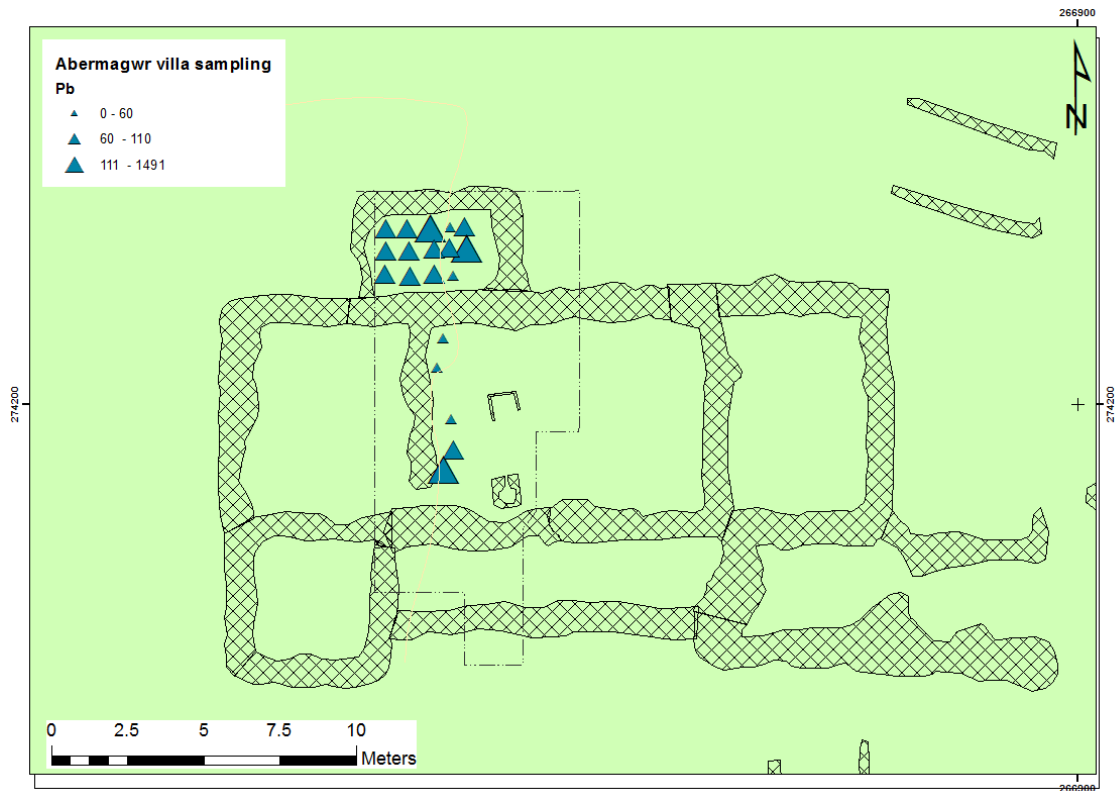
**Table 27.** Main geochemical findings from Abermagwr.



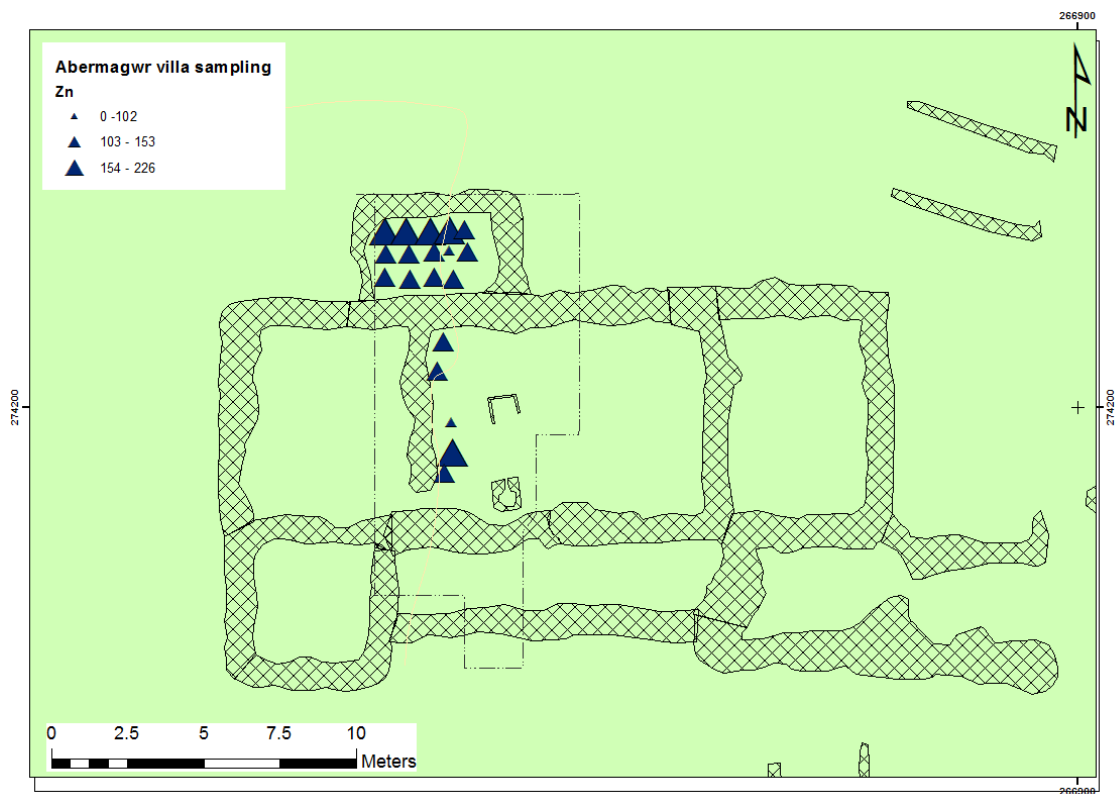
**Figure 137.** Outline plan of Abermagwr villa and the sampling through excavation trenches A and C.



**Figure 138.** Soil analysis of exposed floor surface for Cu at Abermagwr villa (all values in ppm).

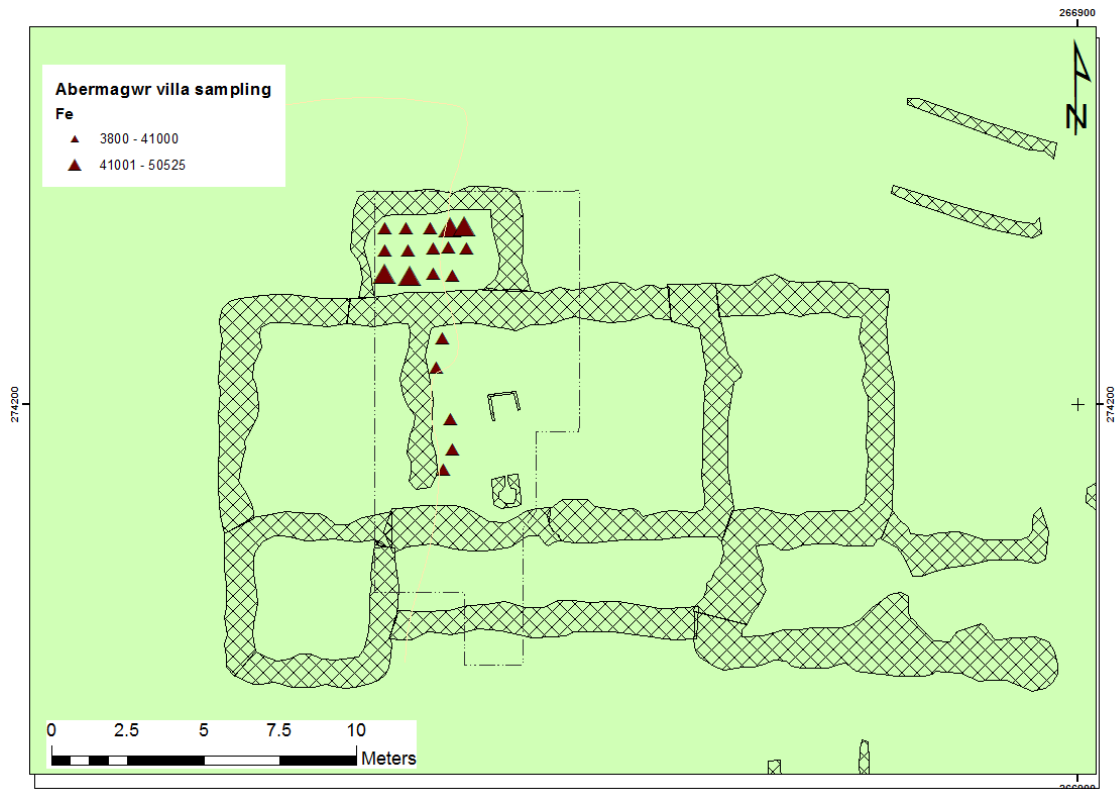


**Figure 139.** Soil analysis of exposed floor surface for Pb at Abermagwr villa (all values in ppm).



**Figure 140.** Soil analysis of floor surface for Zn at Abermagwr villa (all values in ppm).





**Figure 141.** Soil analysis of exposed floor surface for Zn at Abermagwr villa (all values in ppm).

Overall, zinc was within both the local back ground and control values. Copper was above the local average with eight samples showing three times the average. The pXRF analyses recorded lead levels at between 2 – 22 times above background levels of 39 - 110 ppm in rooms 2 and 6.

The dried, milled and re-analysed samples were three to five times higher with maximum values being possibly 4000 - 5000 ppm if the wet sample values are extrapolated to dry weight sample values. The high lead values suggest lead may have been worked within the villa. However, it is difficult to establish if it was prior to or after its abandonment. Copper was also elevated above back-ground but the local lode is primarily galena and sphalerite, so the copper may have been from another source, but is difficult to establish which.

#### 5.6.4 Interpretation

There is evidence to suggest either Roman or post Roman metal working was carried out at this location. But given smelting would not have been carried out within a

confined dwelling, it may be plausible that if any lead was initially worked here, it was possibly a small metal workshop, possibly used for reworking lead items in room 6. The fire pits within rooms 1, 2, 3, 4 and 7 [see Chapter 3, Figure 42], may have been created post abandonment as both their number and location do not suggest they were part of the original villa's fire places or ovens, and they possibly contributed to the villa's eventual dereliction.

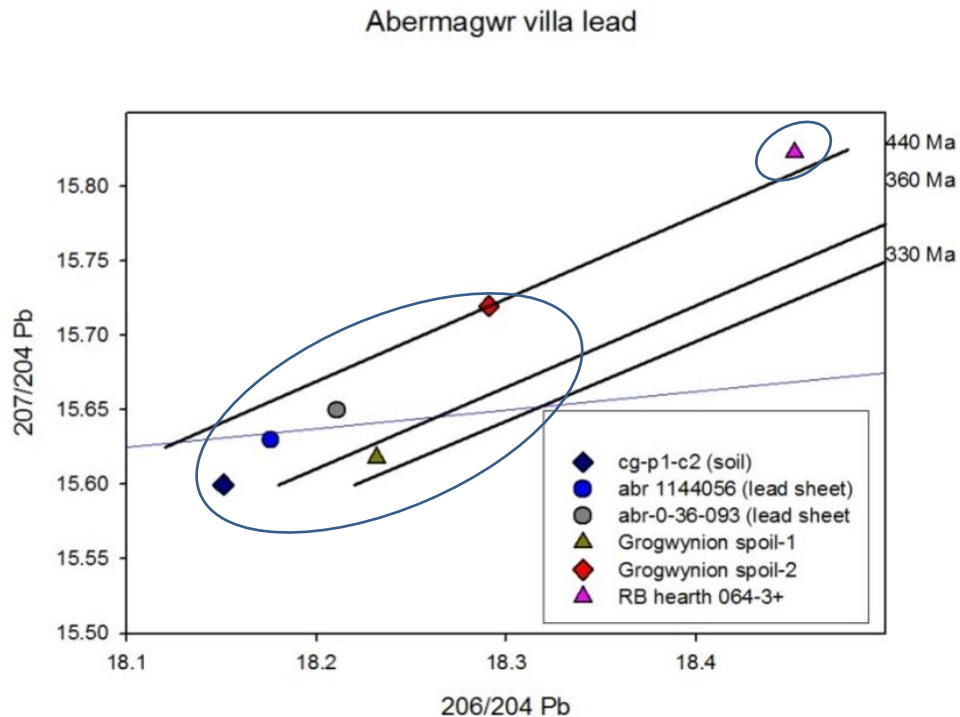
#### 5.6.5 Isotope analysis on lead section



**Figure 142.** Lead section recovered from the villa's 2011 excavation.

Isotope provenance of the lead sheet [see Figure 142], was established by direct comparison to spoil and galena samples obtained from Grogwynion mine 7 Km to the east of the villa. The results were compared with the work of both Rohls (1996) and Fletcher *et al.* (1993) whose work has concentrated on lead isotopes outlining many isotope signatures of local ores in mid Wales. Furthermore, the ratios of  $^{207}/^{204}$  lead

to 206/204 lead were plotted into a Cummings Richard model to identify the geological period in which the mineralisation was formed.



**Figure 143.** Plot of the 6 materials analysed.

Top: the isochrones (black) and growth curve (blue) of mineralisation events correlating to early complex (A1) 440 -360 Ma yrs. and late simple (A2) 360-330 Ma yrs. period mineralisation both, using the Cumming – Richard model.

The lead artefacts from the villa, abr 1114056 and abr-0 36-093 were in strong agreement with the isotope signature of local mineralisation that match both Grogwynion spoil 1 and 2, all falling into isochrones of earlier complex phase (A1) mineralisation 440 to 360 Ma. One other spoil sample cg-p1 c2 was plotted into the late simple phase (A2) mineralisation 360 - 330 Ma, but was still consistent with local mineralisation. Interestingly, the soil sample from one of the fire pits RB hearth 064-3+ within the excavation does not fit either phase and may be either exotic or possibly consists of mixed leads. Overall, some of the mineralisation isotopes give similar results to the outcomes of both Fletcher *et al.* (1993) by comparison to the Cummings – Richard model, and Rohl's (1996) catalogue of isotope data on ores found both in the

Cambrian Ore Fields and the Mendip hills of North Devon, where galena was also mined from the Late Iron Age onwards (BGS, 2014).

Lead Isotope Provenance for the Romano-British villa Abermagwr: Mineral phases of the Cambrian ore fields				
	sample	Early Phase (A1)	Late Phase (A2)	Unknown =C
1	Grogwynion spoil -1		B	
2	Grogwynion spoil -2	A		
3	abr 11 44056 ( lead sheet)	A		
4	abr 0-36-093 (lead sheet)	A		
5	RB hearth 064 -3 +			C
6	cg p1-c2 (soil )	A		

**Table 28.** Isotope and mineralisation phases from the soil and lead analysis.

#### 5.6.6 Interpretation

Both the lead artefact provenance and the suggestion that there may have been some exotic or mixing of leads in the villa suggest a relationship with metal exploitation in Ceredigion, and also the possible re-use of the Romano-British villa. But it is still unclear where the smelting site/s may have been situated. It is speculated that these maybe have been nearer to the Frongoch or Grogwynion mines. However, the Roman lead bole at Cors Fochno dates to the period of the villa's construction and may possibly have been the source of the lead, but for now this is unproven.

