

# Linking Bronze Age copper smelting slags from Pentrwyn on the Great Orme to ore and metal

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*ABSTRACT: Linking the Great Orme Bronze Age copper mine to British metalwork by analysing ores, copper prills from Pentrwyn and particles of bronze found in the mine is an on-going project. This paper focuses on the smelting slags and prills recovered during the 2011 excavations from the Pentrwyn site, the only smelting site known from the British Bronze Age. They indicate the use of a simple smelting process which used secondary carbonate ores with only residual sulphides. The unusual slags are low in silica, like the ores, and lack any additives which resulted in only a small amount of glassy phase being produced. Hence, the copper prills must have been recovered by crushing, which matches the small size of the slag pieces. Lead isotope results link the slags to the Great Orme ores. The analyses of the copper prills show variable trace element levels, sometimes with significant levels of arsenic and nickel, consistent with a proportion of British Bronze Age metalwork.*

## Great Orme Bronze Age Mine Research Project

The Great Orme mine is situated on a Carboniferous Limestone headland on the coast of North Wales and is the largest known Bronze Age copper mine in Britain (Dutton and Fasham 1994; Timberlake 2009) or Ireland. The Great Orme has extensive surface workings and over 6km of accessible underground Bronze Age workings. They were discovered in 1987 and since then over 2,400 stone tools and about 30,000 bone tools or fragments have been recovered. The radiocarbon dates range from around 1884 to 406 cal BC but most dates cluster around the late EBA to the early MBA (James 2011).

Linking the Great Orme mine to British Bronze Age metalwork by analysing ores from all parts of the mine, copper prills from the nearby Pentrwyn smelting site and particles of bronze found in the mine (possibly from mining tools made locally), is an on-going research project. Tracing Bronze Age artefacts back to specific mines or regions can help reveal centres of production, exchange networks, and important social and techno-

logical implications. Ideally, this is achieved by using a combination of two independent techniques – a chemical ‘signature’ from trace elements and a lead isotope ‘signature’ (Pernicka 2004). However, these types of studies have to deal with the many factors involved (ore types, ore variability, ore roasting, smelting conditions, smelting additives, volatilization, trace element partitioning between metal and slag, geochemical and isotopic data overlaps between ore deposits and metal recycling). Research in this area could be significantly improved by a deeper understanding of ore geology and ore mineralogy and how it links to extractive metallurgy. In recent years, the modern mining industry has created a new discipline called geometallurgy to bridge the gap between geosciences (ore geology, ore mineralogy and geochemistry) and metallurgy (Bowell *et al* 2011). An appropriate term for the new research approach being used by the Great Orme project is archaeogeometallurgy. Killick (2014) recently pleaded for more training of archaeological specialists in ore geology to improve our understanding of the development of metallurgy because ‘the literature is full of poorly informed speculation about ores used in the past’.

This paper focuses on the results of an investigation into the particles of slag and copper prills from the Pentrwyn smelting site, 1.2km to the east, and the contribution they make to the broader project whose initial results will be discussed elsewhere (Williams forthcoming). Furthermore, brief observations will be made on the implications of this site (should it prove to be representative of larger smelting operations) for our understanding of British Bronze Age copper smelting compared to more prominent sites in other countries.

## Pentrwyn Site Background

The Pentrwyn site is currently the only known British Bronze Age copper smelting site. It is located on the east side of Great Orme's Head peninsula, Llandudno, on the headland of Pentrwyn at SH 7812 8377 (Fig 1). The site lies at about 45m OD on a narrow (2m wide), east-facing ledge, near the base of vertical limestone cliffs (Jones 1999; Smith 2012). It is a few metres above the Marine Drive road (Fig 2), which in turn lies above further cliffs down to the sea. The ledge was originally wider, forming part of a natural terrace route, but most of it was quarried away in the 19th century when the road was built. Hence, the site may have been much larger but if so, the rest has now been lost. The east-facing site is below the cliffs and sheltered from the prevailing westerly winds rather than being in a position to exploit them for smelting. It is 0.3km to the NW of a natural sheltered quay (Smith 2012), which is near to Pigeon's Cave in which a group of 'Late Bronze Age I' metalwork (a looped palstave, two gold 'lock rings' and a bronze 'awl') was discovered in 1898 (Savory 1980).

The Pentrwyn site was discovered by David Chapman in 1997 and he has been actively involved in all the excavations. The Gwynedd Archaeological Trust (GAT) on behalf of CADW, undertook small-scale rescue



Figure 1: Location of the Pentrwyn smelting site and the Great Orme mine site.



Figure 2: General view of the Pentrwyn site excavations.

excavations in 1998 and 2011 in response to continuing erosion (GAT 1999, Smith 2012). The site has yielded a few hundred grams of copper smelting residues (slags and copper prills) mainly as particles less than 10mm in size. The most obvious source of the ore smelted is from the very extensive Great Orme Bronze Age copper mine only 1.2km to the west (Dutton and Fasham 1994). There is also a natural spring, 0.4km WSW of the Pentrwyn site at Ffynnon-y-Galchog at the top of the cliffs, which has been used as an ore washing site. An excavation discovered bone and stone tools there although the only radiocarbon date obtained was early medieval (Lewis 1993).

## Previous Work - Pentrwyn Copper Slags and Prills from the 1998 Excavation

The 1998 excavation recovered 'close to a hundred' possible slag particles (GAT 1999) mainly by wet sieving all the excavated material. The total weight of actual slag particles is not stated, but is estimated to have been around 100-200g (D Chapman pers comm) while other particles or fragments collected turned out to be natural rock or minerals. Most particles were 10mm or less in size, although one particle was around 25mm. Northover and Salter (1999) reported on their examination of 18 particles from several contexts that were mounted as polished sections. Six of them came from 'a small charcoal-rich feature' (021 in Fig 3) in which there was a sub-circular patch of material cutting the main grey silt layer of the site (002 in Fig 4 - section B). The feature (021) was about 200mm in diameter and 30mm deep and had a high concentration of smelting residues. Immediately below was a small conical hole (029) 40mm diameter by 120mm in depth, which contained charcoal rich silt and two further small slag pieces. The bulk sample of charcoal from this context produced a radiocarbon date of 3310±80 BP (Beta-127076), 1755-

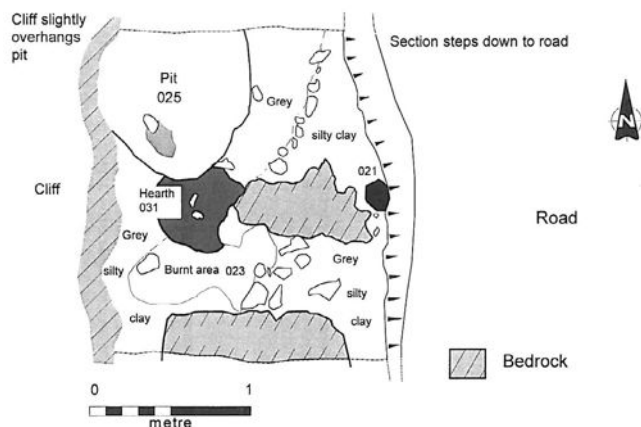


Figure 3: Plan of the 1998 excavations. Feature 021 yielded the most metallurgical particles and charcoal that gave an EBA/MBA date (after GAT 1999).

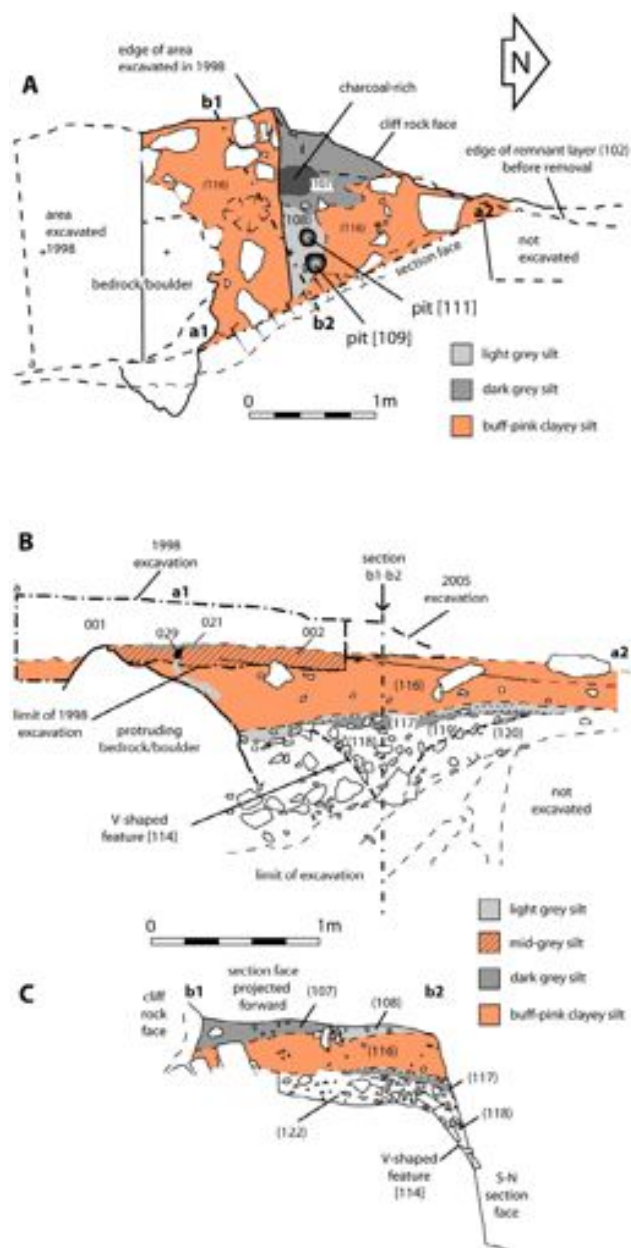


Figure 4: Plan and sections from the 2011 excavation (after Smith 2012).

1415 cal BC at 2 SD, in the Early to Middle Bronze Age, but this is now in doubt following the more detailed radiocarbon dating carried out in 2011 (see below).

