The Great Orme Bronze Age copper mine: Linking ores to metals by developing a geochemically and isotopically defined mine-based methodology

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THE GREAT ORME BRONZE AGE COPPER MINE: LINKING ORES TO METALS BY DEVELOPING A GEOCHEMICALLY AND ISOTOPICALLY DEFINED MINE-BASED METAL GROUP METHODOLOGY

Robert Alan Williams*

Abstract

Understanding the connectivity between Bronze Age communities involving the movement of people, materials and technological knowledge can be assisted by re-invigorating metal provenance studies. Completely rethinking our methodology by switching around from an artifact-based metal group approach to a new mine-based metal group approach based on the discovery of major Bronze Age mine sites in recent decades. This approach relies on using expertise from geological disciplines combined with the latest analytical techniques and are here applied to the Great Orme mine in north Wales which is one of the largest surviving Bronze Age copper mines in Europe. The results show this mine to be a major source of arsenic–nickel metal contrary to low impurity claims of the past literature. The evidence suggests that the 'golden age' of production at the Great Orme was around 1500 to 1400 BC in the early Middle Bronze Age (Acton Park), when it probably dominated the metal supply in Wales and Lowland Britain with some exchange to the near continent.

Key words: Bronze Age, Britain, Wales, Great Orme, metal, copper, mines, provenance, mine-based metal group, arsenic, nickel, Acton Park, exchange, connectivity, geology, geometallurgy.

Resumen

La comprensión de la conectividad de las comunidades de la Edad del Bronce implica el movimiento de personas, materiales y conocimiento tecnológico y en este sentido los renovados estudios sobre procedencia del metal pueden ser de gran ayuda. Es necesario repensar nuestra metodología cambiando el enfoque desde el grupo metálico basado en el objeto hacia un nuevo enfoque de grupo metálico basado en las minas a partir de la identificación de las principales minas de la Edad del Bronce realizado en las últimas décadas. Este enfoque conecta los conocimientos de disciplinas geológicas con las últimas técnicas analíticas y aquí se aplica al caso de la mina de Great Orme en el norte de Gales, que es una de las minas de cobre de la Edad del Bronce más grandes que sobreviven en Europa. Los resultados muestran que esta mina fue un recurso importante de metal con arsénico y níquel a pesar de que anteriormente se le ha considerado con nivel bajo de impurezas. Los datos sugieren que la «edad de oro» de la producción en el Great Orme Fue alrededor de 1500 a 1400 a.C. en la Edad del Bronce Medio temprano (Acton Park), cuando es probable que dominó el suministro de metal en el País de Gales y de las tierras bajas de Inglaterra con algunos intercambio con el área continental próxima.

Palabras clave: Edad del Bronce, Inglaterra, Gales, Great Orme, metal, cobre, minas, procedencia, grupo metálicos basado en minas, arsénico, níquel, Acton Park, intercambio, conectividad, geología, geometalurgia.

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METAL PROVENANCE STUDIES AND ARTEFACT-BASED METAL GROUPS

Increasing our understanding of the connectivity between Bronze Age communities involving the movement of people, materials and technological knowledge can potentially be assisted by re-invigorating metal provenance studies. A re-thinking of our methodology needs to be based on bringing in practical expertise from other disciplines. Part of this involves systematic ore sampling and using the latest and most appropriate scientific analytical techniques to provide representative and accurate results.

Many archaeologists in the past have eagerly pursued the hope of being able to analyze Bronze Age metal artefacts and trace them to a mine or mining area. Pernicka (2014) and Pollard and Heron (1996) reviewed developments starting with the aspirations of researchers in Europe in the nineteenth century. In Britain, William Gowland (1906 and 1912), professor of metallurgy, at the Royal School of Mines sought origins of the metals and noted the presence of arsenic and silver in analyses of Irish copper axes. Advances in analytical techniques allowed a larger number of samples to be analyzed with pioneering work by Otto and Witter (1952) in Halle who analyzed 1300 mainly German artefacts but few ores. Also Preuschen and Pittioni (1937) in Vienna who analysed over 6000 artefacts and 2000 ores from Central Europe, unfortunately only recording the presence or absence of elements rather than quantification (Pernicka 2014,240-241). Both these projects proposed their own artifact-based groups with some regard to general ore types.

The scientific approach of the Austrian work influenced British researchers (Davies 1935,v, Coghlan 1958,57). Research resumed after the second world war and in 1945 the Ancient Mining and Metallurgy Committee was set up in Britain chaired by Herbert Coghlan and involved many of the most prominent Bronze Age scholars of the period including Gordon Childe and Stuart Piggott. Eventually this group had, what has subsequently proved to be, a remarkable success in tentatively identifying the unusual fahlore copper ores from «the Cork-Kerry region» in SW Ireland as the probable source of the earliest Irish and British copper (Coghlan 1958, Coghlan and Case 1957, Coghlan *et al*. 1963,15). They also proposed three artefact-based metal groups.