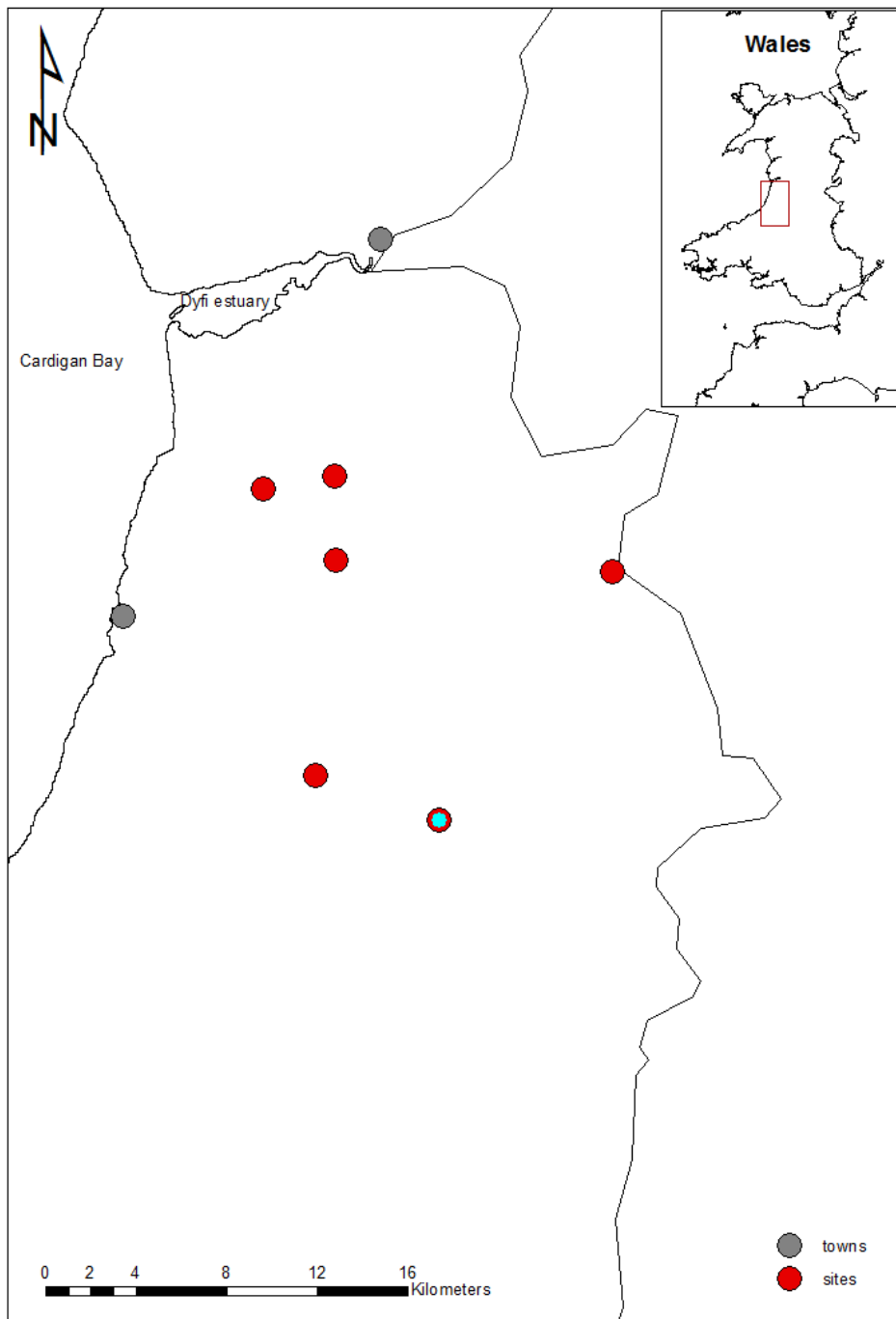
## 5.7 Castell Grogwynion Grid Reference SN72107249

### 5.7.1 Site description

See Chapter 3 for full site description.



**Figure 144.** Castell Grogwynion viewed from the north: Note how the natural topography and earth works have created a defensive northern approach.



**Figure 145.** Castell Grogwynion hill fort position highlighted in blue.



**Figure 146.** Looking 1 km west from Grogwynion hill fort along the Ystwyth Valley towards the Grogwynion mine spoil tips which scar the mountain side beyond the immediate stands of deciduous trees and evergreens.

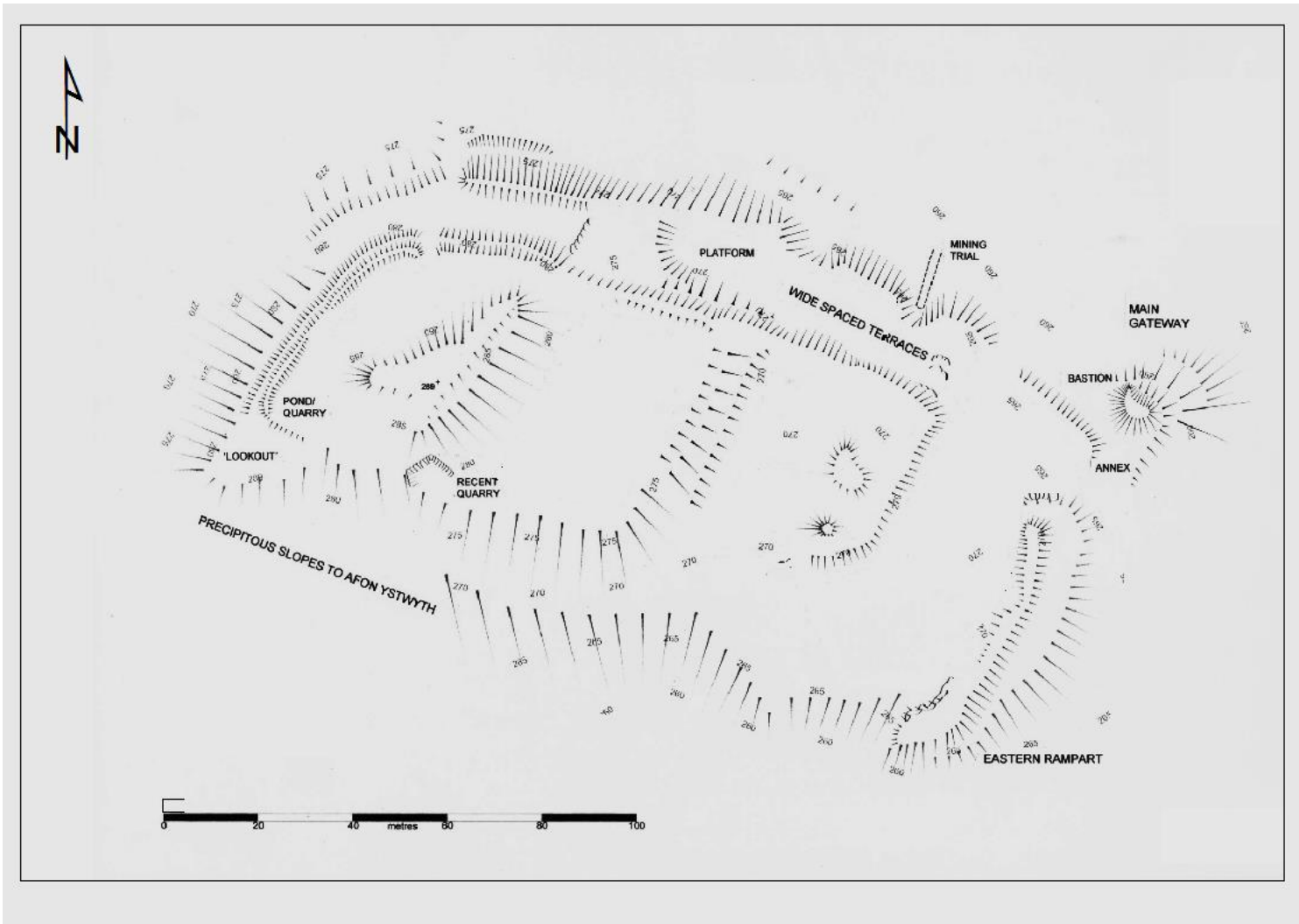


Figure 147. Plan of the hill forts compartments and features. Source: RCAHMW (2012).



### 5.7.2 Survey method

One hundred and eighty five samples were analysed *in situ* to assess all platforms, mining and antiquarian trial pits identified from a recent hill fort plan and the initial field walking. Further sampling at the abandoned Grogwynion mine 1 km to the west was undertaken to establish if natural or anthropogenic mechanisms may have re-mobilised mining spoil, possibly contaminating the site with lead and zinc. These data were geo-referenced and imported into ArcMap to assess if any of the target elements copper, lead, zinc and iron were elevated above background levels and control points, creating clustering or hot spots. Subsequent high resolution analyses and supplementary soil samples were taken on revisits after the initial survey data revealed levels well above the expected values for lead at one of the hill fort platforms.

### 5.7.3 Soil geochemistry

The geochemical analysis of the top soil 10 cm below the turfed surface is outlined in the following geochemical concentration maps. Table 29, outlines the regional geochemistry, stream sediment and soil values for Wales, the site control, and the average of the total survey analyses.

Castell Grogwynion Iron Age	pH 4.5 – 5.6		
Element (ppm)	Regional Geochemistry Stream sediment and soil values for Wales	Site control	Site survey average n=136
Cu	19 - 30	20	7.8
Pb	39 - 110	60	105.71
Zn	130 - 180	30	24.6
Fe	82000 - 98000	21000	11683.06

**Table 29.** Site survey element average compared to the Welsh stream sediment/soil Atlas and site control.

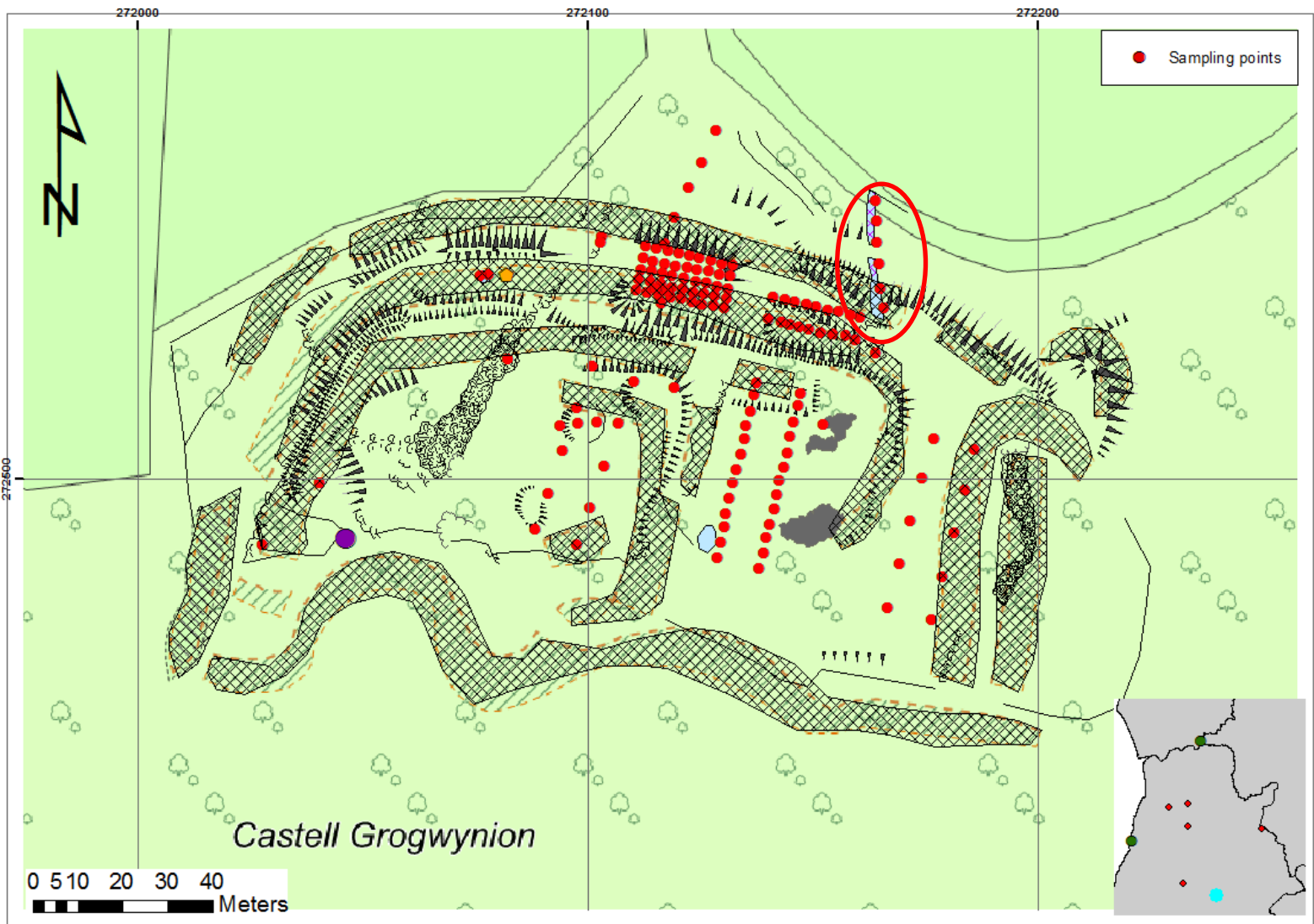


Figure 148. Castell Grogwynion sampling points. Note the possible trial trench circled in red.