A summary of the most relevant key points and conclusions from the Northover and Salter (1999) report is given below:

- Eighteen selected particles were cut, mounted and polished for examination by reflected light microscopy and electron microprobe. Heavy weathering was very apparent in the samples. The particles were interpreted as being from copper smelting rather than any other type of metallurgical residue.
- Copper prills were small, varying in size from a few microns to 3mm. Three of the prills were analysed at various points (13 point analyses on the 3mm prill, 1 to 3 analyses on the other two). Iron levels were high and consistent and finely dispersed metallic iron was observed. There were significant levels of nickel present and, in two samples, arsenic (Table 4).
- The slag did not have the chemical composition or microstructure of fayalitic iron silicate slags normally associated with the smelting of copper sulphide ores. The slags were mainly ‘calcium(magnesium)-iron oxides with a minor silicate component’ and could be termed a ‘lime-ferrite’ slag that would have had a liquidus around 1200°C.
- The high level of copper sulphides in both the slags (with some remnant chalcopyrite grains) and also along the grain boundaries of some of the copper prills suggested the ore used was ‘rich in sulphides’. This could originate from the ‘as yet un-re-discovered disseminated polymetallic sulphides’ described by Ixer (2001) as type 3a ore but not found in the Bronze Age workings.
- There was a problem linking the three Pentwyn copper prills which have a high level of impurities to the Great Orme Bronze Age ores, which Ixer and Budd (1998) state have low level impurity levels. The main ore type seen in the mine excavations ‘would not contain the levels of arsenic and nickel required’. Considering other possibilities, they concluded ‘it is reasonable to presume that they [the ores used] do derive from the Great Orme but, for the present, the connection cannot be regarded as completely certain.’
- The inhomogeneous nature of the slag and remnant ore particles suggested the slag had never become fully fluid and was probably crushed to extract the copper prills.
- The nature of the site and the small amount of slag did not suggest extensive production. They suggested ‘small-scale copper extraction’ using finely crushed ore in a ‘small charcoal-fired hearth’ rather ‘than a



fully operative production site', possibly 'for assay smelting during a period of prospecting'.

- Two lead isotope measurements on two Pentrwyn copper prills gave results consistent with the radiogenic end of the Great Orme ore range.
- The main trace elements in the three Pentrwyn prills analysed had the closest match with the Middle Bronze Age Acton Park Welsh artefact analyses. However, iron levels in the prills were much too high to match the artefacts but refining had probably reduced the iron content. The lead levels also did not match, being at trace levels in the prills, but typically around 1 to 2% in the artefacts, and this was explained by intentional lead alloying. This was believed to also explain why the lead isotope values of the prills did not match the artefacts.

### Archaeological context of Pentrwyn slags and copper prills from the 1998 and 2011 excavations

On a small truncated limestone shelf at the base of cliffs (Fig 2), the 1998 excavation (Fig 3) found a complex of pit features lying above and cut into light and dark grey silty layers (002, 010, 020, 028, 102, 104, 105, 107 and 108) beneath the topsoil (GAT 1999, Smith 2012). One feature was a sub-circular pit (025) whose fill produced fragments of burnt stone and animal bone plus marine shells and a whetstone. This pit cut a smaller pit (031) whose lower fill produced charcoal which gave a medieval radiocarbon date of 840 +/-60 BP (Beta-127077), cal AD 1035-1285 at 2 SD. Pit 031 cut a thin layer of material (023) which contained fragments of charcoal, slag, burnt stone and unburnt animal bone. Within a metre was a sub-circular patch of dark material (021), described above.

Immediately to the north of the 1998 excavated area some limited rescue work in 2005, followed by the work in 2011, discovered two further small pit features (109 and 111) in the light grey silt layer (108) (Fig 4 –plan A and Fig 5). These features are sub-circular in plan, almost vertical-sided, but tapering at the base. The fills were slightly darker and more charcoal rich (Smith 2012), and some copper prills were found when they were first uncovered in 2005, but no obvious hearth lining or vitrified ceramic were found. These pit features were at first interpreted as postholes, however, Chapman and Chapman (2013) have suggested that they could be small furnace pits (90-100mm in diameter, 90-150mm deep), possibly for 'assaying', each with a shallow slot at the west edge, which could have been for a blowpipe, and with the degraded remains of a clay 'collar' (Fig 5).

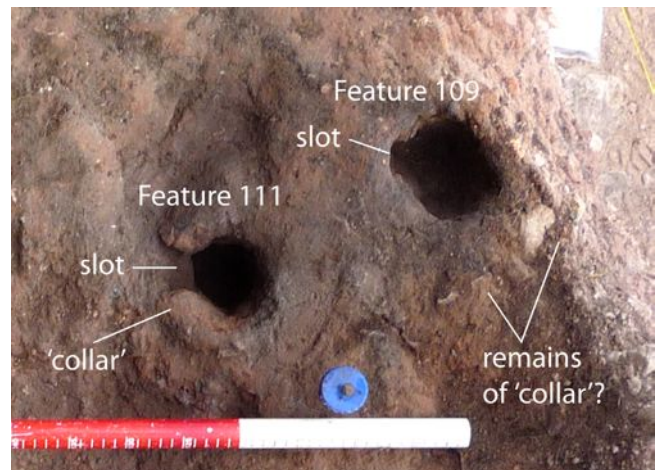


Figure 5: Features 111 and 109 (plan view; after Chapman and Chapman 2013). White portion of scale bar 200mm.

While these features might seem too small to be practical furnace pits, David Chapman, an experienced experimental archaeologist, has succeeded in demonstrating that these features could be used to smelt small amounts of high-grade malachite ore to give blister copper and leave very little trace in the ground (Chapman and Chapman 2013). Obviously, this interpretation does not exclude the possibility that larger more typical furnace pits or hearths were being used at the site, but these have left no traces or were lost when the site was truncated.

The 2011 work excavated some of the dark grey silt layer 107 (Fig 4, section C) that remained from 1998 and yielded the largest concentration of metallurgical particles recovered during that excavation. The underlying buff-pink clayey silt layer also contained some metallurgical particles. Table 1 shows the number of particles recovered from each of the contexts in the 2011 excavations.

The grey silt layers, the thickest of which was 250mm deep, lay abruptly over the deeper buff-pink silt layer (116), which was up to 400mm deep. While this buff-pink layer yielded metallurgical particles they were generally smaller (around 1mm) with very few of the coarser particles (around 10mm) that were more common in the grey layers. The buff-pink layer is regarded as probably a naturally-deposited colluvium. The shallower dark grey silt layer (117) below contained no metallurgical evidence and was interpreted as buried soil layer. It produced a few struck flint flakes and charred hazel nutshell, from which a radiocarbon date in the Mesolithic period was obtained (Table 1).

A major difference between the 1998 and 2011 excavations was the radiocarbon dates obtained from charcoal in the layers in which the main metallurgical particles

Table 1: Pentrwyn metallurgical particles from 2011 excavations by context, and radiocarbon dates on charcoal.

Context	Description	Number of metallurgical particles	Other finds	Radiocarbon dating		
				Lab Ref	Measured age BP	Date cal BC
102	grey silt	16	Pottery (1), animal bone, limpet shell, charcoal, heat-shattered pebbles			see Note 1
104	grey silt	32	Animal bone (3), shells, charcoal, heat-shattered pebbles			
105	grey silt	3				
107	grey silt	270	Charcoal, shell, bone, flint	SUERC-39896	2730±30	929-812
				SUERC-39897	2780±30	1005-842
112	grey silt	122	Pottery (1), charcoal	SUERC-44867	2727±33	930-809 or 968-964 see Note 2
108/116	grey/pink silt	17				
116	buff-pink clayey silt	206	Charcoal, bone, shell			
127	buff-pink clayey silt	27				
117	fine dark grey silt	0	Flint flakes (2), charcoal, burnt bone	SUERC-39901	8775±30	7961-7712 or 7693-7685
118	stony silt	0				
		Total 693				

Notes: 1: The two dates obtained in 1998 came from separate charcoal-rich features cutting the top grey silt layer of the site. One was also rich in slag particles and gave an EBA date of 1755-1415 cal BC. The other feature about 1m away had no slag and gave a medieval date of cal AD 1035-1285.

2: This date is on context 112, the fill of pit 111, cut into grey layer 108.

3: Particles are mostly 0.5-10mm diameter.

were found. Unlike the single Early to Middle Bronze Age date from the 1998 excavation (1755-1415 cal BC) from feature 021, three radiocarbon dates were obtained on carefully selected charcoal, two from the grey silt layer (107) and one from pit 111. These produced dates in the Late Bronze Age (LBA), around 900 cal BC (two sigma ranges from 1005 to 812 cal BC – see Table 1). Smith (pers comm) states that the earlier radiocarbon date from 1998 was obtained from a bulked sample of unidentified charcoal that could have incorporated earlier material while the three dates from the 2011 excavation were carried out on single samples of short-lived material (*Corylus avellana* and *Ilex*), which gives more weight to these new dates. Overall, the original EBA date now looks doubtful, but the original material is unavailable for further examination. For comparison, the Great Orme mine radiocarbon dates range from the EBA to the EIA (1884 to 406 cal BC), but with most dates in the EBA to MBA period. Therefore, the new Pentrwyn dates post-date the peak of mine activity. However, the new dates do appear to be contemporary with the Late Bronze Age metalwork found in Pigeon's Cave nearby.

## Materials and methods

During the 2011 excavation, it was difficult to spot all the metallurgical particles because they were mostly small (typically 1-10mm). Many were recovered by first wet screening every bag of spoil at 1mm and then by visually hand picking on the basis of colour. In addition a powerful industrial rare earth rod magnet was passed over the 1mm screened material resulting in many additional metallurgical particles being recovered. In total 86g of metallurgical material were collected consisting of about 515 particles above 0.5mm diameter, with a few coarser particles up to about 15mm in their maximum dimension. Other material collected turned out, on closer examination, to be natural rock or mineral.

A standard binocular microscope was used for initial examination of the samples. Twenty-one were selected, mounted in resin and the surfaces were ground and polished. Reflected light microscopy (RLM) in polarised light and with cross polars of the polished samples examined microstructures and made preliminary phase identifications.