In the 1960s and the 1970's there was the huge SAM project of Siegfried Junghans and Edward Sangmeister based in Stuttgart and Freiburg using optical emission spectroscopy, which eventually analyzed about 22,000 metal artefacts across Europe (Junghans *et al*. 1968 &1974). They were unable to match artefacts to mines or mining areas and so instead established a classification independent of typology with a view to identifying 'workshops' (Pernicka 2014,242; Roberts 2014,424). They set up 12 and later 29 artefact-based metal groups using the principal impurities found in copper, namely arsenic, nickel, antimony, silver, bismuth, lead and cobalt. These groups were statistically based without proper geological and archeological foundations. The SAM programme and similar ones in other countries have been widely criticized (Tylecote 1970, see Pernicka 2014,244-247 for a review) but form a useful legacy database provided the accuracy limitations of the analytical method used are borne in mind.

In the late 1970s in Britain, Peter Northover's (1980) pioneering work involved analyzing numerous artefacts from the Bronze Age collection in the National Museum of Wales using electron microprobe analyses. He defined 14 artefact-based metal groups based on trace/minor element chemistry, which were later extended to the whole of the Britain (Northover 1991). Later Rohl and Needham (1998) defined 23 British artefact-based groups incorporating trace elements, lead isotopes and a typological/chronological dimension.

The common thread of the various research groups was the setting up of artefact-based metal groups but there was a gradual realization that there were complications in the trace element chemistry approach alone. Firstly, there were some overlaps in the geochemistry between some mines and mining regions. Secondly, there was a split of the trace/minor elements in the ores between the copper metal and slag during smelting. These might vary depending the smelting conditions such as the redox and the temperature although a better understanding was gradually gained (Tylecote *et al* 1977, Pollard *et al*. 1991, Pernicka 2014, 252-253, Hauptmann 2007,27,204-207).

Given these potential weaknesses from using a trace/minor element 'signatures' there was renewed optimism with the introduction of lead isotope measurements which came to prominence in the 1980s and 1990s (Pernicka 2014, 247). This offered, in principle, an isotopic 'signature' or 'fingerprint' that would, in theory, be specific to each ore deposit and would apparently be fully preserved during smelting (Pernicka 2014, 248, see also Pollard and Bray 2014,232). This proved very valuable in excluding deposits as sources of particular copper artefacts (e.g. Rudna Glava mine, see Pernicka 2014, 250-256) even when the actual sources sometimes remained unknown. The whole subject ran into a confidence damaging controversy in the early 1990's over various issues relating to possible fractionation, precision, overlapping ore deposits and the mixing of metal sources (see sum-

mary by Tite 1996, Pollard and Bray 2014,229). However, most of these criticisms were addressed successfully and the technique has re-emerged with more accurate measurements and a clearer acknowledgement of the technique's limitations (Pernicka 2014,263). As with the trace/minor element studies, as more and more ore deposits were analyzed, occasional overlaps between mines or mining areas were discovered (Pollard and Bray 2014,231) and also, where significant uranium or thorium was present in the deposit, some very broad isotopic 'signatures' emerged (Pernicka 2014,249).

While both chemical and isotope methods have some drawbacks, when they are used in combination they can be provide compelling evidence because they are both completely independent methods. Hence, the best practice is to use both methods in provenance studies (Pernicka 2014,263) wherever possible. In addition, information on the date of mining activity in a particular area can further strengthen the evidence linking mines to objects of the same age (Pernicka et al 1997,143). Roberts (2014,433) pointed out another requirement to increase the probability of success of such studies, is that the ore source should have been the dominant source of metal in an area for substantial period of time in order to make an impact on the regional artefacts as the dominant metal composition.