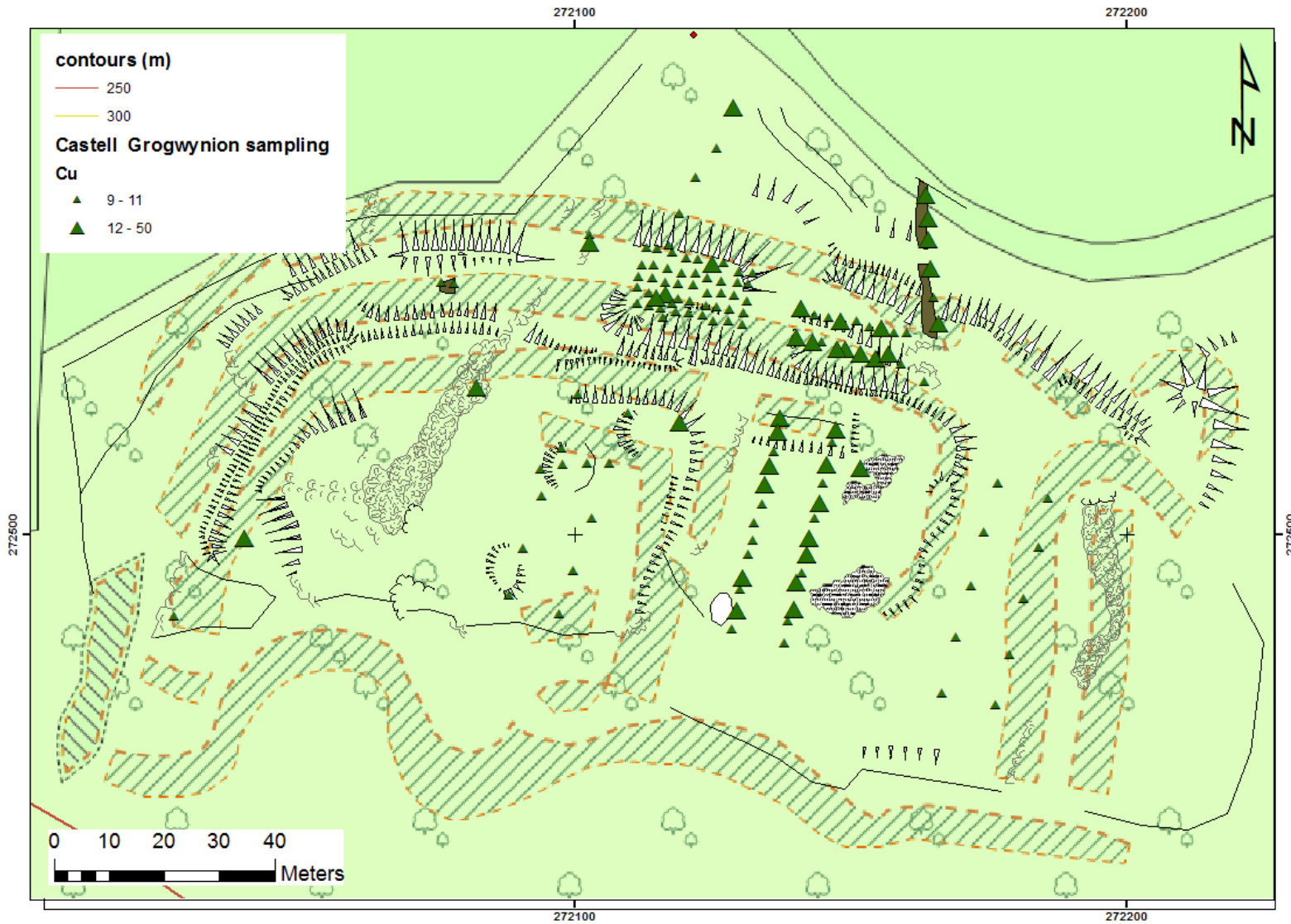
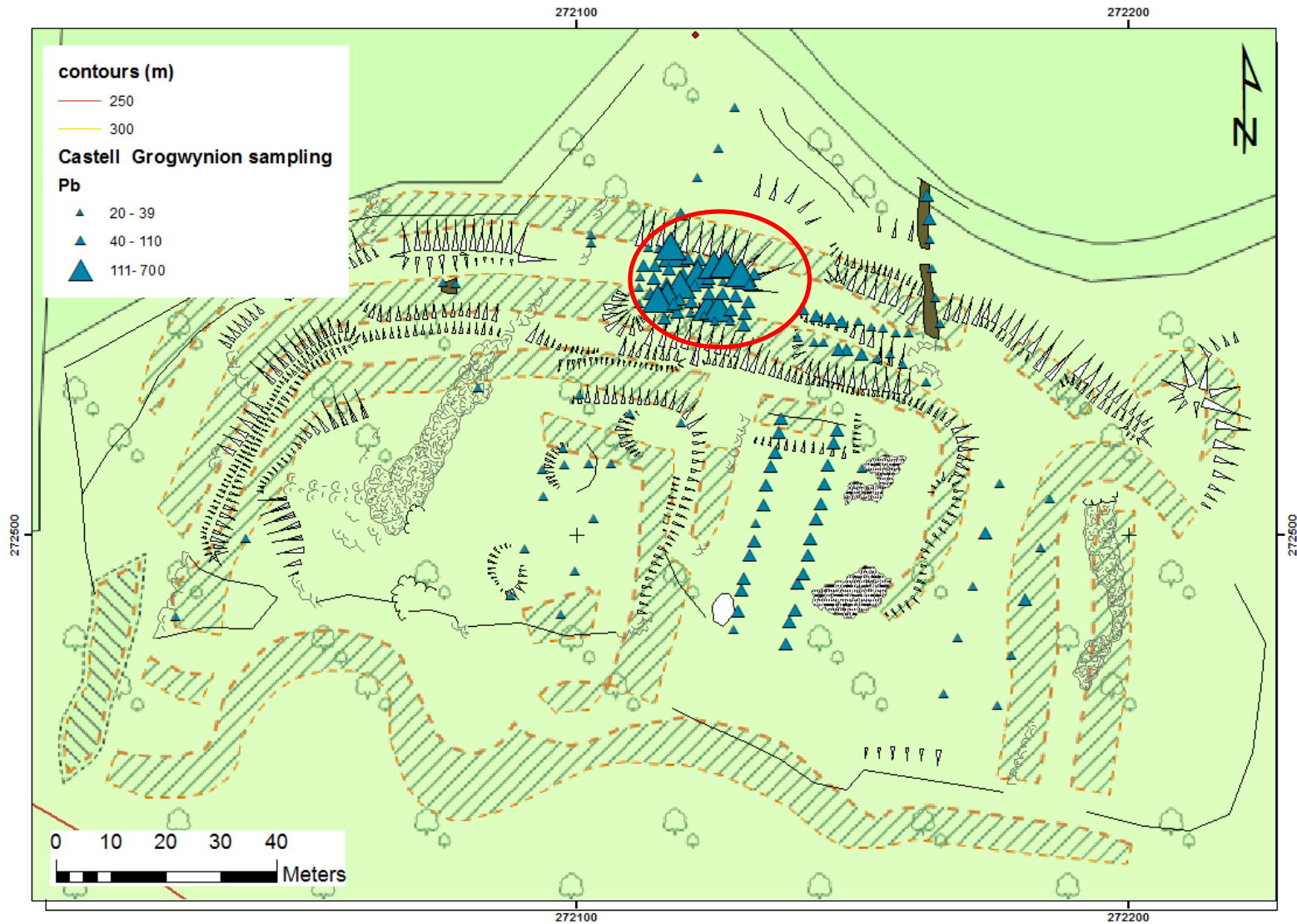


Figure 149. Surface analysis for Cu at Castell Grogwynion (all values in ppm).



**Figure 150.** Surface analysis for Pb at Castell Grogwynion (all values in ppm). Note the clustering of high Pb circled in red.

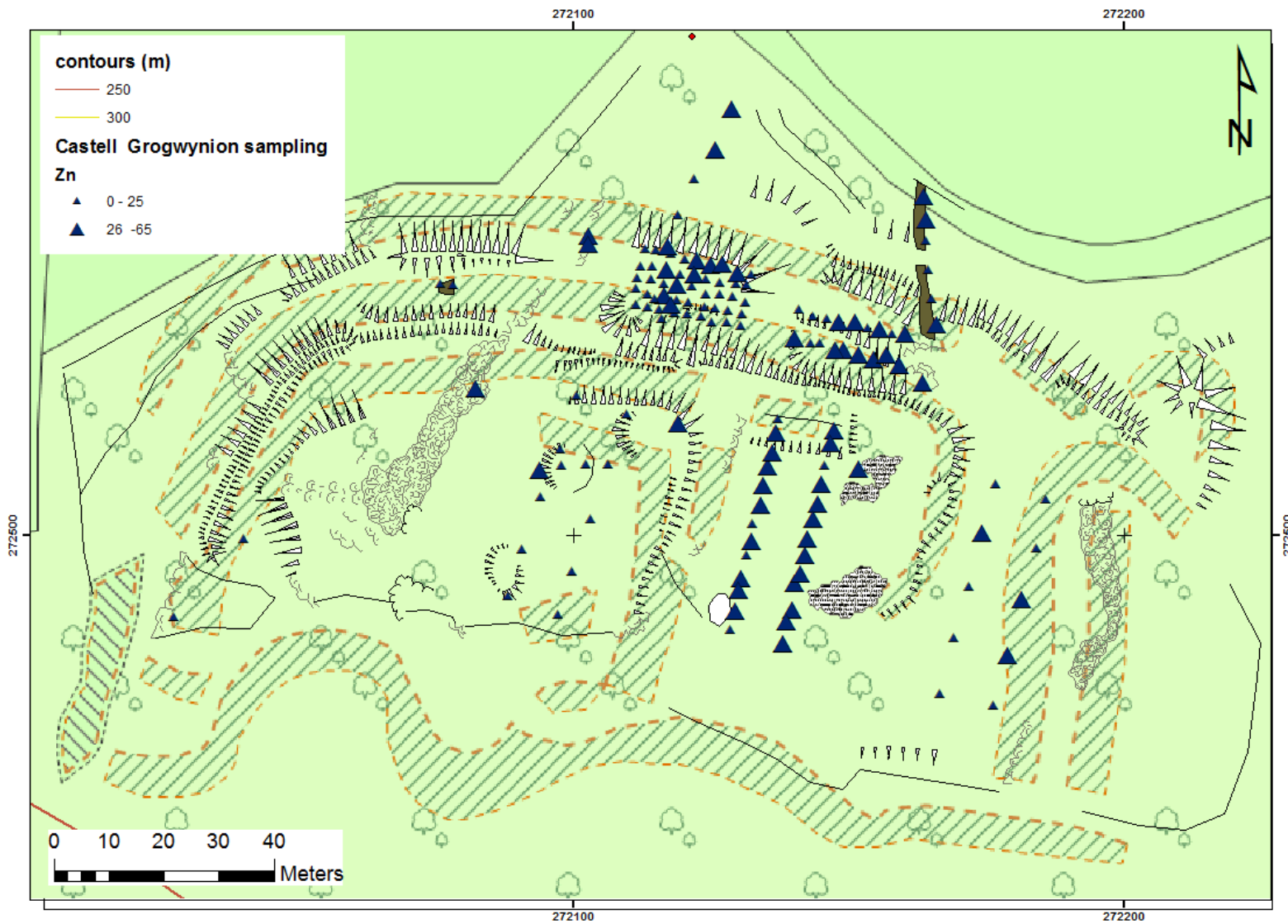


Figure 151. Surface analysis for Zn at Castell Grogwynion (all values in ppm).

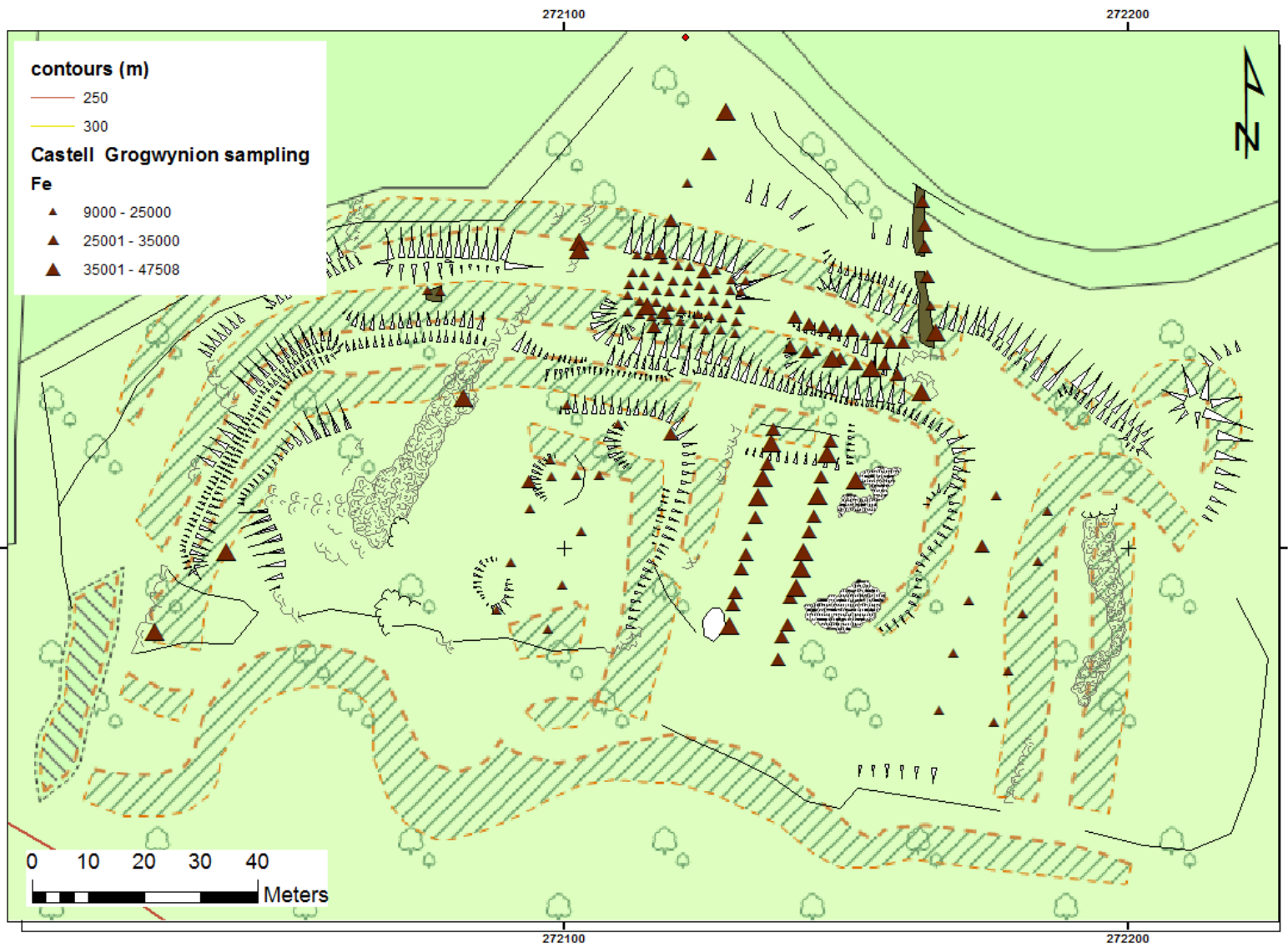


Figure 152. Surface analysis for Zn at Castell Grogwynion (all values in ppm).

The Castell Grogwynion survey found that the distribution of heavy metals over the hill fort were within or below the expected range of element concentrations for zinc and iron. For copper, only 3 analyses were slightly raised above the expected values [see Table 31]. In contrast lead shows elevated concentrations > 110 ppm on the northern platform above the local average and that of the other platforms in the hill fort.

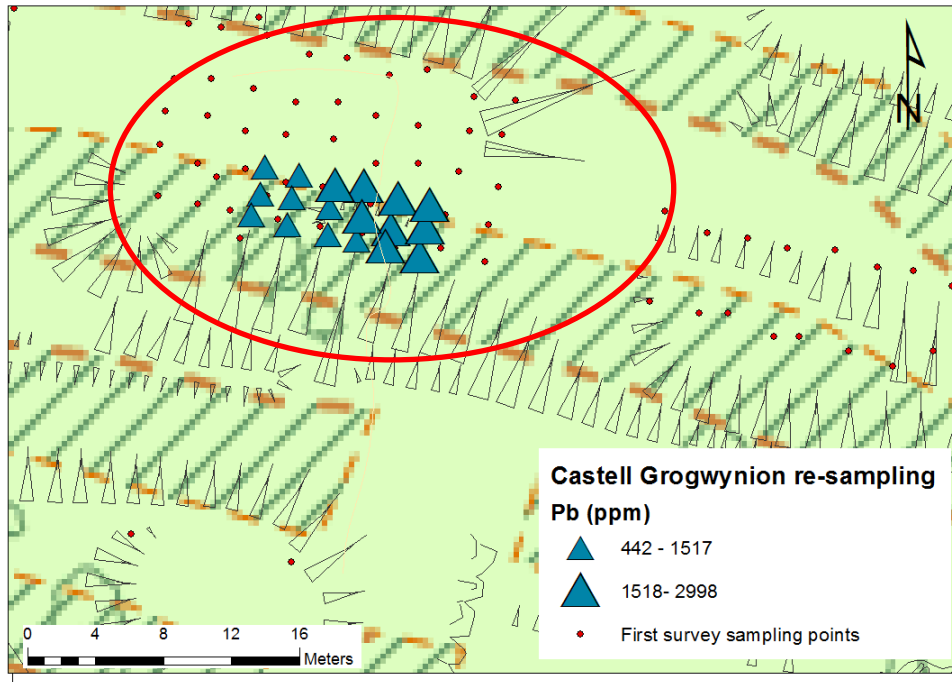
<b>Geochemical survey (Castell Grogwynion)</b>	<b>All values in ppm</b>			
<b>Element</b>	<b>Cu</b>	<b>Pb</b>	<b>Zn</b>	<b>Fe</b>
<b>Median</b>	5.8	88.7	22.4	9280.9
<b>Max</b>	41.0	697.6	64.3	47508.2
<b>Min</b>	< LOD	7.6	< LOD	531.9

**Table 30.** Main geochemical findings from initial survey.

Clustering of high levels of lead on the northern platform suggested this area required resampling at a higher resolution of 1 analysis per 2.5m<sup>2</sup> over a 7.5 x 15 m small raised area section to further corroborate the initial survey's findings.