A scanning electron microscope with energy dispersive spectrographic analysis (SEM-EDS) at the University of Liverpool ACE Department was used to examine microstructures using back scattering mode (BSE) and for phase identification. Quantitative analyses on some of the residues and copper prills were also carried out. The SEM-EDS was a Jeol JSM-5300 with the ED attachment using PGT Spirit software to obtain quantitative data. Calibration was on certified reference materials. All totals on Pentrwyn samples, before normalising to allow for comparison, were between 96% and 103%. SEM-EDS is well known to have limitations at low concentrations due to high background noise levels, although levels down to 0.1% are commonly quoted in the literature albeit with reservations, for example Rehren *et al* (2012), but a limit of about 0.5% is more realistic for many elements. The situation for certain elements is made more difficult due to the interference of peaks (eg the arsenic  $K_{\alpha}$  peak overlaps with the lead  $L_{\alpha}$  one).

X-ray diffraction analysis was carried out on two particles from Pentrwyn using a Panalytical MRD (PW3040).

Due to the limitations of SEM-EDS with regards to detection levels of minor elements and its unsuitability for trace element analysis, another technique was required. An electron microprobe (EPMA) was not available and although atomic absorption spectroscopy (AAS) will be available at a later date, only three copper prills will be large enough for analysis. The method therefore chosen was LA-ICP-MS; the facilities used were at the School of Earth and Ocean Sciences at the University of Cardiff: a New Wave Research laser ablation microscope (model UP213) connected to a quadrupole ICP-MS (Thermo-Elemental X Series 2) using PlasmaLab software. A short 300-400 $\mu$ m line scan with a laser wavelength of 213nm operating at 20Hz with a spot size of 55 $\mu$ m moving at 6 $\mu$ m per second was used. A helium atmosphere was used to flush the ablated material into the ICP-MS unit. Analysis was carried out on the 10 Pentrwyn copper prills that were large enough (>400 $\mu$ m) and 17 ore minerals (Williams forthcoming) on uncoated polished sections. Reference materials used were copper alloys standards (C50.01, C50.03) plus sulphide and silicate standards. The various analytical issues involved in the use of LA-ICP-MS in archaeometric research have been reviewed in the literature (Resano *et al* 2010; 2012; Speakman and Neff 2005; Neff 2012). Calibration has been one of the main discussion points with the technique. A very common strategy is to take as the internal reference sample a major element measured by SEM-EDS on the same sample, and in this study copper was used.

Table 4 provides a useful comparison of copper prill analyses by SEM-EDS and LA-ICP-MS. The differences observed may be due to two main factors. Firstly, while the data applies to the same prill, the exact area analysed differs slightly. Secondly, the SEM-EDS equipment is operating at around the detection limits for the elements present at low concentrations, while the LA-ICP-MS is designed for trace element analysis. The SEM-EDS data appears to be overestimating the low levels of iron, arsenic, lead, zinc and silica relative to the LA-ICP-MS data. Fractionation and other effects occurring during laser ablation cannot be completely discounted because this technique is relatively new in this application. The largest anomaly is with zinc and this is believed to be due to the SEM-EDS software falsely detecting the Zn  $K_{\alpha}$  peak on the shoulder of the large copper  $K_{\beta}$  peak.

To provide new and more accurate lead isotope data than that currently available, three Pentrwyn copper prills from the 2011 excavation were analysed by the NERC Isotope Geosciences Laboratory at Keyworth. For comparison, three ore samples sampled in situ from the Bronze Age workings at the Great Orme mine were also analysed. About 10mg of copper prill and about 50 mg from the more abundant ore samples were ground in a mortar and pestle and then dissolved in 16M HNO<sub>3</sub> with some added HF at 100°C and left overnight. The lead was then extracted by ion exchange chromatography using resins and a series of steps that produce a dry sample. Prior to analysis, the lead fraction was brought into solution using 1ml 2% Telfon distilled HNO<sub>3</sub> and thallium was used as a fractionation monitor. The analyses were carried out on a Thermo Fisher Neptune Plus MC-ICP-MS. The reported propagated analytical errors for the various sample ratios ranged between 0.003%



Figure 6: Metallurgical particles from the 2011 excavation. Several particles proved to be copper prills. Scale units 2mm.



and 0.012% at the two standard error (2SE) level.

## Results

### Copper slag microstructures and composition

Thirteen of the twenty-one particles were copper slags. In this paper the term ‘slag’ is used to cover any residue left over from a smelting charge that is not a copper prill. The Pentrwyn slag is very unusual in typically having a low silica and glassy phase content. This makes it very different from Bachmann’s (1982) definition of slag as ‘vitrified material’ that is ‘mainly silicates’ and is closer to the terminology used by Bourgarit (2007).

Figure 6 shows a typical selection of particles showing irregular shapes ranging from angular to rounded. Externally they were covered by corrosion products, often friable, consisting of brown to black hydrated iron oxides and spots of a green copper compound, confirmed by XRD to be a hydrated copper chloride (atacamite,  $\text{Cu}_2\text{Cl}(\text{OH})_3$ ). Most particles were weakly to strongly magnetic, reflecting the internal presence of magnetic iron oxides (magnetite and/or wustite). When sliced in half, particles were mostly black and exhibited small gas cavities. In oblique light, red cuprite and green atacamite were very apparent (Fig 7), along with the black-brown iron oxides. In reflected light, most phases appear as various shades of grey or brownish grey, except the very reflective copper metal (Fig 8).

Distinguishing the effects of around 3000 years of weathering in a saline coastal environment from the original microstructure that existed after smelting is essential for understanding the smelting process used. A sequence of weathering from copper metal to cuprite and then copper chloride was apparent in many samples

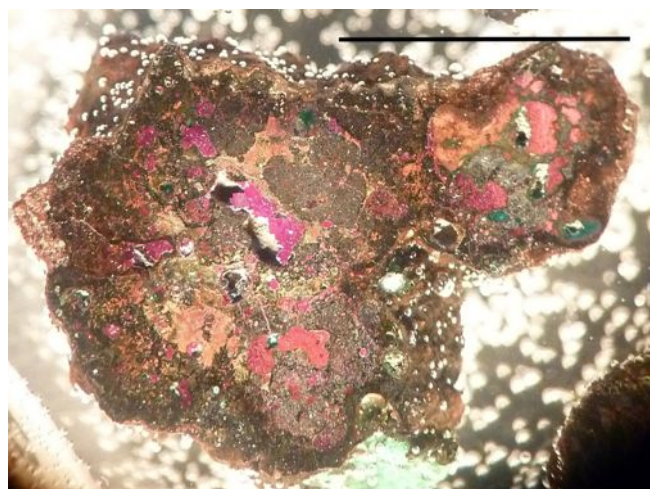


Figure 7: Polished section of a typical heterogeneous slag particle under oblique illumination. Scale bar 5mm.

with some remobilisation of the cuprite and chloride into veinlets and cavities. The magnetite and some wustite produced by the smelting process appear more resistant, but show some conversion at the sample edges to hydrated iron oxides. The small amounts of interstitial glassy or silicate phases have often been weathered or even replaced by atacamite. In the lime-rich sample (P122D), calcite from weathering is present as veinlets and near the surface of the particle.

The typically heterogeneous nature of the slag particles (Fig 8) indicate that the smelt was a long way from being fully liquid. Particle P122C (Fig 9a) is very important as it shows one of the least altered areas of any of the slag particles, revealing the original phase assemblage (Fig 9b) showing some of the included copper prills without any weathering to cuprite, abundant iron oxide and a small amount of interstitial glassy phase. Other samples show the partial or complete corrosion of the copper prills to cuprite. XRD analyses (Table 2) indicate that both magnetite ( $\text{Fe}_3\text{O}_4$ ) and wustite (FeO) are present but delafossite ( $\text{CuFeO}_2$ ) was not detected. A general wide area SEM-EDS analysis of P122C (Table 3) indicates that the particle is principally a mixture of iron oxide and copper oxide with only low silica levels, minor amounts of arsenic, calcium and secondary chloride. The high levels of copper (26%, and up to 48% in other particles) suggest copper losses in the slags were high, unless the slags were re-smelted. An analysis of the glassy phase of this particle (Table 3) shows that it is rich in iron, potash and silica, with low levels of alumina, lime and copper. Another area of P122C shows rounded white areas which were originally probably copper prills but have mainly oxidised to cuprite and, in turn,

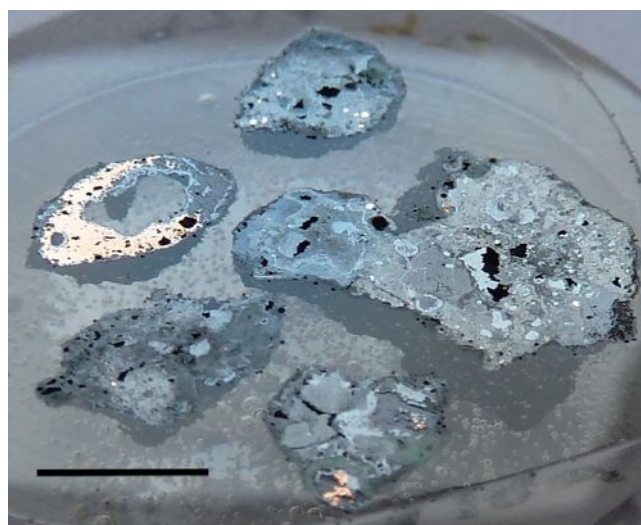


Figure 8: Polished sections of a corroded copper prill (top left) and heterogeneous slag particles (that to the right is also seen in Figure 7). All figures are in reflected light unless otherwise stated. Scale bar 5mm.