Recycling, to some degree, is very likely to have occurred since earliest times. There is some debate about the extent of recycling in the Bronze Age and the degree of volatile loss on re-melting (Pernicka 2014,254-258, Bray and Pollard 2012,854,865). Some recycling would have been of metal objects from one dominant primary source and so the isotopic and chemical signature would be unchanged apart from some possible volatile loss (see below). Even when metals from two different sources were used the resulting metal will lie between the primary sources in terms of trace/minor elements and lead isotopes (mixing lines) but obviously these signatures will become of little use with multiple metal sources (Pernicka 2014,258). Also re-melting metal may reduce the content of volatile elements, particularly of arsenic and antimony (Bray and Pollard 2012,854) under certain redox/remelting conditions and consequently slightly increase the level of non-volatile elements. However, the presence of nickel may inhibit arsenic loss (Sabatini 2015) and also losses may not be significant at low concentrations and with particular redox/remelting conditions. Sudden and dramatic changes in the dominant metal composition (both chemi-
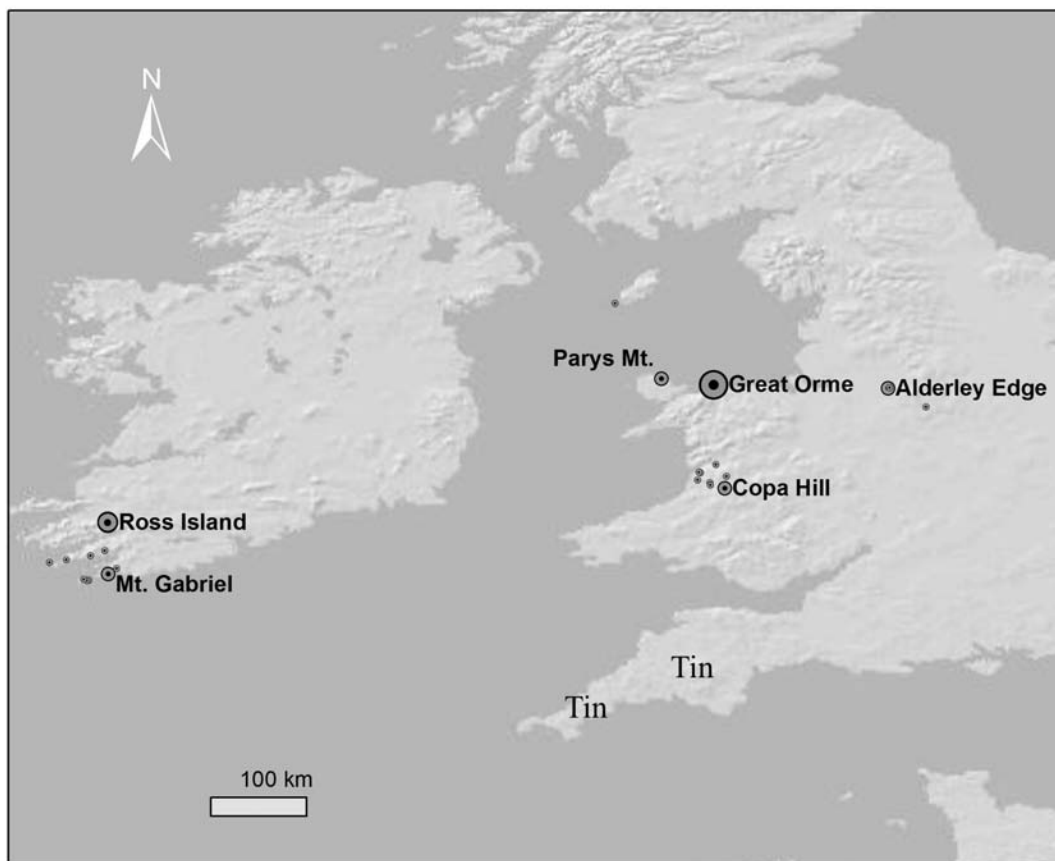

FIGURE 1. *Dated Bronze Age copper mines and trials in Britain and Ireland with main mines named.*
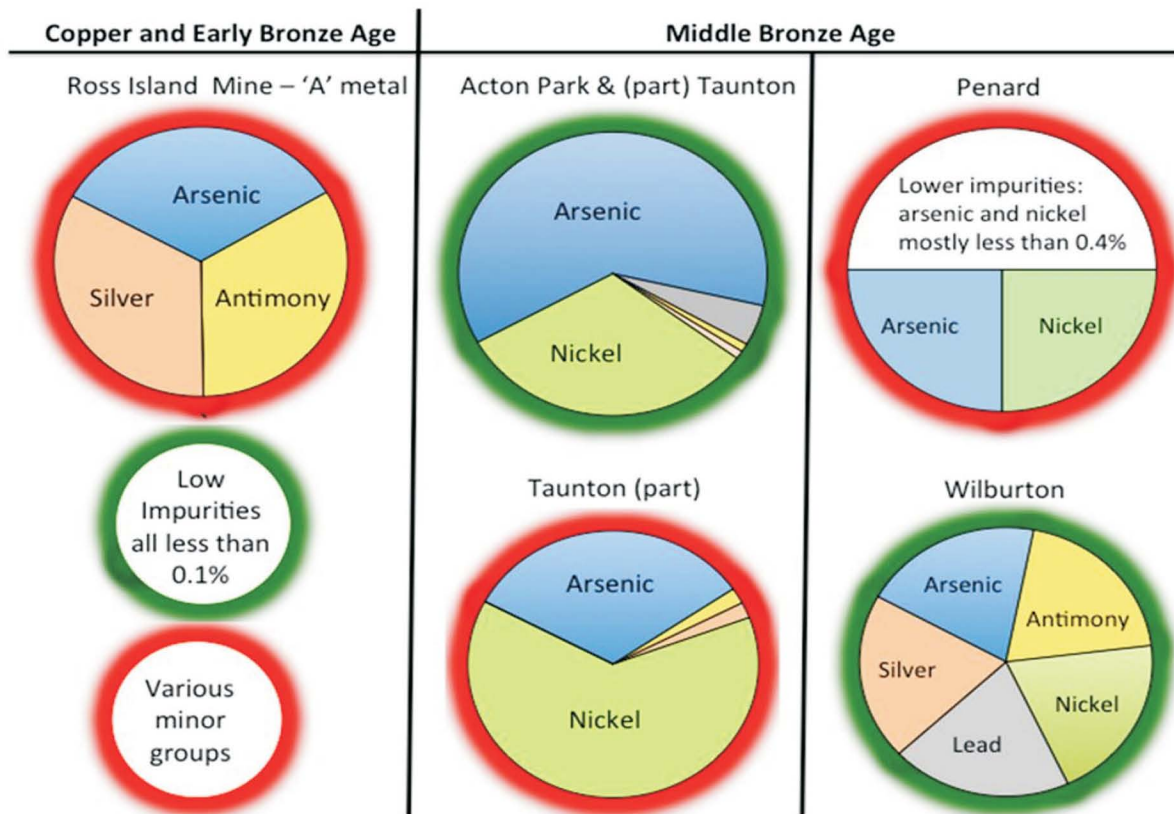
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FIGURE 2. *Seven broadly dominant artefact-based metal compositions in the Copper/Early Bronze Age and in the metalwork phases of the Middle Bronze Age and Late Bronze Age. Note the elemental proportions shown are not to scale and are symbolic only. Approximate correspondence to Northover groups (A, C, M, N, P & S) is indicated. Chemistry can be used to distinguish most groups but those with a thick black border (Groups 4, 5 & 6) require lead isotope to separate them.*