<b>Castell Grogwynion Iron Age re-sampling</b>	<b>pH 4.5 – 5.6</b>		<b>pXRF dry analysis</b>
<b>Element</b>	<b>Regional Geochemistry Stream sediment and soil values for Wales</b>	<b>Site control</b>	<b>Site survey median n=18</b>
<b>Cu</b>	19 - 30	20	40.0
<b>Pb</b>	39 - 110	60	1498.7
<b>Zn</b>	130 - 180	30	71.9
<b>Fe</b>	82000 - 98000	21000	32219.7

**Table 31.** Re- sampling of the northern platform of Castell Grogwynion.



**Figure 153.** Re-sampling over the northern platform. See Figure 150.

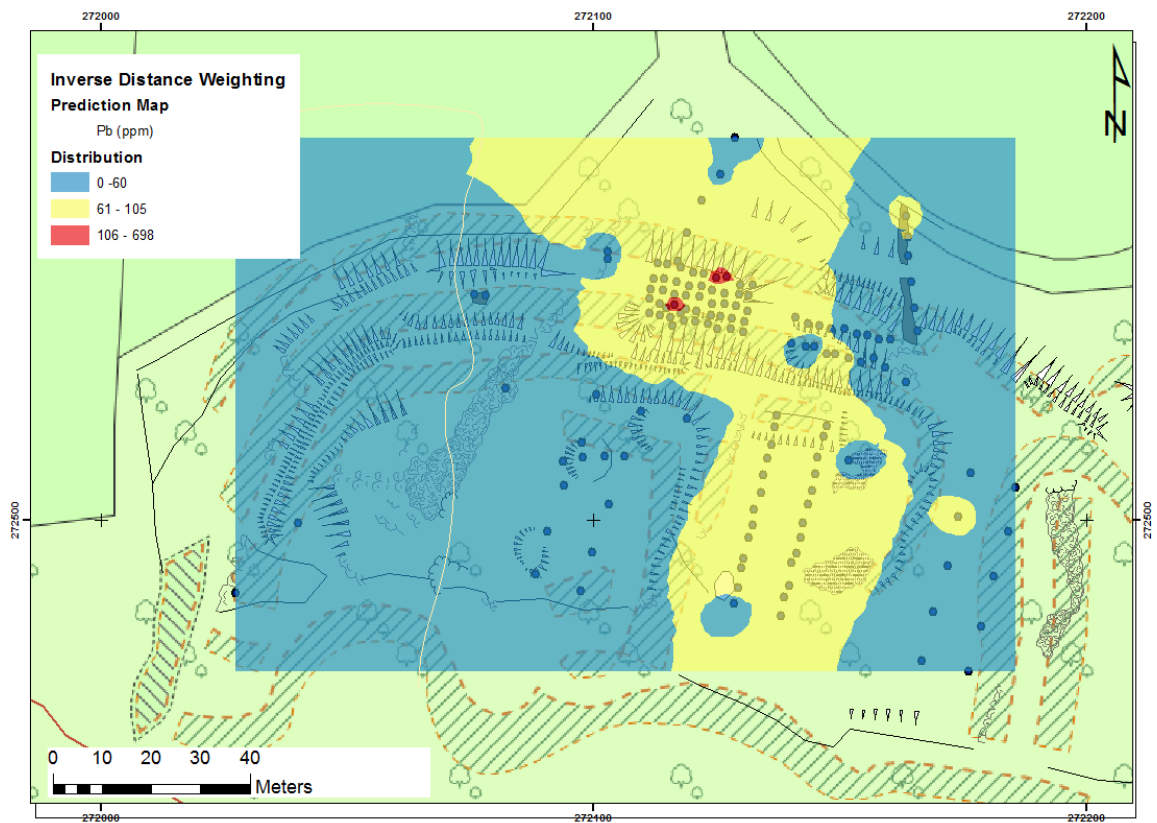
Re-sampling used both *in situ* analyses and supplementary soil samples to further test the lead anomaly. All soil samples were dried and milled [see methodology Chapter] and re-sampled by pXRF. Analyses of the dried, fine fraction confirmed higher concentrations of lead than the initial *in situ* survey, with levels increasing from 700 ppm to 3000 ppm. Not only did this further support the previous interpretation that the high lead anomaly was centred on the northern platform, but it supported the findings on the equipment testing of the matrix effect due to high moisture on pXRF *in situ* analysis.



Geochemical re-survey (Castell Grogwynion)	All values in ppm			
Element	Cu	Pb	Zn	Fe
Median	40.0	1498.7	71.9	32219.7
Max	88.5	2997.8	123.71	35853.9
Min	< LOD	442.5	36.7	27205.4

**Table 32.** Main geochemical findings from Castell Grogwynion re-survey.

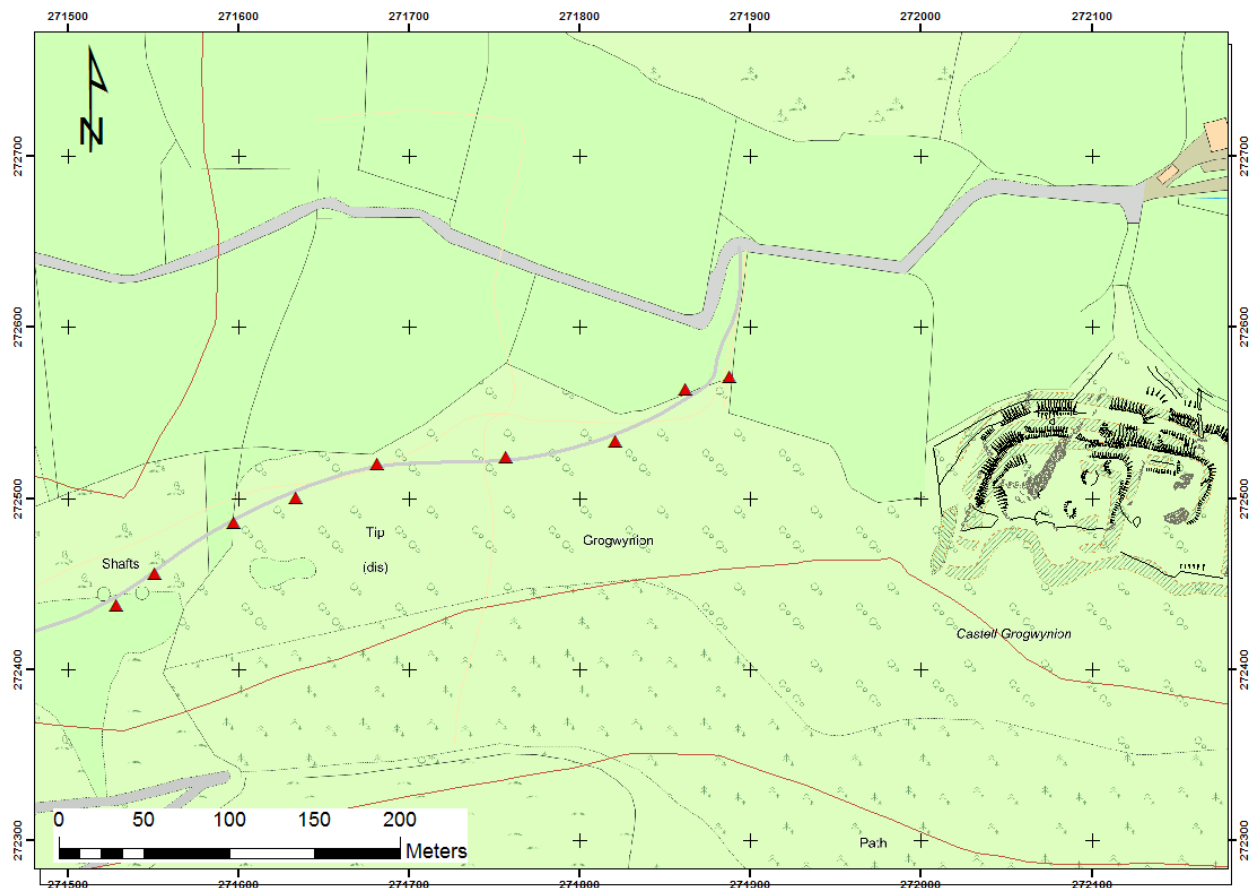
Further modelling by inverse distance weighting confirmed the Northern platform was the centre of the lead anomaly, but also highlighted some lesser effects in the middle platform [see Figure 154].



**Figure 154.** Inverse distance weighting map showing the probability of higher Pb over the northern and mid-section of the hill fort, also suggesting very high concentrations within the northern platform.

### 5.7.4 Interpretation

Although lead concentrations were only *ca.* 3000 ppm the shape and confined area suggests possible anthropogenic distribution with the highest levels within the re-sampled section. However, within 800 m of the hill fort the abandoned Grogwynion mining complex presented a further possibility of surface contamination over the interior of the hill fort. Research by Davies and White (1981) and Johnson and Roberts (2003) high-light the possibility that weathered mining spoil < 2  $\mu\text{m}$  can be spread up to 1800 m in favourable wind conditions > force 4. Assessing this saltation distribution process, analysis of sediment and soil samples from the spoil tips located on the eastern edge of the abandoned mine, [the closest point to the hill fort] was undertaken to within 100 m of the hill fort's perimeter. This was to ascertain whether re-distributed metal-rich spoil had left residual lead over the hill fort, contemporaneous with the spoil tip chemistry of the local mines.



**Figure 155.** Sampling points 1 – 9 along the dirt track probably dressed with spoil from Grogwynion's spoil tips, points 1 - 9 are from left to right.

Distribution of elements from spoil tip to CG		Pb (ppm)
1	1 spoil tip	2682.9
2	2 spoil tip	8834.59
3	3	169.05
4	4	186.91
5	5	60.53
6	6	36.58
7	7	116.01
8	8 road aggregate	787.42
9	9 gate	59.15

**Table 33.** Possible re-distribution of Pb from the spoil tips at Grogwynion mines.

Nine samples were analysed from the eastern edge of the mine spoil tips were taken from west to east [see Figure 155 and Table 33]. The results of these analysis shows the location and reduction of lead levels to between 40 – 60 ppm in locations 5, 6, and 9, which agree with the site control values of lead 60 ppm taken from a control point near the hill fort. However, it is noted the surface dressing to the track [see Table 33], number 8, is elevated to lead 787 ppm and comparable to the highest *in situ* values on the northern platform. But it is highly likely that the road surface dressing was sourced from the mine’s spoil tips, which would be high in metalliferous lead content. Furthermore, if the hill fort interior was contaminated by wind distribution of spoil tip dust, it is reasonable to expect that there would be a homogeneous level of lead over all of the hillfort’s compartments.

### 5.7.5 Geophysical survey

Further assessment of both the extent, and depth of any remnant lead residue or the possibility of a smelting bole, warranted a geophysical survey. Targeting the non-gradiometric aspect, where top soil is more magnetic than the sub soil and the subsoil slightly more magnetic than the geology, it aimed to identify any anomalies suggesting sediment or structures which have been affected by high temperatures. There are exceptions to this, where biological processes in the top soil can change the oxidation states of the iron content, which can have differing magnetic states. But normally soil

will accumulate in negative features such as pits and ditches. These will invariably accumulate metallic soils which have thermo-remnant magnetisation (TRM) produced by exposure to heat. These align with the ambient magnetic field during the settling process creating deposits with remnant magnetisation (DRM), often associated with fire setting or pyro-metallurgy. The principle is to map the accumulated magnetic soils as opposed to any buried structures, as these would be magnetic in their own right i.e. made from brick or tiles previously subject to high temperatures (Roseveare, 2012).



Figure 156. Geophysical survey plan view. Source: Roseveare (2012).

The upper platform survey detected two hut platforms 10 and 13 [Figure 156]. These were also identified by the initial survey, highlighting areas on the northern platform [see Table 34] catalogue numbers 1 – 4. This correlates to the location of the pXRF analyses of elevated lead in a pattern not dissimilar to hearths associated with smelting boles (Timberlake, pers. comm., 2011).

Label	Anomaly Type	Feature Type	Description
1	<b>Strong discrete dipolar</b>	<b>Fill/ Thermal-Hearth</b>	<b>A very strong discrete anomaly, typical of a hearth or pit filled with heated soil</b>
2	<b>Area enhanced</b>	<b>Fill / Deposit-debris</b>	<b>Spread of magnetic material associated with structure [1]. Accumulated heated soil is likely origin, spread/ braided by later cultivation</b>
3	<b>Area enhanced</b>	<b>Fill / deposit - debris</b>	<b>Spread of magnetic material, presumably associated with structure [1] although this is not certain. Accumulated heated soil is a possibility</b>
4	<b>Non-magnetic?</b>	<b>Structure</b>	<b>Anomaly [3] has an abrupt eastern edge and if interpreted as a magnetic fill might imply the existence of a linear structure bounding it</b>
5	Area enhanced	Deposit?	Material on outer face of rampart, otherwise locally deep soil?
6	Area reduced	Bedrock?	Very shallow soil, i.e. outcropping bedrock, might account for this anomaly. Failing that, a mass of stone close under the surface
7	Linear enhanced	Fill - Ditch / deposit	Possible narrow ditch or hollow alongside the inner face of a low bank
8	Linear enhanced dipolar (sample)	Fill - Cultivation	Closely spaced cultivation furrows are aligned along the length of the platform
9	Area enhanced	Fill / deposit - Debris	Uncertain, perhaps a dump of heated soil or similar magnetic material within a hollow
10	Linear enhanced	Fill - ditch	Eaves drip or drain, alternatively the deepest region of fill over a former platform, most likely the site of a prehistoric roundhouse
11	Linear enhanced	Fill - ditch	See [10]
12	Strong discrete dipolar	Fill / thermal - Hearth?	Probable hearth or perhaps a pit with heated soil associated with likely roundhouse [10]
13	Strong area enhanced	Fill / Debris	Possible burnt soil within hood or eaves drip of likely roundhouse [11]
14	Linear enhanced	Fill? - Ditch?	A possible enclosure may be defined by a ditch or hollow up to 1.5m wide, presumably associated with the likely roundhouse sites
15	Variably enhanced	Fill? / Debris?	Possible Midden or spread of similar material across the platform

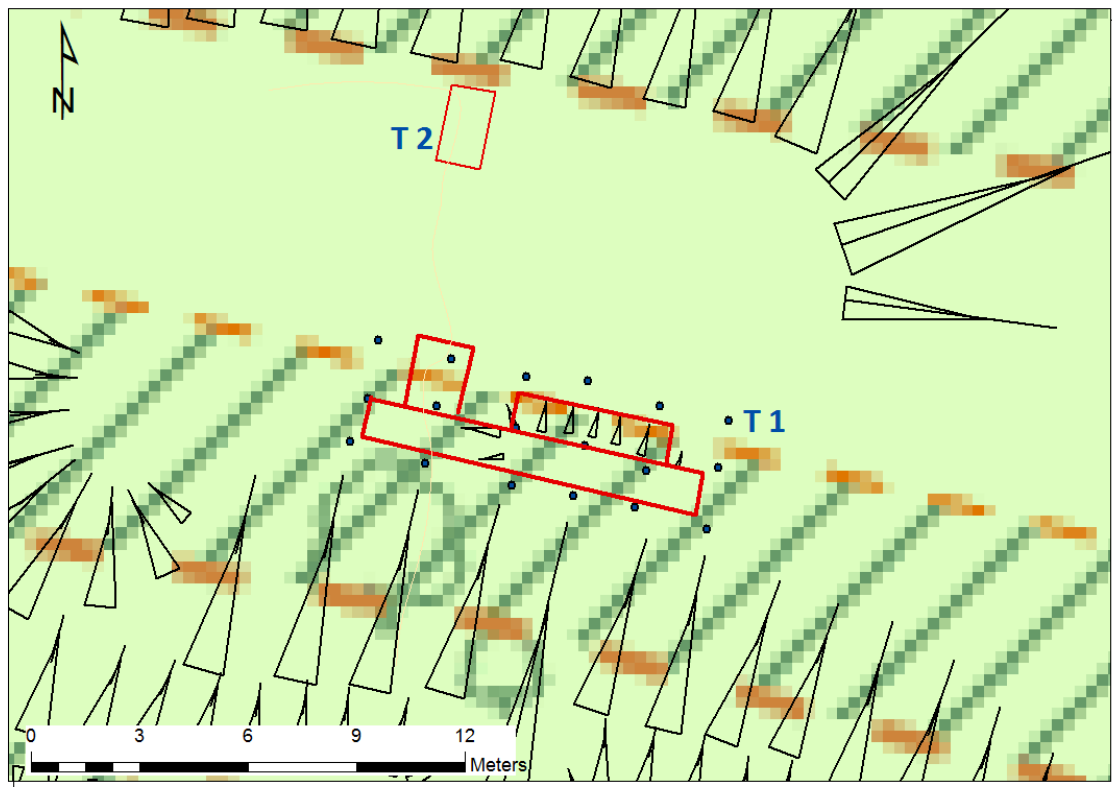
**Table 34.** Catalogue for plan view see figure 156. Note in bold 1 – 4 for the area with high Pb plume. Source: compiled from Roseveare (2012).