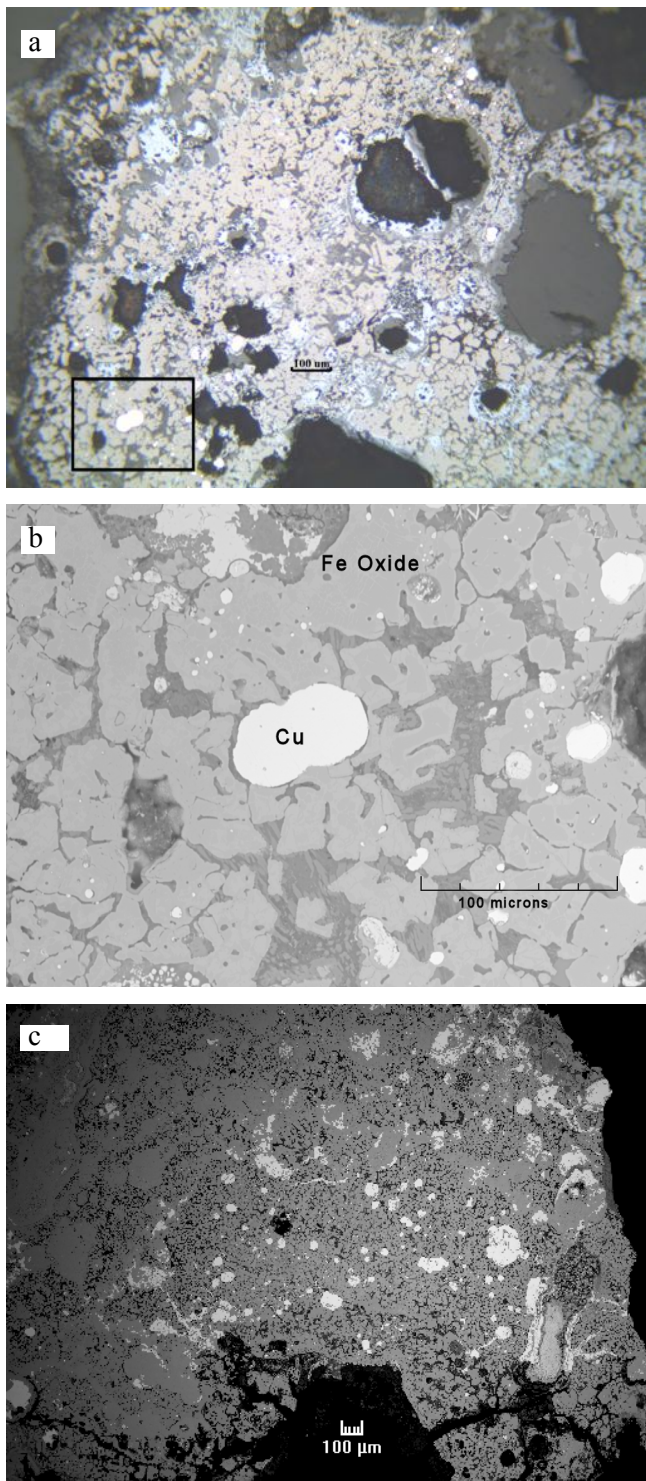


Figure 9: The least weathered slag particle P122C. a) small copper prills (white), iron oxides (brown), cuprite (light grey), atacamite (dark grey) and a small amount of a glassy phase can be seen; b) BSE image of boxed area showing copper prills (white), iron oxide (light grey) and partially devitrified interstitial glassy phases (dark greys); c) BSE image showing probable relict or 'ghost' textures which may reflect the original malachite-goethite ores. Scale bars all 100µm.

are weathering to atacamite (Fig 9c). Note the probable relict or 'ghost' textures which may reflect the original malachite-goethite ores (see below).

Table 2: XRD Results for two Pentrwyn slag particles.

Phase identification	Formula	Comment
<b>Sample P122C</b>		
Atacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	Major phase (P122C is a very weathered sample)
Magnetite	$\text{Fe}_2\text{O}_3$	
Wustite	$\text{FeO}$	
Cuprite	$\text{Cu}_2\text{O}$	
Mg Fe Oxide	$\text{MgO}_{0.239}\text{FeO}_{0.761}$	
Glassy Phase		Curve shape indicates presence of amorphous phase
<b>Sample P122D</b>		
Magnetite	$\text{Fe}_2\text{O}_4$	Major amount
Srebrodolskite	$\text{Ca}_2\text{Fe}_{1.94}\text{Mg}_{0.06}\text{O}_5$	Major amount, Mg-rich variety
Cuprite	$\text{Cu}_2\text{O}$	
Atacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	
Periclase	$\text{MgO}$	Not yet found by SEM
Glassy Phase		Curve shape indicates presence of amorphous phase
Quartz	$\text{SiO}_2$	Small, may be from oxidation of silicon-rich substrate

Particle P122A shows a similar microstructure and mineralogy to P122C, but with fewer copper prills surviving (Fig 10). The overall SEM-EDS analysis of this particle (Table 3) is similar to P122C.

Other particles serve to show further variations in microstructure, phases and composition, which suggests the samples are from several different smelting events. P10B (Fig 11) shows a similar microstructure to the previous particles, but locally has more glassy phase in which dendrites of iron oxides (probably wustite) have grown. Besides the probable replacement of copper prills by cuprite (then altering to atacamite), there is a later mobilisation and redeposition of cuprite in cavities as euhedral cubic crystals and as veinlets cutting across the particle. P16C shows the same major phases (cuprite, iron oxide and atacamite) and the presence of some laths of an iron silicate phase, but with a more irregular texture partly related to weathering.

P122D (Fig 12) is a lime-rich variant containing up to 16% Ca, while most other samples contained less than 1% (Table 3). While the copper prills, cuprite and iron oxides are still present, there is an additional phase, a calcium-iron oxide identified by XRD (Table 2) as probably a magnesium-containing variant of srebrodolskite



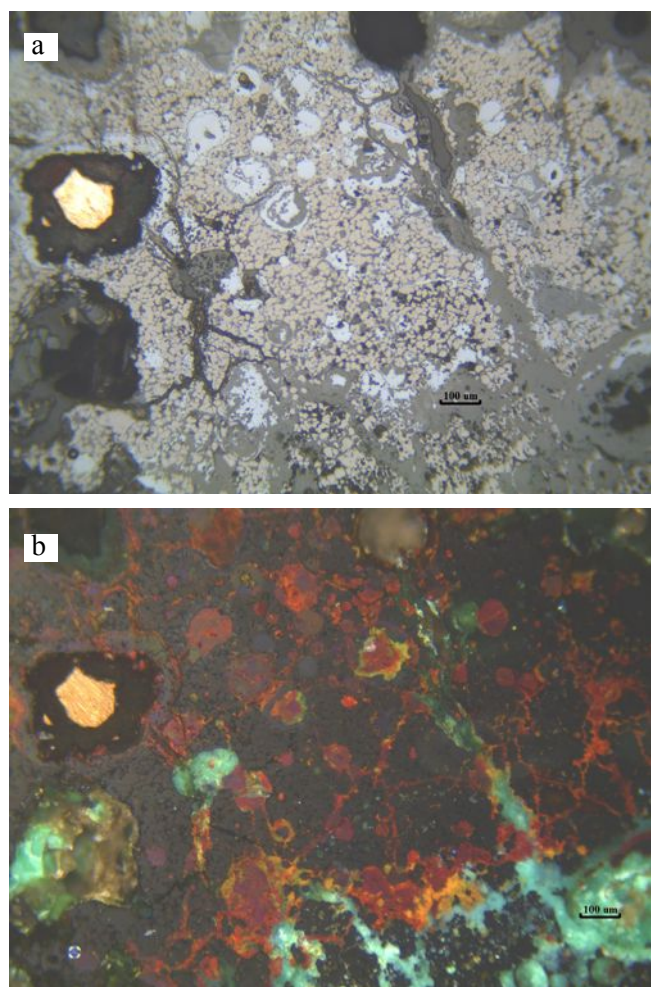


Figure 10: Slag particle P122A. a) in reflected light, and b) under cross-polars. The iron oxide appears buff in a) but black in b), cuprite light grey or red, and atacamite dark grey or green. Scale bars 100 $\mu$ m.

(Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>). XRD also suggests the particle contains periclase (MgO), but this has not been confirmed by

Table 3: Pentrwyn slag analyses (SEM-EDS, normalised wt%).

Sample	Comment	Cu	Fe	As	Ni	Pb	Co	S	Cl	Al	Ca	Mg	Si	P	K	O
P16b	General analysis	48.3	30.7	0.4	nd	0.1	0.1	0.3	0.9	0.2	0.1	nd	0.8	0.1	nd	18.0
P122C	General analysis	26.4	40.3	1.9	0.1	nd	0.2	0.1	0.9	0.6	0.4	nd	2.4	0.2	0.2	26.2
P122A	General analysis	21.7	45.1	nd	0.2	0.4	0.4	0.2	3.3	0.7	0.3	0.4	2.3	0.4	0.2	24.4
P122D	General analysis A	20.6	22.1	0.4	0.3	0.1	0.3	0.7	1.3	0.5	16.0	0.7	3.2	0.6	nd	33.0
P122D	General analysis B	3.4	50.6	nd	nd	nd	nd	nd	0.8	1.4	7.0	3.2	5.1	0.2	nd	28.5
P122D	General analysis C	8.5	48.9	nd	nd	nd	nd	nd	1.8	1.9	5.8	3.0	4.8	0.4	nd	24.9
P122A	Cuprite (Cu <sub>2</sub> O)	82.2	1.4	0.4	nd	nd	nd	nd	1.0	nd	nd	nd	nd	nd	nd	15.0
P122A	Cuprite (Cu <sub>2</sub> O)	87.3	0.5	0.6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	11.7
P122A	Iron oxide	1.3	75.2	nd	nd	0.1	0.8	nd	0.6	0.1	nd	0.1	0.4	nd	0.1	21.2
P122C	Iron oxide	0.8	70.4	0.4	nd	nd	0.9	0.1	0.5	0.9	nd	nd	0.2	nd	0.1	25.7
P122C	Glassy phase	1.2	14.1	0.4	nd	nd	0.1	0.2	0.3	3.2	1.6	0.2	19.0	0.9	18.2	40.5
P122D	Ca Fe oxide	1.0	35.0	nd	nd	nd	0.4	nd	0.4	1.6	30.5	0.2	0.8	0.3	nd	30.1
P122D	Fe Ca oxide	0.7	57.6	0.2	nd	nd	0.3	nd	0.5	0.4	13.4	0.2	0.3	0.2	nd	26.2

Note: All data calibrated using certified reference materials. Original totals between 96-103% before normalisation. nd = not detected. Analyses are expressed as elements, so for example 2.4% Si is equivalent to 5.1% SiO<sub>2</sub>.