cally and isotopically) are sometimes clearly visible in the archaeological record. For instance, in Britain from the Early to Middle Bronze Age (Arreton to Acton Park) and later in the Middle Bronze Age (Penard to Wilburton). This suggests that the effects of recycling, at least in some periods and in particular regions, can be muted or diluted to low levels when a major flow of new primary metal becomes established. This type of sudden change may correlate with a major change in the dominant exchange network due to broader societal changes and/or the exhaustion/discovery of particular ore deposits.

The discovery in Ireland and Britain of numerous Bronze Age mines and trials since the 1980s (Fig. 1) has transformed our understanding of potential copper sources (Timberlake 2009, O'Brien 2004) but probably not many of them made a significant contribution to the metal supply. At the Ross Island mine in SW Ireland, the application of lead isotopes combined with the very distinctive chemistry of the grey fahlore copper ore (As, Sb and Ag in tennantite-tetrahedrite) matched the artefact-based metal group 'A' which dominated the Irish and British Copper Age and Early Bronze Age (Fig. 2).

Smelting experiments with samples of probable ore proved difficult but eventually three copper prills were micro-analysed and were found to be consistent with 'A' metal (O'Brien 2004, 532).

However, since the Ross Island work, the matching any of the other dominant metal groups during the rest of the British Bronze Age to British, Irish or continental mines has stalled. This has been partly due to the papers in the late 1990s onwards, which claimed that most British (and some Irish) Bronze Age mines could only produce copper with low impurity levels (Ixer and Budd 1998,26). However, this conclusion was based only on mineralogical studies without any geochemical analyses. This low impurity claim only matched a minor metal group, mostly in the Early Bronze Age, while the Middle Bronze Age was dominated by arsenic-nickel compositions (Northover 1991,65) (Fig. 2). In addition to this difficulty, the wide range of lead isotope signatures in British mines and artefacts, revealed by pioneering work of Rohl and Needham (1998), seemed to make the whole business of unraveling which artefacts were from British mines too difficult and so little further work has been done. There has been some debate about

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a possible minor Copper Age copper source(s) in SW England (Budd et al 2000, Bray 2012, 60) based on rare highly radiogenic artefacts but the location of the source mine(s) remains elusive.

MINE-BASED METAL GROUPS – A NEW APPROACH

A new approach is required to give fresh impetus to the stalled process of matching Bronze Age artefacts to the copper produced by the principal British Bronze Age copper mines discovered over the last 30 years. The new approach involves establishing the concept of mine-based metal groups by harnessing knowledge from other disciplines, namely ore geology, ore mineralogy, geochemistry, geometallurgy and pyrotechnology. Now that numerous Bronze Age copper mining sites have come to light there is the opportunity of turning the usual provenance question around. Rather than seeking to assign the relatively artificial artefact-based metal groups to mines/mining regions we can now define mine-based metal groups, each of which might partially or fully overlap with several existing artefact-based groups.