The combination of both pXRF and geophysical data created a strong argument that this site contained evidence of pyro-metallurgy.

### 5.7.6 Excavation

Data from the pXRF and geophysical surveys outlining the preliminary findings within the northern platform, with details outlining the excavation method and site remediation, were submitted to CADW for consideration to carry out a small test excavation. Scheduled site consent was given for a 25 square metres test excavation over the northern platform of the hill fort.

Between the 6th and 10th October 2013, two trial trenches were excavated by hand by members from the EMRG and the RCAHMMW.



**Figure 157.** Footprint of the Castell Grogwynion excavations.

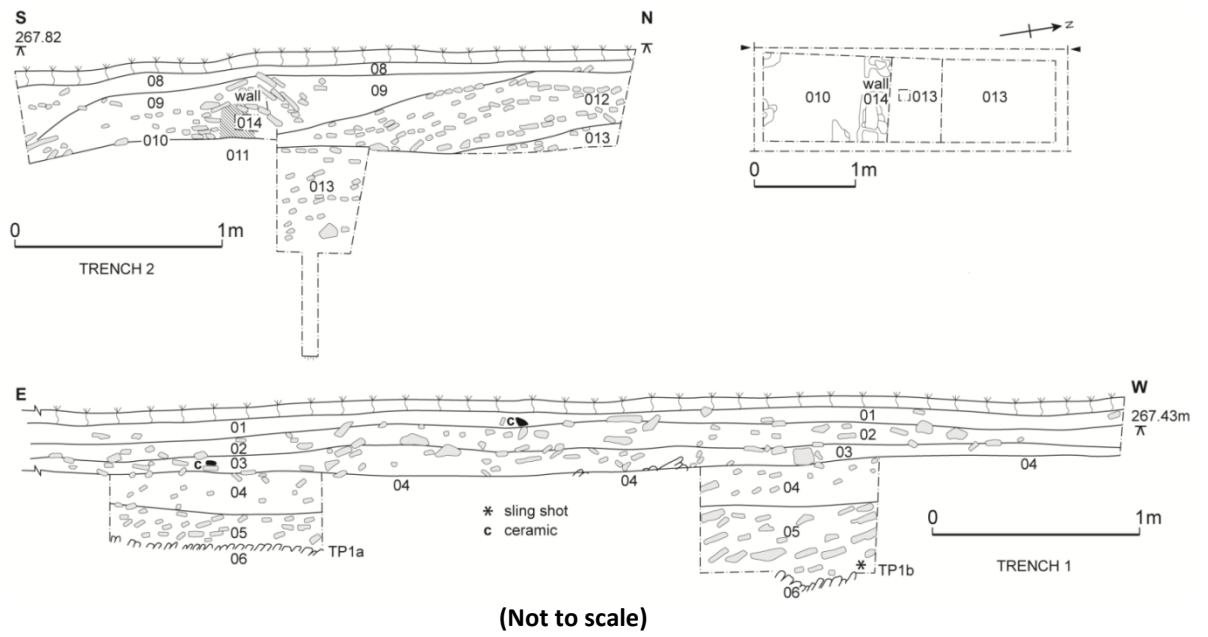
One trench of 8.83 m in length was oriented approximately east to west with a further 2 and 3 m sections added, making a total of 13.93 m<sup>2</sup> in area. A second trench was

added to the northern edge of the platform measuring 0.88 x 1.58, 1.6 m<sup>2</sup>. In total the trenches covered a combined area of 15.53 m<sup>2</sup>.



**Figure 158.** Trench one upper looking east and lower looking north.

Trench 1 explored the high lead anomaly, with Trench 2 being used to identify the edge of the earthworks, or whether there was a garden perimeter abutted to the platform edge.



**Figure 159.** Trench plans for Castell Grogwynion identifying all of the lithofacies. Re-drawn by A. Smith from Timberlake *et al.* (2014).



**Figure 160.** Trench 2, with exposed walling, possibly and abutted perimeter wall.



### 5.7.7 Trench 1 description

Height: OD 267.43 m.

Lithofacies numbers can be identified in Figure 159.

Surface - 10 cm. A low mound consisting of dumped stone mixed with topsoil in sharp contact with lithofacies 01. Matrix supported sub-angular to angular clast from 3 – 5 cm on the A axis.

Munsell colour = 10YR 3/2- 3/3 very dark grayish brown - dark brown.

Modern soil with high organic matter.

Lithofacies 01. 10 - 20 cm. With minor assemblages of medieval pottery, some iron nails and animal bone. Beneath which were two further thin layers; one of dark brown ashy soil containing disseminated charcoal with large amount of broken post medieval pottery, nails, glass and roofing slate, with sub angular clasts 5 – 7 cm on the A axis all matrix supported packed with soil and silt.

Munsell colour = 10YR 3/2- 3/3 very dark grayish brown - dark brown.

Lithofacies 02. 20 – 30 cm. Mixed colluvium and flat lying natural mud stone scree, with a small amount of re-deposited medieval pottery fragments. Both clast and matrix supported with silt and clay. Clasts are angular and vary in size from 4 - 8 cm on the A axis, sharp contact with the lower level.

Munsell colour = 10YR 3/2- 3/3 very dark grayish brown - dark brown

Sharp boundary between modern soil and Denbigh Mor phase soil.

Lithofacies 03. 30 – 40 cm. This stratum appears to represent the horizon where the base of the cultivated meets a disturbed area associated with a possible Midden which overlays significant hill wash infill of small angular clasts, silt and clay from the northern platform.

Sharp boundary.

Colour as above. (Denbigh Mor phase, brown stoney clay loam over bedrock).

The next two lithofacies describe the deeper test pits excavated at the bottom of the initial trench TP 1b and TP 1b. See plan and section drawing.

Lithofacies 04. 40 – 50 cm. This sterile layer comprises of well mixed loose shale, gravel and soil in equal parts.

Sharp boundary.

Munsell colour 10YR 5/3 - 5/4 Brown - yellowish brown.

Denbigh Mor phase, brown stoney clay loam over bedrock.

Lithofacies 05. 50 - 70 cm (variable) large angular clasts > 25 cm on the A axis clast and matrix supported with smaller shale, gravel, clay, and silt.

Sharp boundary.

Munsell colour 10YR 5/3 - 5/4 brown - yellowish brown.

Denbigh Mor phase, brown stoney clay loam over bedrock.

Lithofacies 06. Bedrock and mud stone with some splitting and erosion with angular edges. Dip 30° east apparent, base unseen.

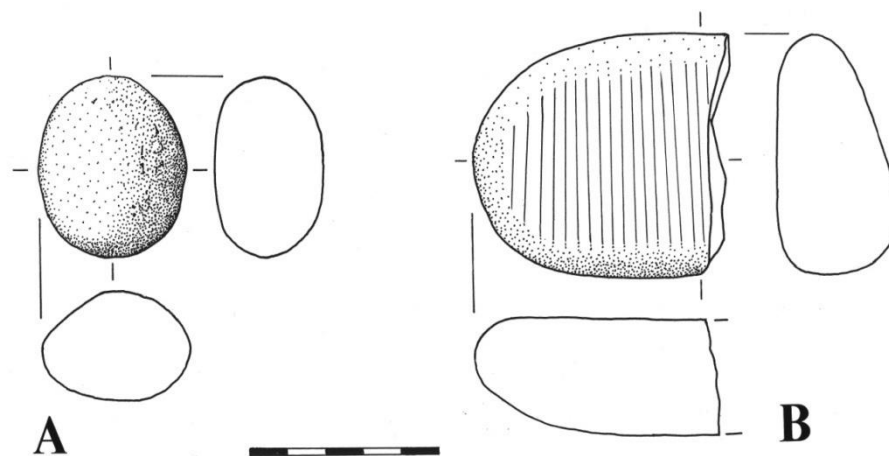
Colour 5YR 4/1 – 5/2 dark gray - olive gray.

Within TP 1 at ca.70 cm depth there was a single small oval pebble (45 x 37 x 25mm). These are often associated with sling stones and were most likely to have been collected from the nearby beach at Tanybwllch or other beaches near Pen Dinas hill fort, Aberystwyth. Given the name of the hill fort 'Castell Grogwynion'; meaning white pebbles, further finds of squared quartz blocks within TP 1 may have formed part of the hill fort's revetments or bastions and been buried within this anomaly.

A larger fragment of local greywacke sandstone (65 x 60 x 30 mm) uncovered in TP 1 with a smooth flat upper surface showed traces of possible wear. This may be part of a

whetstone. The date of this is difficult to estimate as re-deposition in context of its current location may be questionable.

Nineteen pieces of clay tobacco pipe comprising 13 stem fragments; of pottery consisting of five un-decorated bowl fragments and a flared foot bowl possibly produced in Broseley Staffordshire were unearthed. Other finds included glass fragments, 20 nails with other fragments of Iron gate hinges, bone fragments and roof tiles with vestiges of nail holes. These were also mixed amongst 575 pottery shards (Timberlake *et al.*, 2013) of type and period described later in this chapter.



**Figure 161.** Castell Grogwynion (A) Slingstone. (B) Whetstone? Source: B. Craddock, Early Mines Research Group (2013).

### 5.7.8 Trench 2 excavation description

Height: OD 267.82 m.

Trench 2 lithofacies follow trench 1 numerical, i.e. trench 1. 01 - 07, trench 2. 08 - 14

Lithofacies – surface was cut into the edge of the retaining bank of the north terrace. Here, it a thicker layer of top soil 10- 15 cm in depth was revealed.

Munsell colour = 10YR 3/2- 3/3 very dark grayish brown - dark brown.

Modern soil with high organic content

Lithofacies 08. Overlying colluvium mixed with small amounts of Midden charcoal and pot shards. Sharp contact at base with lithofacies 09; at the southern limit it dips 20° apparent.

Colour and description as of surface lithofacies.

Lithofacies 09. Possibly equivalent to Lithofacies 02 and 03 of trench 1, where the horizon has sealed an earlier collapsed stone faced wall.

Munsell colour 10YR 5/3 - 5/4 Brown - Yellowish brown.

Modern soil and Denbigh Mor phase soil.

Lithofacies 10. Bottom of the southern section of trench 2 (similar to 09) base unseen.

Munsell colour 10YR 5/3 - 5/4 brown - yellowish brown.

Transient boundary between modern soil and Denbigh Mor phase soil.

Lithofacies 11 – 14. Possibly the retaining wall of the later terrace was developed during the post medieval re-occupation. It has been cut in to a gently sloping bank to the north. Constructed of flat lying mud stone but collapsed at the north end in to lithofacies 09. Mainly clast supported with some infill or in-wash. Clasts 15 – 35 cm, sub angular mud stone.

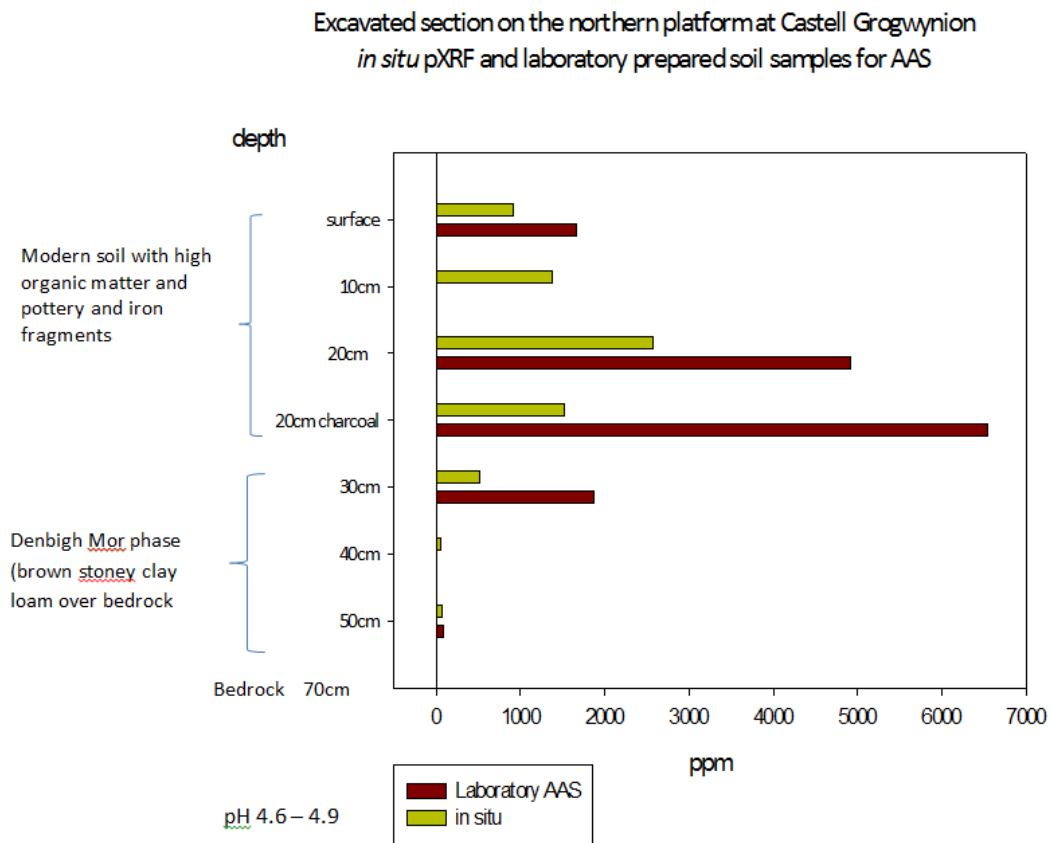
Lithofacies 12 – 13. To the north of the terrace wall it dips 15 - 20° north to south from litho 08 at the edge of the platform to the front of the terrace wall, suggesting that this collapsed section was part of the original Iron Age earthwork. Large angular clasts > 25 cm on the A axis, clast and matrix supported with smaller shale, gravel, clay, and silt. Sharp boundary.