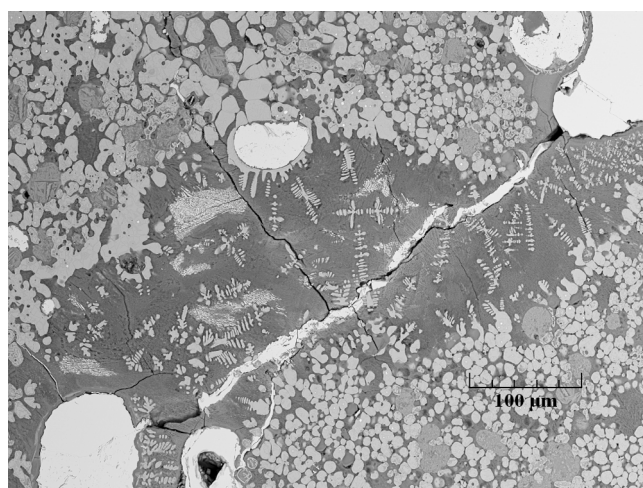


Figure 11: BSE image of slag particle P10B. The copper droplets are replaced by cuprite (white) which is also redeposited in veinlets; iron oxide dendrites (light grey) have grown in the glassy phase (dark grey); the rounded phase is iron silicate (mid grey). Scale bar 100 $\mu$ m.

SEM-EDS. A copper-iron silicate was detected by SEM-EDS and calcite (CaCO<sub>3</sub>) has formed around the weathered edges of the particle. This particle would be consistent with smelting the type of Great Orme ore that is rich in calcite.

P16A (Fig 13a) is the most weathered of the samples examined, showing almost complete conversion to copper chloride (atacamite) thereby destroying most of the original microstructure. However, the particle is still of great interest as it also contains apparently skeletal remnants of copper sulphides, chalcopyrite (CuFeS<sub>2</sub>) and probably covellite (CuS). This was the only sample from the 2011 Pentrwyn excavation in which any trace of sulphide minerals was found, apart from a minute grain

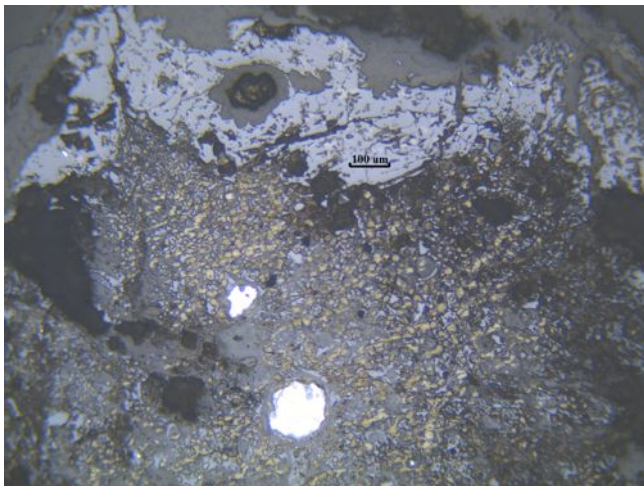


Figure 12: Slag particle P122D is a lime-rich slag variant with an additional calcium-iron oxide phase (light brown) with weathering at the edges to calcite (the pale grey zone near the top). Scale bar 100 $\mu$ m.

in particle P16B. Northover and Salter (1999) found a lot more sulphides in the samples they examined from the 1998 excavation. Another interesting feature of sample P16A is that it contains small (100 by 200 $\mu$ m) pieces of an aluminosilicate material (Fig 13b) identified by SEM-EDS which could be fragments of a ceramic or vitrified clay, but it would be unwise to draw any conclusions about the use of crucibles or clay lining from such minute fragments.

### Copper prill microstructures and composition

Eight particles were essentially copper metal prills with little or no slag. In addition, many slag particles contained microscopic copper prills. For the purpose of discussion, they have been grouped into three types based on size and microstructure.

**Type A:** The microscopic copper prills (a few microns to around 200 $\mu$ m), generally rounded or sub-rounded, that are present inside pieces of slag. They have often not achieved a full spherical shape, which is probably due to the limited formation of a glassy phase. They are generally uniform in appearance without any gas cavities and only a few inclusions but many show weathering to cuprite and/or atacamite, mostly around the outer surface (see Figs 8-10).

**Type B:** The macroscopic prills (3-10mm) that are composed of copper metal or its secondary weathered products. The prills have some rounded surfaces. In section they exhibit numerous gas cavities and inclusions, mostly of cuprite and often around crystal boundaries; this results in a speckled or dirty appearance. In one copper prill (P16D) spheres of metallic iron, about 5 $\mu$ m in diameter, were detected; they were also observed

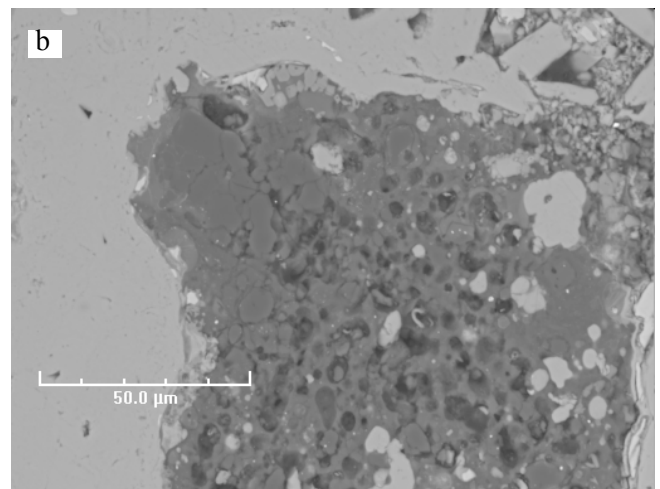
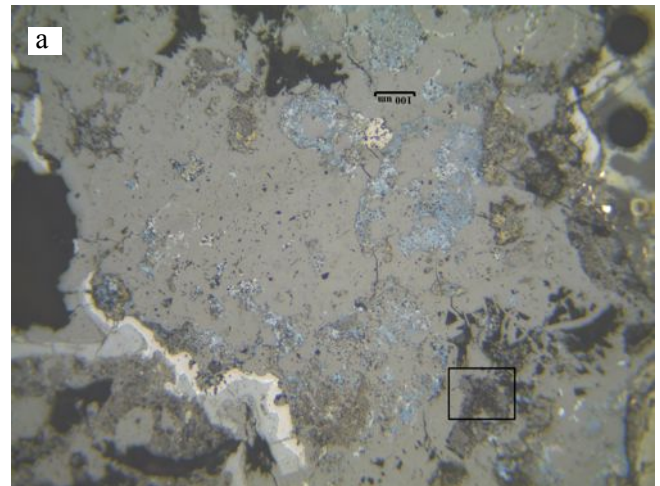


Figure 13: Weathered slag particle P16A. a) residual sulphides show as blue and yellow. Scale bar 100 $\mu$ m. b) boxed area shows an aluminosilicate material. Scale bar 50 $\mu$ m.

by Northover and Salter (1999) in one of the prills they examined. All the prills show varying degrees of weathering to cuprite and atacamite ranging from major areas of conversion in P16D with irregular remnants of copper in the cuprite (Fig 14) to less severe alteration in P12A. Only one of these larger prills (P16B) was attached to a piece of slag.

**Type C:** These are also macroscopic particles that are slightly smaller (around 4mm) than type B and are distinguished by a much 'cleaner' appearance without large gas cavities and inclusions, although some show weathering to cuprite and atacamite.

The larger prills (Type B) suggest that in at least some parts of the smelting process, the copper metal was able to locally aggregate together to form impure 'raw' metal prills up to 10mm in size. However, many very small droplets of copper metal did not come together, which suggests that the slag was crushed down to a fine grain size to extract the copper prills possibly involving



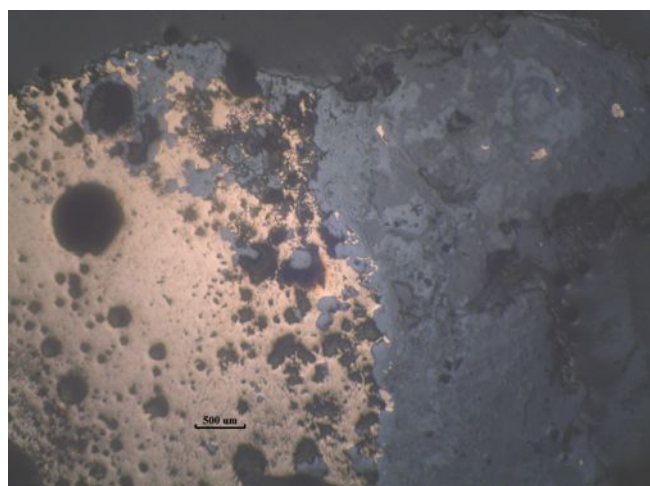


Figure 14: Copper prill P16D. Note the numerous gas cavities in the copper metal, the weathering to cuprite and atacamite (grey phases) and the irregular remnants of copper in the cuprite. Scale bar 500μm.

a concentration process based on the high density of copper metal (eg panning).

Eleven copper metal prills from the 2011 excavation were analysed using SEM-EDS and (with one exception) LA-ICP-MS, which has much lower detection limits for minor and trace elements. Table 4 shows the analytical results obtained and illustrates the known limitations of SEM-EDS at low concentrations. Planned AAS analyses should further clarify these results. Copper levels determined on freshly polished surfaces by SEM-EDS vary between 86.3% and 93.8% with minor amounts of oxygen and chloride, probably both from oxidation products. The balance, based on the LA-ICP-MS results, includes iron, sulphur probably as sulphide, arsenic and nickel. One very small prill (122D) contained higher arsenic and nickel levels. Other trace elements at low levels include silver, antimony, cobalt, cadmium, zinc

Table 4: Pentrwyn copper prill analyses (wt% unless marked ppm).