A mine-based metal group is based on extensive and systematic ore sampling from actual Bronze Age mine workings, from which are produced numerous macro or bulk homogenized crushed samples for analysis. The major weakness of some previous studies is that selected micro-sized grains of a copper mineral in the ore was used rather than the whole suite of minerals in the ore. The mine-based metal group is defined in two independent ways. Firstly, by establishing in detail the broad natural geochemical range ('signature') for all the key impurities and secondly, by defining the full lead isotopic range ('signature'). A crucial aspect is deciding upon the correct ores to sample, which depends on a detailed mineralogical understanding of the ores (Baron et al 2013,2 , Killick 2014,11) in parallel to an archaeological/geological understanding of the mining remains. For instance, the presence or absence of separate or contemporary lead mineralizing events with the copper mineralization can be crucial in lead isotope interpretation. Overall, this approach is much more likely to reveal the probable metal composition range and isotopic range that the ore deposit could have produced. In the past, the inherent assumption has often been that a mine's ores would produce a narrow metal composition whereas in reality a range of compositions would usually be produced given the natural variation of ore deposits. Combining this approach with smelting experiments, using the actual ores from the Bronze Age workings of a particular mine,

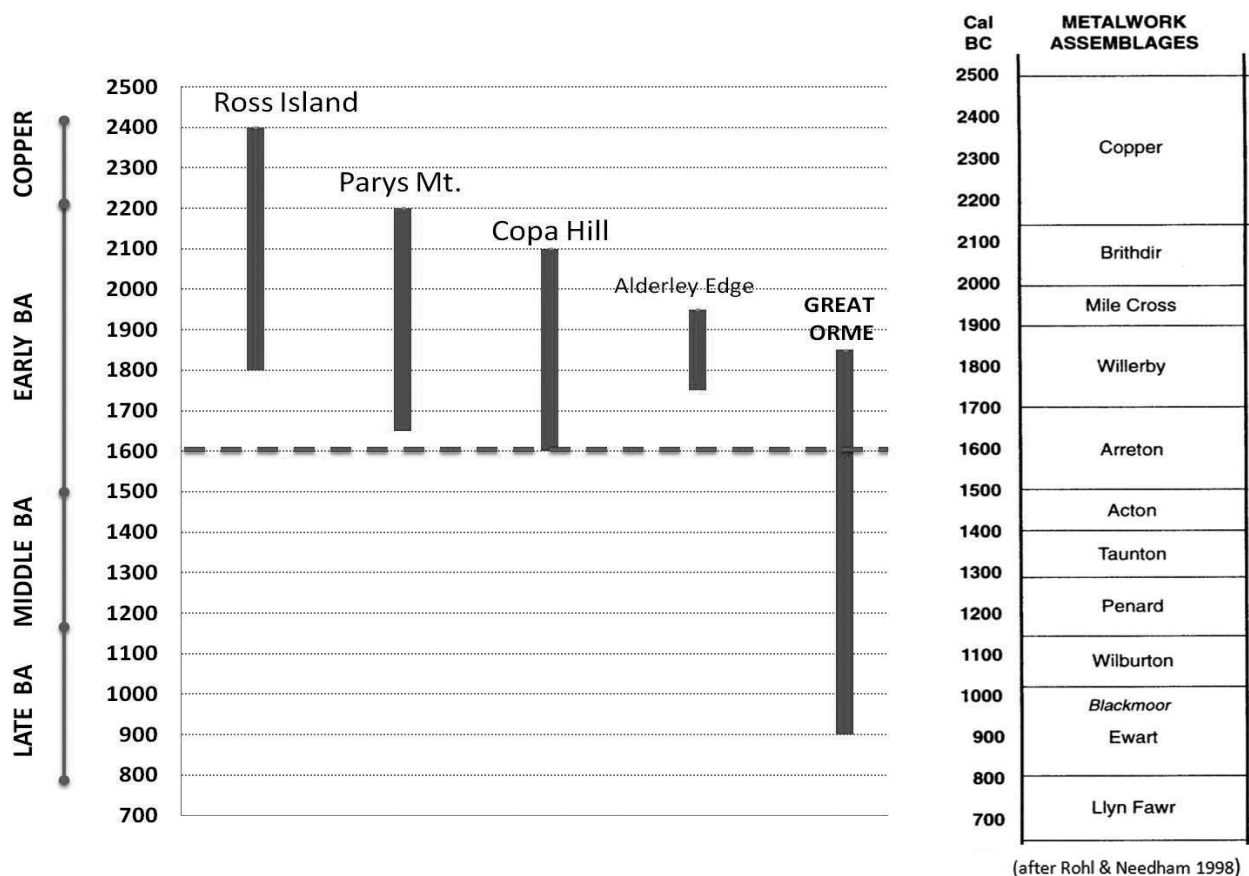FIGURE 3. *General view of the Great Orme mines.*

FIGURE 4. *Bronze Age chronology of main mines and approximate radiocarbon. Date ranges at the 2 sigma level and associated metalwork assemblages. Radiocarbon data from Timberlake and Marshall (2013).*

can lend further strength to the defining the limits of a mine-based group and to allow for an understanding of the split of trace/minor elements between copper metal and slag.