Munsell colour 10YR 5/3 - 5/4 brown - yellowish brown.

No finds were recovered from this trench apart from a few small pottery shards.

In tandem with the excavation the exposed lithofacies of trench 1 were analysed at 10 cm intervals, with supplementary soil samples for laboratory analysis, both to assess the depth of the lead anomaly and lateral variation. Lead contamination within the

excavation was limited to the top 30 cm and from 30 - 70 cm only registered back ground levels. This possibly suggests that lead within the upper levels had been dumped as no evidence of an ore lode or any smelting evidence was identified directly beneath the excavation.



**Figure 162.** Depth model of the Castell Grogwynion trial excavation showing the extent of the Pb anomaly.

No evidence from the excavation indicated a smelting site, which was suggested by both the pXRF and geophysical survey results. The lead anomaly was diffused and spread laterally across 15 m of the sampled area of the platform and 25 – 30 cm deep within the upper soil stratum, combined with other finds of disseminated charcoal and 575 pottery shards.

### 5.7.8 Interpretation

Although the pXRF and geophysical survey strongly suggested evidence of deep burning and elevated lead concentration, indicating an area subject to smelting or smithy works, this for now cannot be confirmed, but it raises further questions on the source of the lead anomaly, or the excavation method.

1. The excavation may have missed evidence of smelting.
2. The pottery may be the source of the lead anomaly;
  - It is necessary to try to establish if the mass balance of pottery lead to soil equate.
  - It is necessary to try to establish if the pottery have similar isotope signatures to local ores.
3. There may be a possibility of small scale exploratory work within the northern platform of the hill fort to look for lead lodes (evidence of a trial pit is noted 30 m to the north-east of the northern platform).
4. They may have been a small smithy works located within the hill fort as part of re-use and re-occupation during the 18th Century.
5. The site may have been used as a privy dump from the nearby farm at Pengrogwynion.

Some of these points are conjecture that can only suggest how the anomaly was deposited, but the first point can be addressed to a certain extent.

When compared to other similar sites that have produced smelting evidence, later agricultural ploughing has often been known to re-distribute smelting detritus over a larger area in both a vertical and lateral context (Navazo and Diez, 2008; Brooks *et al.*, 2009). The geophysical survey of Castell Grogwynion suggests similar analogies on the north and central platforms by the plough marks seen on the site's geophysical report and annotated plan [see Figure 156]. The considerable experience of the EMRG and RCAHMW makes the suggestion that the excavation missed the mark or vital evidence

(Timberlake and Driver pers. comm., 2014) is unlikely. Furthermore the excavation was precisely centred over the highest point of lead concentration by DGPS. However, the possibility suggested in No. 1 cannot be totally dismissed, as the trial excavation covered only *ca.* 10 % of the initial pXRF and geophysics survey.

Alternative hypotheses as to the source of the lead anomaly considered whether or not lead rich glaze had leached into the surrounding soil. There is sufficient evidence that soil with pH values between 4.6 - 5.6 which are similar to the soils found on the upland sites surveyed during this study, can transfer lead from lead rich glaze into surrounding soils (Azzoni *et al.*, 1981; De Mejia and Graigmill, 1996; Tite *et al.*, 1998 and Hernberg, 2000). Acidic soil will affect fractured or stressed areas of pottery, often associated with broken pottery that has formed craquelures through age.

Provenance of lead within pottery glaze can determine the origin of the lead used, with even small amounts allowing successful measurements and identification of the lead source. Brill and Wampler, (1967) achieved this on a few flakes from Roman 1st Century (Flavian) period pot sherds found in Caerleon South Wales, identifying them as being from the Gaul region of Europe.

Therefore, if the lead could be provenanced to a local ore source and if mass balance of the soil to lead glaze ratio could establish the amount of lead required it may give an answer as to the origin of the lead may be found.

#### **5.7.9 Pottery assemblages Pb content**

The pottery assemblage from the excavation site amounted to 575 sherds (6543 g). All were post medieval with a date range from the 16<sup>th</sup> to 18<sup>th</sup> centuries (Timberlake *et al.*, 2014). Selected samples of pottery sherds relating to the excavation were selected in order to evaluate element composition and ore provenance. Research and the cataloguing of lead isotope data for Wales and England by Brill and Wampler, (1967); Fletcher *et al.* (1993) and Rohl, (1996) were used for this evaluation. Using ICP-MS in tandem with the laser element, lead isotope provenance of a representative selection of pottery sherds was carried out [see method Chapter 5 for full description on preparation and analytic equipment used].

The collection of clay pipe fragments was not used as datable evidence in this study, however, statistical evaluation of the clay pipes' length and bore has been used in the past to determine their dates (Walker, 1967).

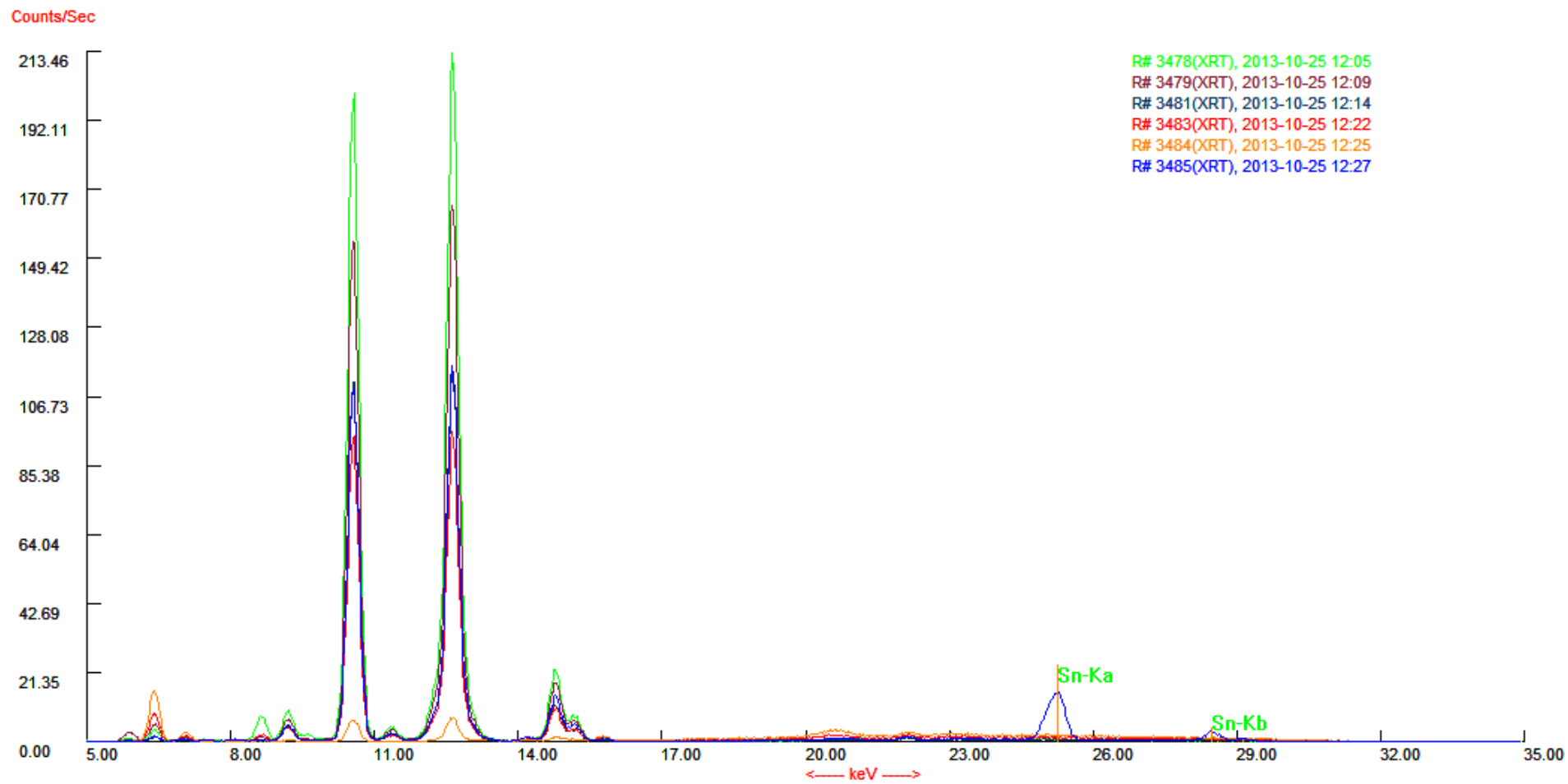
Analysis of all pottery types utilised three methods: pXRF, AAS and ICP-MS, the latter for isotope provenance.

	Castell Grogwynion pottery finds pXRF data wt. %	Sn	Sn Error	Pb	Pb Error	As	As Error	Bal	Bal Error
1	pottery black and cream	0.554	0.051	84.950	4.176	2.039	0.146	10.629	4.375
2	pottery black	0.442	0.047	62.827	3.008	1.192	0.107	33.097	
3	glass	0.000	0.015	0.027	0.009	0.004	0.003	98.517	0.135
4	pottery brown on glaze	0.507	0.059	55.794	3.124	1.449	0.122	41.707	3.256
5	pottery dark brown and light brown	0.487	0.050	56.198	2.736	1.785	0.119	40.104	2.895
6	pottery dark brown and light grey	0.095	0.022	17.373	0.479	0.510	0.040	80.419	0.533
7	pottery dark brown and light grey 'back'	0.000	0.014	1.501	0.048	0.029	0.014	93.929	0.171
8	pottery-blue on white	7.564	0.417	43.011	1.972	0.918	0.089	47.974	2.427
9	pottery brown on glaze	0.615	0.059	69.925	3.604	1.716	0.132	25.919	3.795
10	Blank								

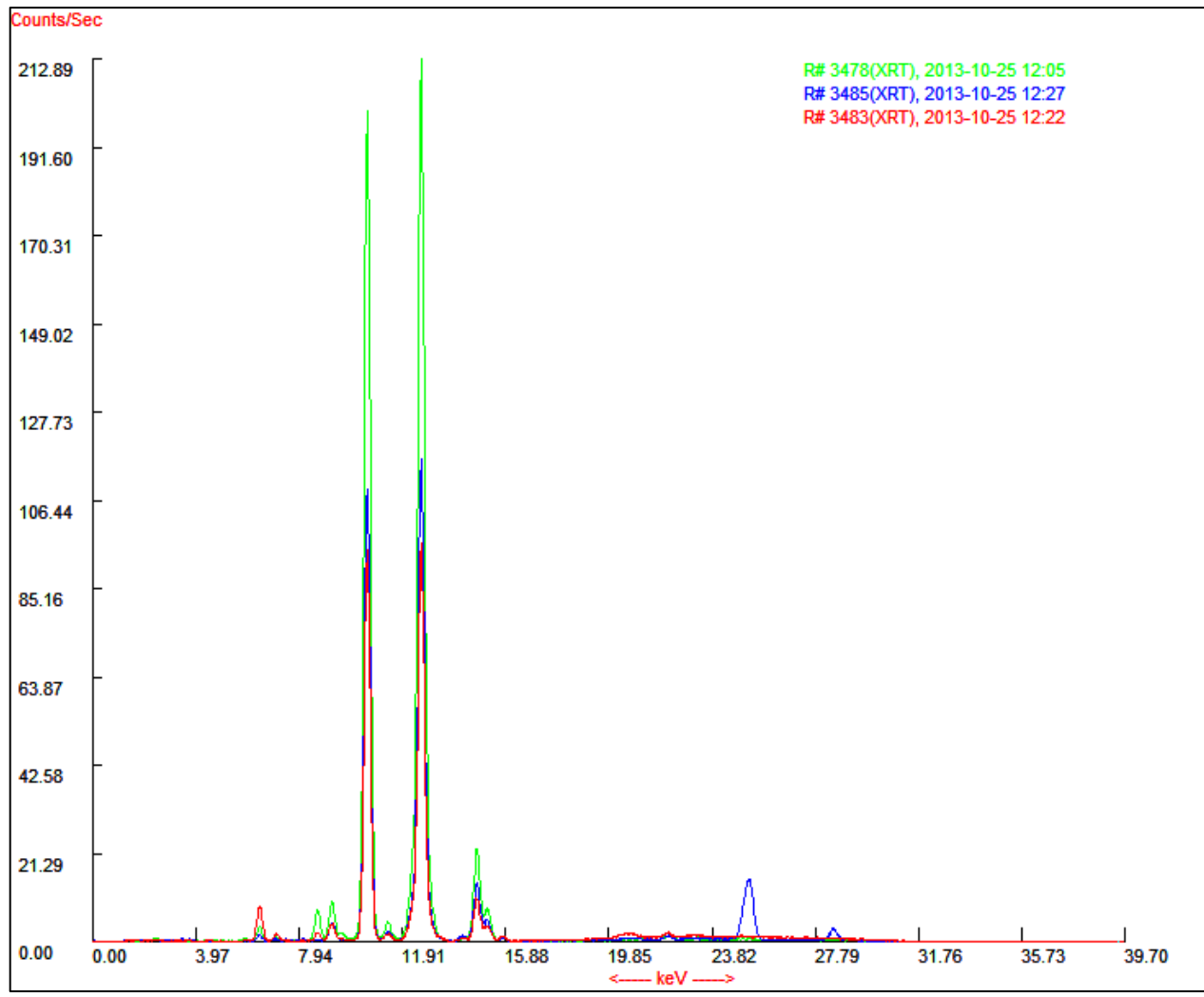
**Table 35.** Initial pXRF data showing the main elements within the pottery glaze.

Initial pXRF analysis of the pottery items confirmed high levels of lead within the glazed surfaces, but higher than normally seen for this type and age of pottery (Zucchiatti *et al.*, 2008). The spectral signatures [see Figure 163 and 103] highlight the difference in pottery types with a peak of tin for the blue and white coloured tin glaze earthenware pottery, which is spectrally different from the two Staffordshire pottery items which had little or only slight background amounts of tin.





**Figure 163.** Six overlaid spectral signatures from the pXRF of the lead base pottery glaze fall in to a distinct pattern, but with one (R# 3485(XRT), 2013-10-25 12:27) is also rich in tin (Sn) glaze.