Sample	Method	Cu	Fe	As	Ni	Sb	Ag	Pb	Zn	Cd	Co	S	Sn	Cl	Si	O
<b>Samples from 2011 excavation</b>																
122D	EDS	86.5	2.3	2.7	1.4	nd	nd	0.2	1.1	nd	nd	nd	0.6	0.5	0.2	4.6
	LA-ICP-MS	Too small														
16B	EDS	90.4	1.9	nd	0.4	nd	nd	0.3	0.9	0.2	nd	0.4	0.1	0.7	0.2	4.5
	LA-ICP-MS	90.4	0.63	1266ppm	0.07	14ppm	109ppm	49ppm	94ppm	<50ppm	197ppm	<0.2	<18ppm		<0.06	
P27	EDS	93.8	0.3	0.6	0.3	nd	nd	0.1	0.8	nd	nd	0.1	0.1	0.4	0.3	3.2
	LA-ICP-MS	93.8	<0.06	1438ppm	<0.05	23ppm	135ppm	27ppm	<20ppm	<50ppm	132ppm	<0.2	<18ppm		<0.06	
P5	EDS	93.0	0.2	0.3	0.2	nd	nd	0.2	1.3	nd	nd	0.2	nd	0.6	0.2	3.7
	LA-ICP-MS	93.0	<0.06	500ppm	0.13	19ppm	10ppm	106ppm	<20ppm	355ppm	121ppm	<0.2	<18ppm		<0.06	
P16D	EDS	91.2	2.7	nd	0.2	nd	nd	nd	1.0	nd	nd	0.1	nd	0.3	0.2	4.1
	LA-ICP-MS	91.2	1.38	1576ppm	<0.05	18ppm	144ppm	16ppm	157ppm	<50ppm	80ppm	<0.2	<18ppm		<0.06	
P12A	EDS	92.1	0.3	nd	0.3	nd	nd	0.4	1.0	nd	nd	nd	0.2	0.8	0.3	4.8
	LA-ICP-MS	92.1	<0.06	817ppm	<0.05	15ppm	172ppm	31ppm	<20ppm	511ppm	8ppm	<0.2	<18ppm		<0.06	
P12B	EDS	88.4	2.1	1.1	0.1	nd	nd	1.5	0.8	nd	nd	nd	0.2	0.6	0.4	4.8
	LA-ICP-MS	88.4	0.71	616ppm	0.08	132ppm	173ppm	12417ppm	346ppm	593ppm	345ppm	0.29	<18ppm		<0.06	
P14B	EDS	88.1	3.4	0.4	0.1	nd	nd	0.1	0.9	nd	nd	nd	nd	1.0	0.4	5.6
	LA-ICP-MS	88.1	1.10	1837ppm	<0.05	27ppm	114ppm	63ppm	107ppm	107.0	90ppm	<0.2	<18ppm		<0.06	
P15	EDS	90.6	3.0	0.3	0.1	nd	nd	0.3	0.5	nd	nd	0.8	nd	0.7	0.3	3.4
	LA-ICP-MS	90.6	2.48	952ppm	<0.05	18ppm	211ppm	74ppm	843ppm	407ppm	238ppm	2.99	<18ppm		<0.06	
P10A	EDS	90.0	2.7	nd	0.3	nd	nd	0.1	0.5	nd	nd	nd	0.2	1.2	0.4	4.5
	LA-ICP-MS	90.0	0.84	2291ppm	<0.05	33ppm	202ppm	145ppm	225ppm	<50ppm	310ppm	0.38	<18ppm		<0.06	
P10B	EDS	86.3	3.5	0.4	0.3	nd	nd	0.5	1.1	nd	nd	0.9	0.1	0.7	0.3	5.8
	LA-ICP-MS	86.3	0.97	2848ppm	0.09	32ppm	244ppm	68ppm	268ppm	<50ppm	204ppm	0.47	<18ppm		<0.06	
<b>Samples from 1998 excavation</b>																
2222	EMPA	Mean of 3	96.95	2.83	0.62	0.29	0.00	0.03	0.08	0.00	-	0.09	0.02	0.00	-	-
		Min	94.87	2.62	0.18	0.27	0.00	0.00	0.03	0.00	-	0.08	0.02	0.00	-	-
		Max	98.65	3.04	1.29	0.31	0.00	0.05	0.15	0.00	-	0.11	0.03	0.01	-	-
2227	EMPA	One analysis	98.24	2.44	0.00	0.82	0.01	0.16	0.02	0.04	-	0.17	0.08	0.01	-	-
2237	EMPA	Mean of 13	94.39	2.74	0.52	0.20	0.01	0.07	0.04	0.02	-	0.04	0.04	0.01	-	-
		Min	92.19	2.25	0.00	0.14	0.00	0.00	0.00	0.00	-	0.02	0.00	0.00	-	-
		Max	95.50	3.22	1.48	0.24	0.05	0.10	0.09	0.06	-	0.06	2.67	0.03	-	-

Notes 1: LA-ICP-MS uses the copper value from EDS as the internal standard.  
 2: The EDS data was calibrated using certified reference materials and then normalised. nd = not detected. Original totals 98-102%.  
 3: The data for the prills excavated in 1998 is taken from Northover and Salter 1999. - = no data given. Totals are 98-102%.



and lead (except P12B, which contains 1.5% lead).

The iron level is of particular interest when considering the smelting technology, according to Craddock (1995, 140). He suggested that the virtually 'non-slugging' low temperature poorly-reducing smelting model for high-grade ores would give very low iron levels of around 0.05%. Many artefacts from the British Bronze Age are generally low in iron, but with exceptions. For Pentrwyn copper prills, the iron levels, with a few exceptions, are high to very high, being between 0.63 and 2.48% (Type A and B). Northover and Salter (1999) obtained EPMA results for iron that were also high at 2.25-3.22%. These iron levels suggest that at times the smelting may have achieved moderately or highly reducing conditions and this is supported by the presence of at least some wustite, some metallic iron particles in certain prills and the apparent absence of delafossite in the slag. However, in the 2011 copper prill results, there are three exceptions all containing far less iron (<0.06% Fe by LA-ICP-MS). Two of them are particles P27 and P5 which are 'clean' inclusion-free copper prills (Type C). The other one is P12A, which is a large prill but with gas cavities (Type B).

How then do we explain the very low iron levels in these three prills, two of which come from the buff-pink layer rather than the grey silt layers? One possibility is that they have been through a secondary refining process resulting in the lowering of the iron level and this would also explain their 'cleaner' appearance. Another explanation is that some low iron prills were formed directly during the variable smelting conditions, in areas of lower temperatures and less reducing conditions.

The indications are that there were several stages to the process used. In the initial smelting stage the malachite in the ore formed copper prills of varying sizes while iron oxides present in the ore transformed from goethite to magnetite and wustite with only a small amount of glassy phase due to the low silica content of the ores. The

prills must then have been released by crushing and then concentrated by hand picking and possibly washing. The next stage would involve re-melting the combined prills to refine and cast the metal, presumably using crucibles (although no clear fragments have yet been identified) at this site or elsewhere.

### Linking Pentrwyn copper prills to British Bronze Age metalwork

Considering all the data in Table 4, it shows variable trace element levels, often with significant arsenic and nickel levels and generally low levels of antimony, silver, and cobalt. If we assume, as previously discussed, that the iron levels were reduced by refining and that lead was an accidental or deliberate addition, then the Pentrwyn copper is consistent with several of the Early and Middle British Bronze Age metalwork groups defined by Northover (1980; 1991), particularly the Acton Park metalwork assemblage. The broader Great Orme project is defining a mine-based metal group (to be used in parallel with artefact-based groups) based mainly on numerous analyses of ores from the Bronze Age workings. Supporting evidence is being drawn from the Pentrwyn prill analyses in this paper and the analyses of small pieces of bronze found in the mine, possibly from mining tools, which may have had a local origin. All this evidence should reveal the full range of metal compositions that the Great Orme mine could have produced. The initial analytical results from the ores will be reported elsewhere (Williams forthcoming) but the arsenic and nickel levels normalised for copper are similar to, and often much higher than those obtained from the prill analyses reported here, even allowing for some smelting losses. All the new evidence differs from the influential 'trace element poor' view of Great Orme metal proposed in the past (Ixer and Davies 1996, Ixer and Budd 1998 and Ixer 2001), which would not match much Bronze Age metalwork. The new evidence supports the views expressed by others about the probable importance of Great Orme metal, particularly in the Middle Bronze

Table 5: New lead isotope data for three Pentrwyn copper prills and three Great Orme ores.

Sample	NIGL Batch No	206Pb/204Pb	2SE%	207Pb/204Pb	2SE%	208Pb/204Pb	2SE%	207Pb/206Pb	2SE%	208Pb/206Pb	2SE%
<b>Pentrwyn copper prills</b>											
P16C	P625:6	19.874	0.006	15.708	0.008	38.731	0.01	0.79037	0.003	1.9488	0.0050
P13	P625:7	18.979	0.007	15.667	0.009	38.589	0.011	0.82548	0.003	2.0332	0.0052
P16A	P625:10	19.470	0.012	15.689	0.009	38.593	0.011	0.80584	0.01	1.9822	0.0092
<b>Great Orme mine malachite-goethite ore samples (E1 near galena vein)</b>											
E1	P625:8	18.317	0.007	15.632	0.009	38.344	0.01	0.85345	0.003	2.0934	0.0050
G33	P625:9	19.147	0.006	15.674	0.008	38.702	0.01	0.81859	0.003	2.0213	0.0050
G15	P625:11	19.917	0.012	15.697	0.014	38.664	0.017	0.78812	0.003	1.9413	0.0064

Age (Rohl and Needham 1998, Northover and Salter 1999, Timberlake 2009 and Bray 2012).

### Linking Pentrwyn slag and copper prills to Great Orme mine: lead isotope results, ore type and composition

Lead isotope analysis offers another route to link ores to smelting slags/prills and metal artefacts. Unlike most copper ores from British Bronze Age mines, those from the Great Orme mines are strongly radiogenic. Therefore, instead of occupying a small specific area on plots of lead isotope ratios, like many other mines, it occupies a long linear zone stretching far beyond the area of ores from other dated mines and also of most analysed British Bronze Age metalwork. Figure 15 plots the new data for three Pentrwyn copper prills and three Great Orme ores (malachite-goethite) (Table 5) as well as previous Great Orme data (Joel *et al* 1995; Rohl and Needham 1998; Northover and Salter 1999) which includes ores (malachite (6), azurite (3), chalcopyrite (5) and galena (2)), two Pentrwyn slag samples and five bronze particles from the mine.