The research team at Ross Island (O'Brien 2004) went in the direction of the new approach being proposed, however, they were unable to sample primary and probable secondary ores from the extensive flooded Bronze Age workings in order to establish the full range of ore compositions in the mine. In addition, with the ore fragments that were selected, they relied on micro-analysis (electron micro-probe) of tiny individual ore mineral phases within naturally heterogeneous ore samples rather than on crushed and homogenized macro ore sampling, encompassing all phases present for geochemical analysis. This prevented the full range of practical 'run of mine' ore compositions from being established. Hence, there was a heavy reliance on the artefact-based metal group ('A' metal) to define the full range of metal compositions that the mine probably produced rather than being defined independently by the mine's ores.

THE GREAT ORME BRONZE AGE COPPER MINE

The ideal candidate to test the mine-based metal group approach is the Great Orme Bronze Age copper mine on the coast of North Wales (Figs. 1 & 3), which is generally agreed to be one of the largest Bronze Age copper mines in Europe (O'Brien 2015,146). There is access to around 6km of Bronze Age workings with many areas having residual ore in situ. In addition, there are two additional sources of material to test the whether the mine-based group established from the ores is likely to be correct. Firstly, there are the bronze fragments excavated in the mine, which are probably from metal mining tools made with the local ore, and secondly, the copper prills from the near-by fragmentary smelting site.

The Great Orme Bronze Age copper mine is located on a Carboniferous Limestone headland above the seaside town of Llandudno and the workings include a large opencast and tunnels up to 70m metres deep. The extensive ancient workings were found under the nineteenth century mine tips in 1987. Excavations have found over 2400 stone hammers and around 30,000 bone fragments, often used as mining tools (Jen-

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kins and Lewis 1991, Dutton et al 1994, Lewis 1996, Wager 2001, James, 2011). A mining museum was opened in 1992.

At this point it is worth noting a recent review of the chronology of known British Bronze Age copper mines (Fig. 4) based a Bayesian analysis of radiocarbon dates (Timberlake and Marshall 2014). This has suggested that after earliest metallurgy from the Irish Ross Island mine from around 2400 BC (until around 1900/1800 BC) there was a wave of exploration in western Britain, possibly from Ireland, in Mid-Wales and north Wales from around 2100 BC. This appears to have lead to many trials and the opening of mines at Parys Mountain and Copa Hill mines (Fig. 4) plus, slightly later, some workings in central north-west England (Alderley Edge and Eaton) but all had closed by around 1600 BC. The only exception is the Great Orme mine whose radiocarbon dates stretch from around cal. 1884 to 933 BC (2 sigma range, James 2011, 45) indicating that it continued after all the other known British mines had closed. The closures may have been related to the Great Orme's rich and easily worked oxide ores, which contrasted with poorer less oxidised deposits in much hard rocks at the other mines. What is not highlighted in the literature is that the initial British exploration activity, around 2100 BC, corresponded with the relatively sudden change to full tin bronze in Britain and may suggest the wave of exploration also revealed the cassiterite deposits of Cornwall and/or Devon in SW England. Gold has also being recently linked more to this area (Standish et al 2015,18) than the traditionally assumed sources in Ireland.

The Great Orme mine's radiocarbon dates go back to the late EBA although most dates lie in the MBA. Northover (1991,65) noted the sudden change in the dominant metal composition between the CA/EBA (As-Sb-Ag 'A' metal) to the MBA (nickel-arsenic metal). He suspected a source for the nickel-arsenic metal in north Wales (possibly Snowdonia) or Shropshire. Given the discovery of the very extensive Great Orme Bronze Age mine in 1987 with its many MBA radiocarbon dates, this would seem to be the obvious source. However, during the late 1990s a series of influential papers stated this was definitely not the case (Ixer and Davies 1996, Ixer and Budd 1998 and Ixer 2001). They stated that «… the mineralogy of the ores shows that they could only produce trace element poor copper metal like most Bronze Age ores from the British Isles … and that their usefulness in provenancing Bronze Age metal work based upon distinctive trace element signatures is very limited» (Ixer & Budd 2001,218). This conclusion was reflected in a number of other papers including Budd (2000) «…the Great Orme ores contain no ar-

senic whatsoever» , Craddock (1994,76) «…copper from the Great Orme cannot be identified in the contemporary bronzes…the ore is characterized by very low nickel contents» and Northover (1999,223) «…..it is incompatible with the vast bulk of Middle Bronze Age metal». This view has persisted and is stated in a recent book on prehistoric copper mining in Europe, « The copper produced was high purity, making it difficult to follow its circulation in the wider pool of metal in that period» (O'Brien 2015,150). Hence, the consequence of this low impurity conclusion was that the Great Orme mine was not considered as important in the Bronze Age as the size of the workings would suggest. However, Ixer's conclusions were based on mineralogical observations only (noting the lack of specific arsenic or nickel minerals) but without geochemical analyses, which might have detected high levels of impurities within the structure of the various copper minerals and other major gangue (waste) minerals (particularly iron oxides) present in the ore.