**Figure 164.** Three overlaid pottery spectral signatures from pXRF for; (top) Tin Glaze Earthenware (Blue); (Middle) Stafford marbled -feathered slipware (Green) and (bottom) Staffordshire manganese mottle ware (Red)

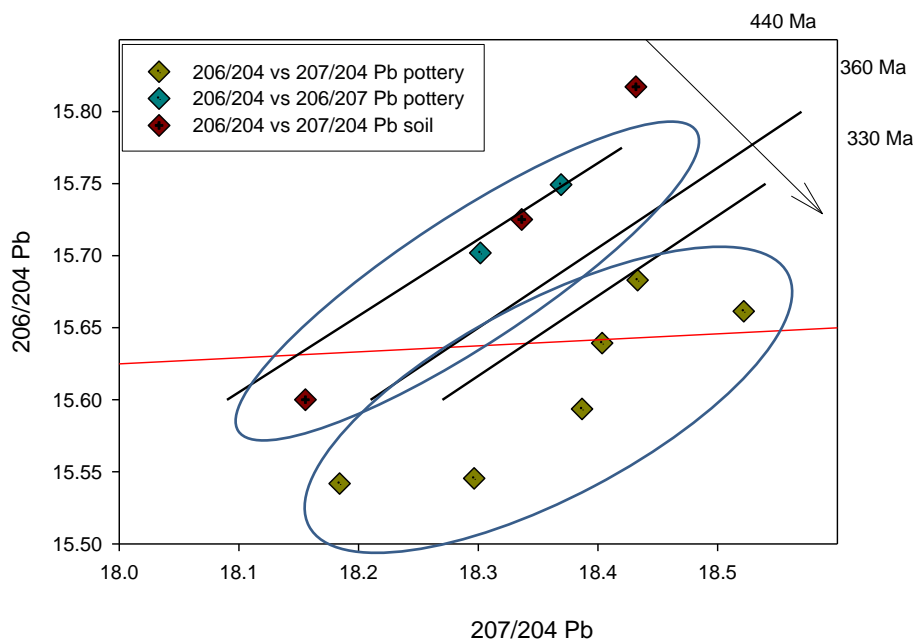
When pXRF analysis was compared to the AAS results, it showed high variation of lead concentrations, but, confirmed significant levels of lead. Lack of comparative values in lead from both analytic processes may be due to poor preparatory work with undetermined amounts of clay rich material introduced creating a bulk matrix effect in the lead sampling.

Isotope signatures of lead can be specific to the host lithology where the mineralising events have occurred (Bird, 2011). In this case isotope data from Rohl, (1996) and Fletcher *et al.* (1993) was used. This categorises specific lead isotopes to both area and period, i.e. the period when the host rock was first deposited and the area in which the host rock is now underlying or outcropping. Contaminated soil from the lead anomaly at Castell Grogwynion and ore sourced from local mines at Grogwynion were used to act as a benchmark for the comparison of the pottery finds uncovered from the excavation. If the pottery items matched the isotope signature of the soil, there is a possibility that the pottery could be the cause of the lead contamination. Analysis of the local ore can also be used to provenance the lead in the soil, if derived from Grogwynion or the nearby Frongoch mines. It should be remembered that the soil may have also contaminated the pottery.

Using the Cummings – Richard model with isotope data from Fletcher *et al.* (1993) shows both the soil and pottery isotope plots. Five of the pottery items taken from the excavation in green diamonds fall within the 330 Ma isochrone, which marks the transition from the Devonian to Carboniferous geological period. In other words, the mineral isotope signature is too young to have been formed within the host rock of the Cambrian Mountains, which were formed within the Ordovician 470 Ma to Silurian 417 Ma hosting the ‘early complex A1’ and ‘late simple A2’ mineralisation respectively, [Figure 165].

However, two of the pottery plots indicated by light blue diamonds fall within the latter category of late simple A2 mineralisation and are similar in fractionation to the soil isotope indicating a similar isotope signature, [see Figure 165]

### Pottery and soil isotope data from the excavation at Castell Grogwynion



**Figure 165.** Pottery isotope scatter plot using the Cummings –Richard model. The growth curve is in Red and Isochrones in Black Re-drawn from the Cummings-Richard model.

It must be noted there are inliers within the Cambrian Mountains that host Carboniferous bedrock which could host local mineralisation, but not near this site. Given the pottery description and place of production, primarily North Devon and Staffordshire (Timberlake *et al.*, 2013), it is reasonable to suggest that the lead isotope signature is derived from mineralisation formed within Carboniferous host rock prevalent in both these areas (Toghill, 2007; BGS 2000) [see BGS Bedrock Geology UK South].

Calculating the mass balance or ratio of lead content within the glaze to the weight of excavated soil with pottery assemblages, may also give a good indication of whether the pottery has changed the background levels sufficiently to parallel the high levels of lead found in the pottery rich soil stratum.

The excavated pottery all measured between 0.26 - 0.33 cm in thickness but varied in length on the long and short axis. Calculating the glaze to fabric ratio required three samples which were all weighed with surface glaze intact and after the glaze had been removed. This determined the ratio of glaze to pottery. However, it is subject to

variation in glaze thickness and the subsequent estimation of the glaze lead content which is shown to vary [see Table 36].

Pottery and glaze fraction and % of lead in glaze					
	Mass of pottery and glaze (grams)	Mass of pottery with glaze removed (grams)	Mass of glaze (grams)	Estimated % of total pottery glaze	Estimated % of lead concentration in pottery glaze
samples					
1	3.611	3.265	0.346	9.569	3.828
2	4.341	3.912	0.429	9.872	3.949
3	2.707	2.438	0.269	9.921	3.968
Total					11.745
mean % $\pm$ 10%					3.915

**Table 36.** Mass of pottery and glaze, with % of lead contained within the glaze.

Estimate of total lead in the pottery assemblages = **3.915 %**

Calculating the soil mass measures the depth of stratum in which the pottery was recovered and the area of the excavation footprint:

Depth \* Area = 0.30 m x 11.5 m<sup>2</sup> = **3.450 m<sup>3</sup>**

Mass of soil = mixture of wet loose dirt (X) and wet loam(Y)

X= wet loose soil = 1250 kg/m<sup>3</sup>

Y= wet loam = 1280 kg/m<sup>3</sup>

X+Y /2 = 1265 kg/m<sup>3</sup> x mass of the soil 3.45 m<sup>3</sup> = 4364.25 kg

Total mass of the pottery excavated = **6543 g**

3.9% of the pottery = **255.18 g**

$$\therefore \frac{\text{pottery (Pb)content(g)}}{\text{mass of soil (t)}} = \frac{255.18 \text{ (g)}}{4.364 \text{ (t)}} = 58.48 \text{ ppm}$$

g = grams

t = tonnes

N.B. Mass of soil types taken from engineering toolbox.com (2014).

Adding the estimated lead from the pottery to the natural background levels of 110 ppm there is, at best, a maximum of 168.5 ppm of lead throughout the pottery bearing soil stratum if well mixed. It seems unlikely that the pottery has a sufficient content of lead to influence the anomaly at Castell Grogwynion which ranges between 400 and 6000 ppm. The likelihood of this is reduced further by the fact that the provenance of 40% of the pottery North Devon and Staffordshire by their typology, fabric and isotope signature. Thus, this can be removed from the overall calculation. Furthermore, the curvature of the pottery may have had some slight effect on the pXRF sampling, but it would have only reduced the sample signal.

However, it must be noted that a third of the pottery identified as Buckley Coarse ware from north-west Wales, which has earlier Carboniferous host bed rock similar in age to north Devon and Staffordshire bed rock.

#### 5.7.10 Interpretation

Although the coarse wares cannot be closely dated, the fine wares suggest that a start date for the assemblage is no earlier than the middle of the 17<sup>th</sup> Century, and in fact there are no wares that can be definitively dated as 17<sup>th</sup> rather than 18<sup>th</sup> Century. Timberlake *et al.* (2014) comments that the scarcity of cream wares suggests that occupation [or at least deposition of domestic refuse in the lazy beds] ended around the middle of the 18<sup>th</sup> Century, with the pottery assemblages covering a period of 100 yrs. from mid-17<sup>th</sup> to mid-18<sup>th</sup> Century.

It is difficult to determine whether this dump of broken pottery and bottle glass originates from a settlement cottage inside the hill fort, or the farm of Pen Grogwynion located a few hundred metres to the north-east. If it is the latter, why was the material

dumped 200 m from the farm? It may have been mixed with for manure and taken from the farm's own midden or privy pit for use as fertiliser on lazy-beds.

#### **5.7.11 .Summary**

The excavation was designed to investigate a high lead/burning anomaly within a low earthwork on the northern terrace of Castell Grogwynion hill fort, identified during the pXRF surface sampling and subsequent geophysical survey. However, excavation found no evidence of burning, or a furnace bole that had been previously postulated.

With reference to the geophysical and topographical surveys, it seemed possible that both the pottery and the charcoal could have been associated with a range of materials dumped here and subsequently mixed into the soil during intensive manuring of these lazy beds 35 m to the west of a possible post medieval house platform.

In attempting to identify the source for this lead anomaly one that was suggested as lead-rich glaze present on the surface of pottery sherds from coarse ware and fine ware pottery, all dated to mid-17<sup>th</sup> - mid-18<sup>th</sup> Century AD, may have been etched by the slightly acidic soil conditions common in these upland soils. Testing for the isotope signature alongside the mass balance calculation does not agree with this supposition. Lead isotope ratios present both in the pottery glaze and in the soil are different. The level of soil-based lead contamination could not all have been derived from the pottery, equally, the isotope signature within the soil was generally different from that present within the analysed pottery. Rather, the nearby mine ores suggest that the source of the pollution may be from the post-medieval lead test pits which are evident within the fort.

As yet there no evidence for prehistoric, Roman or medieval lead smelting at this site, However, analysis of the site suggests later re-occupation of these settlements consistent with the finding from the excavation of a possible post-medieval cottage settlement, associated with a series of lazy beds containing the excavations finds. This

adds further evidence to the notion of a relationship between metallurgy and Iron Age hill forts, even if this is not within the hill fort's initial Iron Age occupation.

## **Chapter 6 Discussion**

The aim of this study was to investigate whether there was a relationship between metallurgy, Iron Age hill forts and Roman settlements in North Ceredigion, using pXRF for *in situ* analysis of the surface soil and sediments. Surveys were conducted with the aim of identifying elevated values of the target elements: copper, lead, zinc and iron, suggesting evidence of anthropogenic alteration to these archives contemporaneous with past metallurgical exploitation throughout Wales and other poly-metalliferous rich lodes along the Atlantic fringe.

Evidence of Bronze Age exploitation has been identified in North Ceredigion with major finds at Cwmystwyth (Budd *et al.*, 1992; Johnston, 2008; North, 1962; Timberlake, 1987, 1994, 2001, 2002, 2004, 2011; Timberlake *et al.*, 2002, 2009; Timberlake and Switsur, 1988) and reflects similar exploitation throughout Wales and in a wider pan European context (Jenkins 1997, 2001; Ixer and Bud, 1998; O'Brien *et al.*, 1989, 1995; Needham *et al.*, 1997).

Iron Age metallurgy has also been widely reported throughout Wales with evidence at Bryn Castell and Breiddin Hills (Musson *et al.*, 1991, 1992; Quinnell *et al.*, 1994) and in North Wales (Crew, 2002). Further postulated evidence of votive offerings were found in Llyn Cerrig Bach (Giles, 2007), all suggesting the continuum of Iron Age metal exploitation but which has not been identified in the hill forts of North Ceredigion.

Roman period lead and copper metal exploitation is well documented in North and South Wales with gold and silver also having been exploited. But until now only proxy evidence has been found in North Ceredigion.



## 6.1 The Study's major findings

The study has found increased metalliferous deposition of high lead values at Castell Grogwynion. This was fixed within a stratigraphic layer located on the Northern platform of the hill fort. Also, at Banc y Daren, a small inclusion similar to smelting debris contained high levels of copper and lead with a further metal rich halo in the soil surrounding the inclusion. The Abermagwr Romano-British villa survey also revealed high levels of lead in numerous fire pits identified during the 2012 excavation. It also identified that lead sheet sections recovered from the earlier excavation were most likely used in the villas construction and that they contain isotope markers concomitant with local ores found 5 km east at Frongoch, Gwaithgoch and Grogwynion mines, where it has been suggested there was exploitation since before the medieval period (North, 1962; Coflein 2014).

Although it is suggested that Roman lead exploitation started within a short time after their conquest of England with evidence in the Mendip hills (Tylecote, 1964) and the South Pennines (Xiangdong and Thornton, 1993), the evidence in North Ceredigion is chronologically later, dating from the 2<sup>nd</sup> and 3<sup>rd</sup> centuries AD (Mighall *et al.*, 2009). Although it cannot be established exactly where the ore for these North Ceredigion sites was extracted, evidence in this study supports the suggestion that Roman period pyro-metallurgy was practised here.

The lead find at Abermagwr is possibly the first piece of smelted lead produced from local ore found in North Ceredigion. It may not reflect the larger lead ingots or pigs possibly associated with the North Flintshire Halken Mountain ore fields, which were dated from *ca.* 60 AD onwards (Museum of Wales, 2014), but all of this evidence points to the exploitation of metal bearing ores throughout Wales. This evidence has been sought through conventional methods of soil, sediment and peat deposit archives, and site and artefact typology, using well established benchmark methods of AAS and ICP-MS, geophysics and excavations.

## 6.2 Outcomes of pXRF testing and application

This study has used pXRF to analyse the soil and sediment in North Ceredigion to establish the relationship of metallurgy with the Iron Age and Roman settlements in North Ceredigion. The process of testing pXRF and its application to geochemical enquiry is compared against other similar geo-archaeological and geochemical research techniques using laboratory and pXRF or similar equipment for *in situ* and *ex situ* analyses.

Comparable work using pXRF in the Near East (Grattan *et al.*, 2014), successfully identified copper concentrations to differentiate mining waste from beneficiated ore. This was from later prehistory and Classical period mining and suggested pyrometallurgical processes that had been ongoing since the Chalcolithic period. The results identified the rich copper *in situ* in the adits and mines and showed that through beneficiation copper is increased by the removal of the gangue, with the inferred nearby waste tip depleted in copper. Clearly, the one problem that this study did not need to assess is matrix effect from high moisture content. This was one of the underlying problems identified for the current study and formed a significant part of the testing of pXRF during subsequent surveys and laboratory testing.

Shuttleworth, *et al.* (2014) also carried out comparable work with similar equipment, the Niton XL3t 900 being comparable to the XLt 700 used for this study's analytic work. The *in situ*, *ex situ* and standard laboratory sampling were also similar to this study's method, but they used peat samples with high moisture content in contrast to the less moisture rich soil sample used here. Both used a similar number of samples (40 - 52 respectively), and range of concentration from LLOD -1700 ppm. Comparing the linear regression results on lead rich samples by Shuttleworth, *et al.*  $R^2$  0.99 for *ex situ* (dried and milled samples) vs. wet chemistry laboratory analysis is similar to this study's results of  $R^2$  0.996. Furthermore, the comparison of results against pXRF and ICP-AES and pXRF and ICP-MS for the Crooks *et al.* (2006) and this study respectively, agree with a high  $R^2$  of 0.99 for both methods of analysis. This high correlation in the relationship between both methods gives robustness to the pXRF quantitative results for this study. [The comparison of ICP-AES and ICP-MS are reported on in Moor *et al.*

(2001). For the matrix effect on sample near to LLOD, Al-Rashdan *et al.* (1991) comment on the improved detection levels of ICP-MS compared to ICP-AES].

Crook *et al.* (2006) also suggest that moisture has a matrix effect on *in situ* sampling. Using the Niton XLt 700, their assessment on how values reduce in a direct relationship with moisture content is comparable to this study, (see Chapter 5, [Table 10]).

The linear reduction for samples with 20% and 40% moisture content with a spiked sample containing 1649 ppm of lead, returned results of 19.0% and 31.7% which are similar to this study's results of 19.8% and 31.1% but contained a slightly higher spiked lead 2723 ppm content. Both this, and Shuttleworth *et al.* (2013) study used similar correction protocols for high moisture content, but this study's evaluation of bias did not compare the corrected data with the re-sampled dry analysis as it was considered that this to be purely academic. Simply drying and milling the samples for re-analysis as was done in this study was also the preferred method suggested by Shugar and Mass (2013).

Shuttleworth *et al.* (2014) also comment on how TOC can create a matrix effect. This was not tested during this study but has been acknowledged as some of the samples possibly contained organic matter. Time and precision in this study were also comparable those of Shuttleworth *et al.* (2014), both noting that the optimum time was no more than 120 seconds for *in situ* analyses. This study's *ex situ* analysis used a maximum of 120 seconds as the decrease in error was only minimal after this threshold and not practical in field conditions.