The Pentrwyn copper prills give similar radiogenic results within the range of Great Orme ores and this leads to the conclusion that the prills are a good match with the most obvious ore source. Ores from other dated British Bronze Age mines are not so markedly radiogenic and lie in the top right hand corner of Figure 15 but with no overlap with the Great Orme ores in that area, except for ore from Alderley Edge (Williams forthcoming). While about half the lead isotope results for Great Orme ores and prills lie in the area where most Bronze Age artefacts

plot in Figure 15, the other half do not. An explanation for how copper with these lower ratios could shift into the main isotope area of Bronze Age metal artefacts is provided by the presence of veins of galena in the Great Orme deposit, which appear to geologically predate the copper mineralisation (Ixer and Davies 1996). The lead isotope values measured on three Great Orme galena samples (PbS) are well within the region of most British Bronze Age metalwork. Many of the prills and the main ore minerals that lie away from the metalwork region in Figure 15 mostly have very low lead contents (Table 4). It would therefore take very little lead mixing from the areas around the lead veins in the copper deposit to swamp the radiogenic lead isotope signal in the copper minerals and so bring them into the area of the other Great Orme ores, which is in the main area of British Bronze Age metalwork. This suggestion is supported by the copper ore sampled near to a known galena vein, which contained over 1% lead and whose isotopic results are in the main metalwork area. One prill (P12B) has a high lead content (over 1.2%), but a lead isotope measurement has not yet been made. Another possibility for the isotope ratio shift in the metal is that it is the result of deliberate, rather than accidental, lead alloying where the copper ore/metal result is swapped by the added lead (which could still have originated from the Great Orme lead veins). Significant lead levels are common in certain British Bronze Age metalwork assemblages (*eg* Acton Park). This topic will be revisited when the lead isotope part of a Great Orme metal group is defined.

While the full details of the parallel study on the copper ores from the Great Orme Bronze Age mine workings will be reported separately (Williams forthcoming),

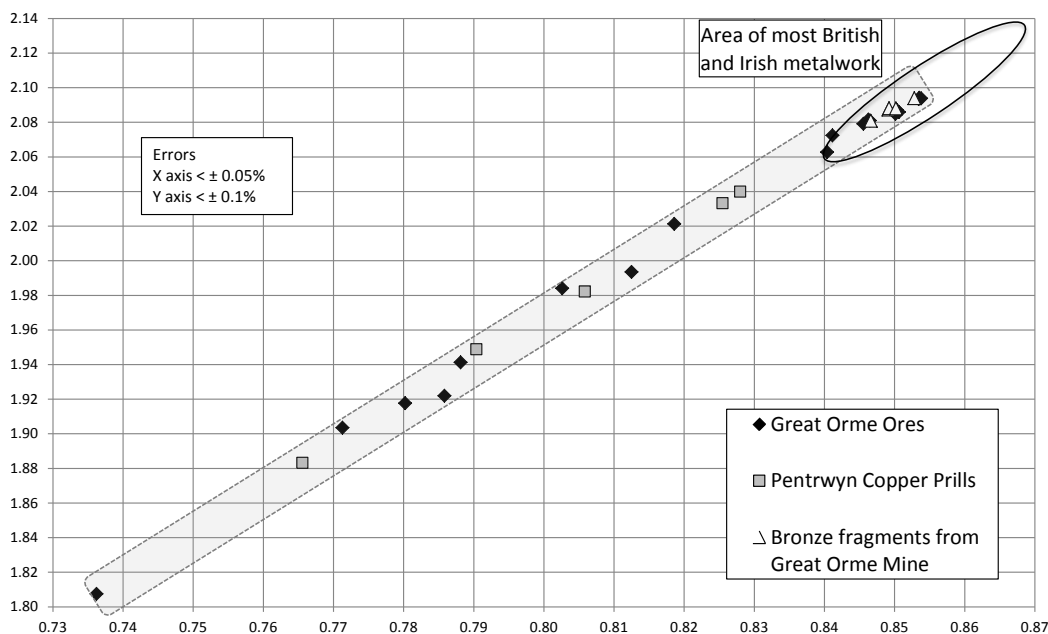


Figure 15: Lead isotope data for Great Orme ores, Pentrwyn copper prills and bronze particles from the mine. Data from Table 5, Rohl and Needham 1998, Joel *et al* 1997 and Northover and Salter 1999.

some key findings are very relevant when discussing links between the smelting slags/prill and ore composition and microstructure.

- It has been established that the dominant ore found in nearly all the Bronze Age mine workings is a malachite-goethite ore (Fig 16) formed by the in-situ oxidation of primary chalcopyrite sometimes containing small amounts of residual sulphide (elsewhere there are smaller amounts of other types of secondary ore).
- The initial bulk analyses of two Great Orme ores show some similarities to the Pentwyn slags, with low silica levels and similarities in the major, minor and trace elements that are present or absent.
- Some of the ‘ghost’ textures in the Pentwyn slags have similarities to those seen in the malachite-goethite ores (Figs 9c and 16).

### Interpretation of the smelting process used at Pentwyn

Views on the copper smelting techniques used in prehistory have evolved over the last 50 years. At the famous sites of Timna in Israel and Faynan in Jordan, major copper smelting sites were revealed which had large tonnages of prominent black silica-rich fayalitic copper slags that are almost indestructible. At Faynan, there is an estimated 5,000 tons of Early Bronze Age II slag (3100-2300 BC) over 13 sites with up to 200,000t from the Iron Age and Roman periods (Hauptmann 2007). Silica-rich tap slags have also been found in parts of Alpine Europe from the Middle and Late Bronze Age, including the Mitterberg in Austria and Trentino in Italy (Craddock 1990 and 1995; Stöllner 2010).

However, it has become increasingly apparent in more recent years that the earliest copper smelting, mostly associated with mainly high grade secondary carbonate or oxide ores without added fluxes, used simple or so-called ‘primitive’ smelting processes usually on a small-scale, which leaves very little trace in the archaeological record. Hauptmann (2007), for example, described Chalcolithic crucible smelting at Faynan in oxidising conditions, without added fluxes, only partial liquid formation and minimal slag. This was based on the availability of rich oxide ores (33-66% Cu), which was likely to have made a more complex slagging technique ‘unnecessary’. One option he proposed was the use of a simple stone structure powered by wind and a two-step process where the copper prills produced were separated from the slag and re-melted in crucibles. Bourgarit (2007) reviewed the growing evidence for the ‘Chalcolithic’ (the second half of the 5th to the 3rd millennium) copper smelting at twenty sites in the

Middle East and Europe. These simple processes were very variable, but typically involved the use of simple furnaces (eg ‘hole in the ground’). They generally had no added fluxes, poorly-reducing conditions, produced mostly high viscosity ‘immature’ non-equilibrium slags and used crushing of the smelt to release the copper prills produced, often leaving very little slag waste. Of his twenty examples, he thought sixteen smelted either oxide or mixed oxide-sulphide ores, with four possibly having smelted sulphide ores.

Craddock (1995) and Bourgarit (2007) have reviewed the major change to a fully slagging process by the 3rd millennium BC in the Middle East. The new process used substantial furnace structures and produced low viscosity liquid slags in which the copper droplets could sink to the bottom. The low viscosity slag composition was often achieved by the addition of one or more additives (eg iron oxide, silica or manganese oxide). Craddock (1995) considered the advantages of the new process were fuel efficiency and the ability to smelt lower grade ores. The furnace operation could be kept going longer with the ability to tap off the waste as slag. All this allowed larger scale production. By the Middle and Late Bronze Age, fully slagging processes were also being used in parts of Alpine Europe (eg Mitterberg and Trentino). The importance of the various factors in stimulating innovation or resulting in a decision to switch to the new process can be debated. Fuel shortage may have been a factor in the barren regions even where oxidic ores were available (eg Timna and Faynan) and/or allowing lower grade oxidic ores to be

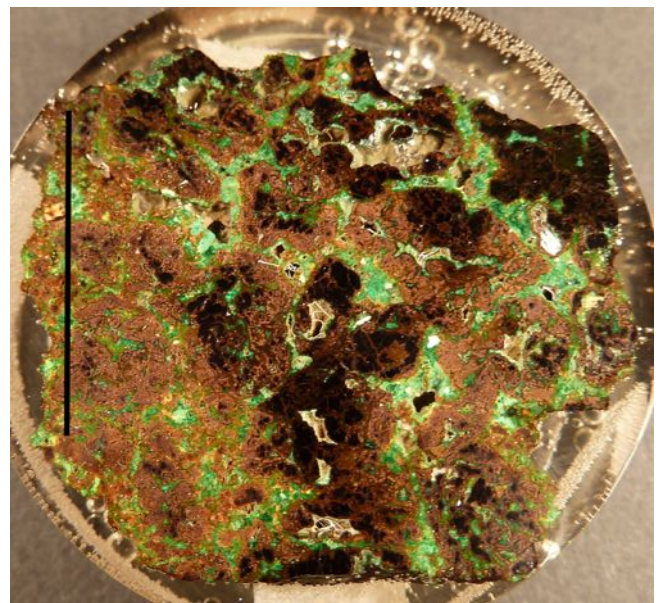


Figure 16: A typical ore from the Great Orme Bronze Age workings in oblique light showing an intimate intergrowth of brown/black goethite and green malachite the product of supergene weathering of chalcopyrite. Scale bar 15mm.



used. Elsewhere, the slagging process may have been part of the technology required to successfully smelt more difficult ores, particularly sulphide ores.

However, there is increasing evidence that in parts of Western Europe variations on the old simple or 'primitive' smelting process using rich oxidised ores continued throughout the Bronze Age. Rovira (2002) reviewed the evidence in Spain where there were numerous small deposits of copper carbonate (malachite) and oxide ores. A 'very simple' or so-called 'primitive' smelting process was used, which involved ceramic bowls ('reduction basins') probably using blowpipes and poorly reducing conditions, followed by the crushing of the slags with stone hammers. This process appears to have continued to be used in the Iberian Peninsula for about three millennia until the early Iron Age. (Figueiredo *et al* 2010, Rovira 2002, Rovira and Montero-Ruiz 2013).