Some scholars such as Rohl & Needham (1998,111,181) using some lead isotope data points and others (Northover in Lynch et. al., 2000,99, Timberlake 2009,115, Bray 2012,60) expressed the view that the mine may have been an important source of MBA metal (and some EBA metal) but offered no explanation to resolve the conflicting mineralogical, geochemical, smelting, isotopic and artefactual analysis evidence. Using the mine-based metal group methodology at the Great Orme should not only demonstrate the methodology in practice but also unravel the various claims made about this mine in the past.

MATERIALS ANALYZED (ORES, BRONZE PARTICLES AND COPPER SMELTING PRILLS)

Three groups of materials have been studied and analyzed in detail, copper ores, bronze particles and copper smelting prills. Firstly, the copper ores from the several kilometers of Bronze Age workings at the Great Orme mine were sampled using specialist knowledge of the ore geology to guide the sampling process. This work established for the first time that the main ore type was a dark malachite-goethite ore formed by in situ supergene oxidation of the primary chalcopyrite (copper-iron sulphide) in north-south trending anastomosing veins which in places merge to form larger ore bodies mined out in large chambers. Associated with the goethite (α-FeO(OH)) are amorphous iron oxides and the general overall term 'limonite' has been used by Ixer (2001,215) to encompass all the iron oxides present. Traces of unconverted sulphides are

present in some ores. There are minor amounts of green malachite-only and azurite-only ores, usually heavily diluted by gangue (waste) minerals, where the copper has moved away from the main primary veins in solution and precipitated in other locations in the surrounding area (e.g. within mudstone layers). An important observation is that there is at least one vein of lead ore (galena) that crosses and predates the copper deposit (Ixer 2001,217). This is important when considering the lead isotope results and the accidental or deliberate alloying of lead with the copper metal produced. A key feature of the malachite-goethite veins is that they were usually easy to extract with bone tools because the dolomite each side was soft and friable (Lewis 1996,78). Ixer (2001,216) attributed the phenomena to the supergene weathering causing local dedolomitization and partial dissolution of the dolomite host rock locally adjacent to the vein. This made an enormous difference to the ease of working and probably explains why fire-setting remains are not very common.

The second group of materials analyzed are the copper prills from the nearby small truncated Late Bronze Age (around cal. 900 BC) smelting site at Pengwern about 1.2km from the mine excavated in 1998 and 2011. An archaeometallurgical study of the prills and slags was recently published and revealed the simple smelting of oxidised ores producing copper prills without a full molten slag and showing geochemical links to the Great Orme ores (Williams 2014,104,108).

The third group of materials analyzed are the bronze particles excavated in the mine in the 1990s plus a bronze tip that was found in 1831 by the miners in an ancient working (Lewis 1996,131 and Williams, forthcoming). These fragments could be from bronze picks like those found in the Hallstatt salt mines (Kern et al 2009) and in the Mitterberg copper mines (O'Brien 2015,211).

ANALYTICAL TECHNIQUES

Several analytical techniques have been used to ensure the data obtained is robust and not affected by the peculiarities of one particular technique. The accurate quantification of the minor and trace elements in rich copper ores is a significant analytical challenge because the very high levels of copper and iron in the ores. This results in a wide range of emission or absorption peaks that sometimes interfere with those from other elements of interest and so development work has been required to ensure good quality data. The chemical data presented in this short paper was obtained by using atomic absorption spectroscopy (AAS) using a Perkin Elmer 3110 and

more recently cconfirmed by microwave plasma atomic emission spectroscopy (MP-AES) using an Agilent 4200, both in the Department of Archaeology, Classics and Egyptology at the University of Liverpool. The results obtained were consistent with the results from other techniques used but not presented here (XRF-WD, pXRF, SEM-EDS and LA-ICP-MS). For the lead isotope work, data was obtained on ore and metal samples supplied to the NERC Isotope Geosciences Laboratory at Keyworth who used a Thermo Fisher Neptune Plus MC-ICP-MS. Certified and standard reference materials were used with all the analyses. Full details of all these techniques will be included in forthcoming papers and a PhD thesis.