Further work by Radu and Diamond, (2009) on abandoned silver mines in Tipperary, Ireland used both AAS and pXRF to assess the spatial extent and contamination levels caused by the mechanics of 'dust blow offs' which could possibly affect local communities. This is similar to the hypothesis proposed at Castell Grogwynion, where the location of the nearby spoil tips of the abandoned mine may be responsible for possible windblown contamination.

Radu and Diamond (2009) used a similar testing protocol and choice of elements: lead, copper, zinc and arsenic to this study. Their results on the linear regression for lead  $R^2$

(0.995) reflect both the results of this and the study of Shuttleworth *et al.* (2014) where results of  $R^2$  0.996 and  $R^2$  0.99 respectively correlate well. Even though there was some slight variation in the results for copper and zinc compared to this study, where, the  $R^2$  for zinc was  $R^2$  0.990, while for this study was  $R^2$  0.849, and copper was also slightly better at  $R^2$  0.99 compared to  $R^2$  0.96 of this study, but both still return quantitative data.

Comparative work on pXRF, AAS and ICP-MS by Kalnicky and Singhiv (2001) and Shackley, (2011) both agree pXRF as an *ex situ* analyser can provide quantitative data when used in laboratory conditions, but that the *in situ* data is often affected by environmental bias. This data is considered to be less robust but is clearly still qualitative. The choice of pXRF for this enquiry has been justified by its extensive use and by the results obtained clearly identifying lead, copper and zinc above expected levels

Unlike the Roman evidence at Abermagwr, this study has not clearly demonstrated a relationship between the Iron Age hill forts of North Ceredigion and metallurgy. However, the application of pXRF and assessment of pXRF has had some success in opening further avenues for research using effective methods to establish this through a stepwise process of hypothesis testing of the metalliferous residue found in the excavated floors of the villa and the interior of the hill fort at Castell Grogwynion.

## **6.2 *In situ* and *ex situ* evidence**

Although this study has not used peat cores as a geochemical archive, work on peat deposition in Northern Spain developed an understanding of the isotope fingerprinting of lodes as little as 5 – 10 km apart, developing a regional understanding of how metals have been exploited. Cortez *et al.* (2002) differentiated the phases of Roman exploitation in the peat mires around La Molina mire, despite the predominance of geogenic source and they discriminated between geogenic and anthropogenic contributions to the mire.

This study has used isotope analysis to provenance lead ore origins using 206/204 lead and 207/204 lead for the pottery and lead rich soil and lead finds to evaluate the local

ore lodes. It differentiated between local and exotic lead lodes used in the lead and pottery glazes, whereby local ore lodes were compared to pottery lead glaze and lead rich soil samples.

Isotope findings for the ores found in Wales and the Mendip Hills ores in the South West have suggested the pottery glaze was not made from the local ores found in Ceredigion. Testing the pottery finds at Castell Grogwynion used a similar method to Brill and Wampler's, (1967) evaluation of pottery glaze from finds in South Wales near Caerleon. Here, pottery fragments were provenanced to lead lodes from the ancient Gaul region of Western Europe, confirming the pottery to be exotic. This is similar to this study's evaluation of the excavated pottery, confirming its origins the Mendips on the basis of the isotopes in the lead-rich glaze lead lodes.

The combined results at Castell Grogwynion of pXRF, isotope analysis and the mass balance of lead to soil ratio strongly suggested the pottery was not the source of lead contamination. But they pose further questions as to where the lead was from. Isotope provenance suggests the local Grogwynion and nearby mines *ca.* 800 m west, but by what process or for what reason is yet to be established. It may simply have been a small farmstead operating a small cottage industry or even some metal prospection.

The data and interpretation of the finds from both Abermagwr and Castell Grogwynion strongly suggest is there has been reuse of these sites after initial construction and occupation. How this has been identified is that the lead anomaly sites are layered within pottery shards which have been dated between the 16<sup>th</sup> and 17<sup>th</sup> Centuries, suggesting these were concomitant in their period of deposition. Although the initial suggestion was that the pottery was responsible for the lead anomaly, further work on the provenance of the lead isotope strongly suggests the lead is derived from a local source.

Other work on this avenue of reuse and occupation of Iron Age hill forts is limited with only some evidence of Roman use during their occupation and later Saxon funereal use. This may be a new avenue of exploration into Iron Age hill forts.

### 6.3 Smelting debris find

The small slag like inclusion found at Banc y Darren which was rich in copper and lead and with signs of vesicular and surface vitrification, is comparable with similar finds of smelting slag. There is some similarity between this sample and findings of copper rich smelting debris from the Kiechlberg Tyro, Austria (Krismer *et al.* 2013), as also with samples from the Faynan copper smelting from the Chalcolithic period (Grattan Pers com 2014). It suggests some process of high heating has produced this sample, but it may have been just a natural windblown fire.

One explanation suggests the extended period of exploitation at Banc y Darren may have seen small smelting activities carried out here and the sample may simply be discarded slag. But in the context of where the slag like sample was found, within the earthwork, it may have been buried during the construction of the hill fort. This requires further investigation. Further work on this find could involve examining the crystalline structure and isotope provenance of its lode. If this proves to be locally derived, further applications for a test excavation through the outer earthwork maybe warranted. However, if this small piece of smelting debris was part of a larger process, there would be further evidence around this site similar to the evidence at Cymystwyth. Here, multiple boles attest to medieval smelting for lead (Anguilano *et al.*, 2010). These have been identified by a geophysical survey similar to that used by used by Crew, (2002) at Crawcwellt in North Wales. This may be the initial approach in answering unanswered questions at Banc y Darren, but if used in tandem with pXRF it would create a strong methodology similar to the methods used at Castell Grogwynion.

Both surveys at Odyn Fach and Llys Arthur do not suggest increased metalliferous signals, even though they are close to the Allt-y-Crib lode and Esgair Lle mine respectively. It is possible that the function of Llys Arthur was simple to protect the mineral asset. Odyn Fach has many other smaller defended enclosures and larger hill forts nucleated within a 2.5 km area, but its size and lowland position mean it is more likely to have been used for agricultural and transhumant practices. This still does not answer the question of where this slag material found during the earlier excavation

was produced (Murphy 1988). Although Pen Dinas (Elerch) is older than Odyn Fach and other lowland sites nearby, it has not presented any evidence of increased metalliferous signals or artefacts associated with pyro-metallurgy. But as with Odyn Fach, the slag material uncovered is still to be explained. The only reasonable answer for now suggests a comparison to the recent find at Glanfred, where an iron smelting hearth has been uncovered and radio-carbon dated to the medieval period (Jones, 2012 unpublished). It may simply be that these sites have been reused during these and other periods after the Roman occupation of 44 – 440 AD.

#### **6.4 Limitations of the study**

It must be acknowledged this study has only surveyed six sites in North Ceredigion for geochemical data that may infer some relationship with the local ores of nearby polymetallic lodes. Expanding this work to other Iron Age hill forts and settlements in this area, concentrating on both the hill fort interiors, and inner and outer annexes may uncover geochemical evidence that will further test the hypothesis formed for this study.

Even though the study has not identified any direct evidence associated with Iron Age period smelting of copper, lead and iron, it has unwittingly uncovered how the later reuse and re-occupation has left other evidence, providing an avenue of research yet to be fully explored. If there is further evidence of this practice within Ceredigion's prehistorical Classical and historical sites, what period was involved and to what use were they put?

Attempting to unravel mixed information where later reuse may have over printed some of the original geochemical signatures from earlier occupation is problematic. This is evident at Banc y Darren where the possible prehistoric evidence suggested by Pickin and Timberlake (1987) and Timberlake (1994) is probably masked by later exploitation of the site. However, it is clearer at Abermagwr, where later reuse is suggested by the fire pits within what would have been a living area. Llys Arthur is another case in point, has the site been re-developed from the possible earlier Roman marching camp to a moated medieval site? What was the site initially used for? The proximity of Cae Gaer 3 km to the east may not have warranted another fortlet so

close unless it was to protect a local asset of metal rich ores at Esgair Lle, similar to the fortlet at Cors Fochno which may have been positioned to protect the assets of Erglodd, Penpompren and Tan y Allt mines which are all within 500 m.

One noticeable outcome of the study is the inability of pXRF to detect high iron deposits above the normal, but ubiquitous levels, when they are buried deep in the soil substrate. This was noted on work carried out on Glan Fred Iron Age enclosure near to Pen Dinas (Elerch) and Odyn Fach, where unpublished work by Jones (2012) uncovered an iron smelter which was carbon-dated to the medieval period. During the investigation, this study was asked to carry out a reconnaissance taking background and smelter iron values with the pXRF. The halo of increased iron was limited to a within. 5 – 10 cm from its source; from this point iron values abruptly return to background levels. Equally at Castell Grogwynion, the cache of iron nails and the hinge found within the excavation remained undetected by pXRF until they were unearthed. This is unsurprising, iron smelting in a pipe-furnace or bloomery hearth does not melt the iron, merely drive off impurities so there is no halo effect. This contrasts with smelting of lead, where the temperature in a pipe-furnace is sufficient to melt the lead and cause some to vaporise which causes the halo. Therefore, pXRF is simply the wrong tool to find iron smelting unless the iron ore contains a distinctive accessory mineral which vaporises to produce a distinctive elemental signature.

Herein lay one of the problems with pXRF and the restrictions that were placed by CADW on the sampling methodology, which was limited to *ca.* 10 cm below the turfed surface. Alternate magnetic susceptibility or caesium vapour geophysics would seem to be a more effective method for detecting iron. However, the use of the latter at Castell Grogwynion in conjunction with the pXRF data suggested a lead smelter was buried at depth within the sediment. This was found not to be so when excavated, but the dipolar signal still suggests deep heating had been carried out there. In this case it suggests that the semi-quantitative and quantitative data may have been misinterpreted and the reliance on scientific applications to underpin the archaeological findings or theories requires both disciplines to serve each other.



## 6.5 Further work

As stated, the number of hill forts and Roman sites surveyed within this study represent < 5% of the sites within Ceredigion. Considering the output from the six sites surveyed, further sites need to be investigated, including their infield and outfield annexes, other nearby enclosures and settlements. This will hopefully add further evidence in answering questions on metallurgy, reuse and occupation of these sites. Furthering the scientific application to aid the understanding of relic geochemical compositions of smelting or smithy artefacts, such research may also incorporate discriminant analysis and ratios of element concentration to see if there is a correlation of geochemical alteration between sites. This would need a consistent sampling methodology and with known environmental bias taken into consideration.

The application of pXRF to the study has had some successes in identifying lead plumes at Castell Grogwynion, the high lead in the fire pits at Abermagwr and the copper in the small smelting detritus at Banc y Darren. But it has failed to identify high levels of iron *in situ*. Alternative testing by geophysics has added to this study's outcomes at Grogwynion, where their parallel use has been developed. If initial pXRF analysis can identify surface anomalies with increased metal values, it may warrant the use of geophysics to identify other iron rich or heated stone or smelting refractories which might suggest pyro- metallurgy.

## 6.6 Outcomes

The data and evidence gained from these six surveys have produced two reports for CADW on the method and initial findings. As well as this, further data was presented in a report to CADW with sufficient evidence to apply for a license to carry out a trial excavation. The findings from this excavation have been published in *Archaeology Wales* (2014) Vol 53, and a short article in *Ceredigion* (2014) Vol XV111 number 2.

The RCAHMW has also benefited from the findings of the survey by adding to the narrative of prehistoric and classic sites in North Ceredigion, with updates to Coflien

[the RCAHMW mapping and data base], and using some of the findings in some posters and reviews.

Further papers are in preparation on the testing of pXRF alongside its application to archaeology in Wales, with a focus on the high moisture bias that causes the matrix effect when using pXRF *in situ* where high moisture levels are encountered. With the isotope provenance of lead considered to have been used in the Romano-British villa at Abermagwr, it presents further evidence on how lead was exploited from the metal bearing lodes of this region during the Roman occupation of Wales. This is another paper that can be taken from this thesis and may possibly be the basis of a larger study in North Ceredigion and Wales. Remote sensing in combination with statistical analysis could be an effective method to create a model for undiscovered sites in south east Wales, where the identification of crop marks has not been as effective as in other areas in Britain. These could be further assessed using pXRF and geophysics for evidence of metallurgy.

## Chapter 7 Conclusion

### 7.1 Iron Age Hill forts and the relationship with metallurgy

This study's aims were to establish if any relationship existed between North Ceredigion's Iron Age hill forts and metallurgy. Whilst the outcomes of this study have to some degree demonstrated that some relationship exists between Iron Age hill forts and metallurgy, it has not established a relationship between Iron Age pyro-metallurgy and these hill forts. Considering the proximal location of many of the lodes that were exploited through the preceding Bronze Age and post Roman period, these hill forts may not have seen metallurgy practised within their interiors. However, this is not to say evidence of pyro-metallurgy may still be found in external annexes or nearer to the mineral lodes, similar to Bronze Age evidence at the Great Orme and Cymystwyth, or sites on the borders and North Wales (Jenkins *et al.*, 2001; Musson, 1992; Crew, 2002, Quinnell *et al.*, 1994).

The first aim was to test whether there was a direct spatial relationship between Iron Age and Roman metallurgy with settlements in North Ceredigion. At Castell Grogwynion, although there was initially strong evidence suggesting a lead smelting bole from both the pXRF analysis and the geo-physics survey, it transpired that this may have been misinterpreted. The evidence of pottery and other waste was in fact evidence of manuring, possibly from a re-occupation during the 16<sup>th</sup> and 18<sup>th</sup> centuries, which also introduced iron in to the lazy beds on these platforms at Castell Grogwynion, but this process is still unclear.

Secondly, did the late Romano-British villa at Abermagwr use locally produced lead in its construction? The study has answered the second question with some degree of confidence through isotope analysis of the lead find at Abermagwr, which correlates with local ores. Although many lead rich fire pits were uncovered at the villa during its excavation, and there were isotope provenances to both local and exotic lead, there is no strong evidence to support the hypothesis that lead was smelted there. This leaves the question of the location of the lead smelting still unanswered. It is, however, suggested this site was re-used after its abandonment which may answer the question as to why there are many fire pits within part of the main rooms of the villa.

During the process of the study, testing pXRF for both accuracy and precision on the target elements compared well to other benchmark standards. But working within an environment with high annual precipitation and soil which can readily retain moisture, it has identified that the matrix effect can reduce the *in situ* values. However, it has still proven to be successful in its overall application in the study.

Further questions include whether Ceredigion's Iron Age hill forts and Roman sites were re-occupied after the Roman's departed Britain and the eventual collapse of their empire. Further evidence like that at Castell Grogwynion, may be found to support this.

Also, were Iron Age hill forts located specifically to both protect and exploit the mineral wealth of polymetallic lodes? While no evidence of pyro-metallurgy was recovered at any of the sites surveyed, it is reasonable to suggest smelting sites may be situated elsewhere, possible nearer to the mineral lodes, or in other outside annexes. These need further examination using LiDAR and ground-truthing the soil chemistry for increased metalliferous content over the expected range. However, it is possible these sites were only used for upland occupation and did not compare to other sites in North Wales and the eastern borders, where smelting of iron, copper and lead has been established.

In conclusion, it is possible these hill forts were constructed only to protect the assets of farming stock, grazing land and control the trade routes that were being established during this period (Driver, 2013), and the ore lodes that were in abundance in the North Ceredigion landscape may not have been exploited for their mineral wealth during the Iron Age period.

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