Bronze Age smelting evidence in Britain is currently limited to the small Pentrwyn site, but the simple process being used there may have been used throughout the life of the mine given the plentiful supplies of rich secondary malachite-goethite ores that were worked for up to one millennium in the Bronze Age. This could suggest parallels with Iberia. The situation in Ireland at the Copper Age/Early Bronze Age Ross Island mine in Ireland looks more complicated. O'Brien (2004 and 2013) believed massive tennantite ( $\text{Cu}_{11}\text{FeAs}_4\text{S}_{13}$ ) was 'smelted using a low temperature, non-slagging technology'. Tennantite, with its low iron content, should be easier to smelt than chalcopyrite, but in addition some secondary oxidised minerals from the Blue Hole mine may have been used. There is no evidence of a slagging process until the 7th or 8th centuries AD when chalcopyrite ore was smelted using a slag-tapping furnace (O'Brien 2004).

The recovery of only very small amounts and small pieces of slag material, as is the case at Pentrwyn, is a common feature of many small prehistoric copper smelting sites that used a simple smelting process (Bourgarit 2007). Some sites only had one or a few actual slag particles (Figueiredo *et al* 2010; Radivojevic *et al* 2010). The lack of slag near mine sites has also been explained by ores being taken away to be smelted at settlements, as was observed in Spain and Jordan (Rovira 2002; Hauptmann 2007). Other factors that reduce the chances of discovering the slags include their crushed form, the low volume produced by high grade ores and their removal for re-smelting elsewhere during later periods, since they had high residual copper contents.

The wide distribution of Pentrwyn particles dispersed over two layers and the variety of phases present (*eg* with and without calcium phases, probably related to the ore type used) suggests that the Pentrwyn slag particle assemblage represents a number of smelts rather than one atypical smelt. The presence of easily recoverable copper prills up to 10mm in diameter suggests a process that was successful in producing copper metal, probably with some aggregation of smaller prills, which had to be released from the minimal slag by crushing, albeit with a significant loss of copper in the slags. Evidence from the ore/slag chemical compositions, lead isotope data and the microstructures of the ore and slag all suggest that the Great Orme malachite-goethite secondary ores with some residual sulphide were smelted at Pentrwyn. There is no evidence for roasting of any sulphide ore or for matte smelting and it is considered most likely that any residual sulphide was ignored and remained in the slag. Some of the sulphide (chalcopyrite) could have reacted to copper metal based on the interactions between mixed oxide-sulphide ores described by Craddock (1995) and Rostoker *et al* (1989). The conclusion of Northover and Salter (1999) that sulphide-rich (chalcopyrite) ores were the principal ore being smelted at Pentrwyn is not consistent with the latest evidence from the ores and slags. The sulphide they observed in the slags is believed to be the residual sulphide present in the mainly oxidised ores and was discarded in the slag.

The level of silica in the slag at around 5%  $\text{SiO}_2$  is exceptionally low compared to most other known prehistoric copper slags (typically 40-50%), whether from a simple process or a fully slagging process (Hauptmann 2007; Bourgarit 2007). This is due to the ore geology at many other ancient copper deposits, which occur in more silica-rich rocks (either the country rock or the presence of quartz as a major gangue mineral).

Apart from the silica content, the Pentrwyn smelting residues fit most aspects of the earliest Chalcolithic smelting described by Hauptmann (2003) at Faynan which was characterised by high-grade ores, no additives, never having been fully molten, producing heterogeneous slags, use of crushing to recover copper prills, high copper levels in smelting residues and poorly reducing conditions. However, the presence of both wustite and magnetite at Pentrwyn suggest reducing conditions could have been stronger locally but variable in the smelting.

The Pentrwyn slags could have been produced in 'hole in the ground' furnace pits which would have left very little archaeological trace as was seen 18 months after

experimental copper smelting experiments at Flag Fen (Timberlake 2007) and in the work of Chapman and Chapman (2013). In the literature, a wide variety of mainly circular furnace pits or holes are described, which ranged in diameter from around 100mm to 1200mm with depths ranging from 100mm to 700mm (Bourgarit 2007; O'Brien 2004). These sources describe sites with and without evidence for the use of a clay or stone lining in the pit, the use of a wide flat crucible or ceramic dish like that seen in Iberia (Rovira 2002), the use of small crucibles (100mm to 150mm diameter; Hauptmann 2007) or where no ceramic was used at all. The very small pit features found at Pentrwyn (100mm diameter with clay side groove) have been shown by Chapman and Chapman (2013) to be capable of smelting malachite operated by one person with a blowpipe without using any ceramic, but output would have been small.

There is currently no firm evidence of crucibles being used at Pentrwyn with the small (200µm) fragments of ceramic material found in slag particle P16A (Fig 13b) being inconclusive. *Ibid* (2013) and Timberlake (2007) have demonstrated that smelting can be achieved without the need for a crucible, at least in the first stage of smelting. Crucibles would have been essential for the following stage of refining and casting, although this may not have been done on the same site as smelting.

What is very clear from the microstructures, mineralogy and chemical compositions of the slags is that there is currently no evidence of a fully slagging process like those at the famous large-scale Bronze Age/Iron Age copper smelting sites in the Middle East or Alpine Europe mentioned earlier being used at the Great Orme. Pentrwyn smelting had more in common with the simple small-scale copper smelting technology of Chalcolithic sites in Europe and the Middle East, which persisted in Iberia until the end of the Bronze Age (Rovira 2002). The Late Bronze Age dates for the Pentrwyn site suggest parallels to the Iberian experience, rather than representing any regression in technology towards the end of the Great Orme mine's life.

Whether in fact a fully slagging process would have offered any decisive advantages in smelting the plentiful high-grade, low silica copper ores of the Great Orme mine is considered very debatable. There is an association in the literature (Craddock 1995) between slag tapping and large-scale production of copper, whether in the Middle East or parts of Alpine Europe. However, one of the main reasons these sites are prominent is because of the survival of large amounts of coarse, highly resistant silica-rich glassy slags in the archaeological record. The

ratio of slag to copper metal at Timna was estimated by Merkel (1990) to be around 15:1, taking into account the ore grade and flux additives. At Great Orme the ore grade is considered to be much higher with no evidence for flux addition and so the figure could have been around 3:1; the slag amount could thus have been up to five times lower. This radically lower volume, combined with its fine-grained nature after crushing and a tendency to weather (because of its low silica content), make it much less visible in the archaeological record, even if copper production levels were substantial. In addition, the charcoal requirements for such high grade smelting would probably have been much lower given the lower slag to metal ratio, even if the main smelting operations may have lacked other economies of scale.

## Conclusions

Detailed analyses of the small particles of copper slags and prills recovered from the Pentrwyn site during the 2011 excavations have revealed strong evidence that a simple or so-called 'primitive' copper smelting process was being used in Britain in the Late Bronze Age using high-grade malachite-goethite ores from the exceptionally rich secondary ore deposit at the nearby Great Orme mine.

Lead isotope data links the Great Orme ores to the Pentrwyn copper prills. The Pentrwyn slag evidence is consistent with the use of the Great Orme malachite-goethite ores, which a recent sampling programme has revealed dominated the Bronze Age workings, though with variable residual sulphide. The sulphide observed in the slags in previous work is believed to be from this residual sulphide (chalcopyrite) and was probably discarded in the slag.

Smelting of the ore probably took place in simple 'hole in the ground' features, either in broad furnace pits, which are no longer visible and/or in the small 'post-hole' type features excavated in 2011. The heterogeneous slag mineralogy suggests the smelt was never fully liquid, and had variable reducing conditions and temperatures. There is no evidence for any fluxing additives (eg silica) and because the ores are remarkably low in silica, they could only produce low levels of glassy phase. This was insufficient to allow full separation of metal and slag, but probably enough to allow some copper metal aggregation. The use of this simple process required the crushing of the smelt to extract the copper prills and therefore must have been followed by a re-melting and refining stage, presumably in a crucible, to reduce iron levels.

Despite the remains at Pentrwyn apparently being on a small scale towards the end of the mine's long prehistoric life, they offer a window onto the simple smelting process that may have been used throughout the life of the mine at larger smelting sites locally or at more distant locations. This has a technological parallel with Iberia where a similar simple smelting process using locally plentiful secondary carbonate and oxide ores was used on a small scale for millennia, including during the Late Bronze Age.

This contrasts with the larger-scale fully-developed slagging process in use by the 3rd millennium BC in the Middle East (eg Timna and Faynan) on oxidised ores and later in Europe (eg Mitterburg and Trentino) on sulphide (chalcopyrite) ores. The reason or reasons the process was developed or adopted at a particular site may have varied but fuel efficiency, lower ore grades and ore types that were more difficult to smelt are probable factors. While the simple or 'primitive' process of smelting of high-grade, mainly oxidic, ores produced very little or no surviving slag, the slag-tapping process produced large amounts of silicate slag.

Given the small scale and late date of the Pentrwyn site relative to the large scale of the mine with a much earlier mining activity peak, there is considerable potential to discover a larger smelting site elsewhere on the Great Orme. One possibility is around the known geochemical anomaly near the summit, a location ideal for wind-assisted smelting. The magnetite in the slags suggests that extensive magnetometer surveys of the Great Orme could detect a larger site. Another possibility is that the ore was smelted elsewhere on settlement sites or in areas with more abundant fuel resources.

This study is part of the broader ongoing project to link Great Orme ore to copper/bronze artefacts in the British Bronze Age metalwork databases (OXALID and OXSAM). The limits of a Great Orme mine-based metal group are being established, mainly based on a systematic geochemical investigation of Great Orme mine ores. Supporting evidence is being drawn from the analyses of the Pentrwyn slags/prills in this paper and the analyses of small pieces of bronze found in the mine, possibly from mining tools, which probably had a local origin. Initial analyses from all these various materials, show variable trace element levels, but frequently with significant levels of arsenic and nickel, consistent with a substantial proportion of Middle British Bronze Age metalwork, particularly the Acton Park metalwork assemblage (Williams forthcoming).

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