For chemical analysis, twenty-eight ore samples were analyzed incorporating intimately associated gangue (waste) minerals in case they were a source of trace elements. Given their inhomogeneity, at least 5 grams (wherever possible) of a hand-picked ore concentrate was crushed and from which a representative 1 gram sample taken. This was dissolved in aqua regia, filtered and then diluted for analysis. The AAS results show very good correlation with key trace elements in the certified standards (As and Ni within 0.6% relative to the certified value). The metal samples (bronze particles from the mine and copper prills from the smelting site) were usually 10 to 20 mg in weight and dissolved in aqua regia according to a well established technique (Hughes et al 1976) and diluted for analysis. MP-AES was used when this new equipment became available during this project and which has a greater sensitivity than AAS. Pre-existing metal analyses have been included from the literature (Lewis 1996,131) and the OXSAM database based on AAS and electron-microprobe data. Twenty new lead isotope analyses were obtained using either 50mg from each crushed ore concentrate or 10mg from the metals (which are more homogenous than ores). The lead isotope data was produced at the NERC Isotope Geosciences Laboratory at Keyworth using a Thermo Fisher Neptune Plus MC-ICP-MS. Pre-existing isotope data has also been included (Joel et al 1995, Rohl & Needham 1998, Northover 1982a)

RESULTS - CHEMICAL ANALYSES

Table 1 shows chemical analysis data on ores for the key elements that are normally used in characterizing copper alloys and were mainly obtained using AAS. The initial data from the other techniques, particularly MP-AES, described above gave generally similar results and included additional major, minor and trace elements and will be reported in a future paper. However,

Ore sample	Cu %	Fe %	As ppm	Ni ppm	Sb* ppm	Ag ppm	Pb ppm	Zn ppm	Co ppm
Major Malachite-Goethite ores (veins in dolomite)									
GO 13	22.9	17.8	4005	546	80	262	724	70	104
GO 15	29.5	20.7	5219	1413	180	287	105	86	470
GO 16	31.1	16.7	3307	1821	90	314	510	259	1168
GO 20	20.5	13.5	2194	1034	70	44	453	260	403
GO 34	17.2	17.5	3053	1037	50	47	192	75	708
GO 40	17.8	15.3	2506	1173	50	230	719	201	602
GO 42	22.2	17.2	4293	2340	<40	97	141	32	692
GO 60	21.5	15.3	3602	1558	60	9	588	176	683
GO 64	36.3	7.0	1511	1529	<40	61	293	115	374
GO 65	23.9	19.3	3179	500	100	147	692	110	262
GO 72	38.6	14.2	2260	1141	<40	156	131	50	140
OC 3	31.6	23.3	3453	497	210	364	1058	86	69
OC 12	21.3	20.1	1918	341	<40	390	1256	1269	151
OC 16	28.3	18.4	1601	773	<40	248	648	268	192
OC 22	37.5	10.7	1771	583	<40	30	90	364	1024
OC 31	24.9	16.8	3597	1635	140	55	665	25	608
OC 39	27.7	17.5	1120	1258	50	75	315	23	86
OC 51	27.3	20.0	3499	464	120	129	635	493	40
EOC 2	29.2	24.2	1381	2501	120	81	17741	36	1044
EOC 3	29.4	19.0	2131	2691	170	135	4723	45	1334
GO 50b	23.7*	26.8*	5179	873	<40	268	394	1004	412
GO 68b	13.4	16.4*	3550	546	<40	136	600	260	303
GO 73d	16.7	23.6*	3983	2806	42	136	334	752	694
Minor Malachite only ores (in mudstone, limestone and dolomite)									
GO 26	18.5	4.3	311	294	<40	16	52	11	52
GO 55	16.8	1.0	334	226	<40	16	37	12	133
GO 62	20.9	1.3	640	354	<40	17	50	46	89
GO 71b	52.6	7.3	365	169	<40	8	23	19	104
Minor Azurite pisoliths in mudstone									
GO 61	16.7	3.4	1013	281	<40	24	134	114	88

All samples analysed by AAS except antimony and *values which were by pXRF.
Certified reference samples used were VS R34 (high-grade copper ore) and GBW 07719 (doped dolomitic limestone)

TABLE 1. *Minor and trace element macro analyses of Great Orme ores using AAS except where indicated*

the AAS results contain the key data required to initially define the main chemical analysis part of a mine-based metal group.

Two key elements to consider are arsenic and nickel and a simple plot is shown in Fig. 6. If the papers by Ixer and co-authors (1996,1998, 2001) claiming only low impurity levels in the Great Orme ores had been correct we would expect the copper ores analyses to lie in the shaded square shown in Fig. 5, in the bottom left hand corner (all below 0.1%). However, plotting the ore results normalized to 100% copper (see below) dramatically shows that there are substantial amounts of arsenic and nickel in all the malachite-goethite ores. Laser ablation ICP-MS work has demonstrated that while the malachite can be low in impurities, the intergrown goethite with its absorbent structure acts as sponge for high levels of trace elements (Manceau *et al.* 2000). The large square in Fig. 5 is the average of all the ore results, which is useful to consider as naturally occurring ores are usually much more heterogeneous than metals (which are mixed during smelting and refining). The much rarer malachite-only ores are lower in impurities and are shown as small triangles.
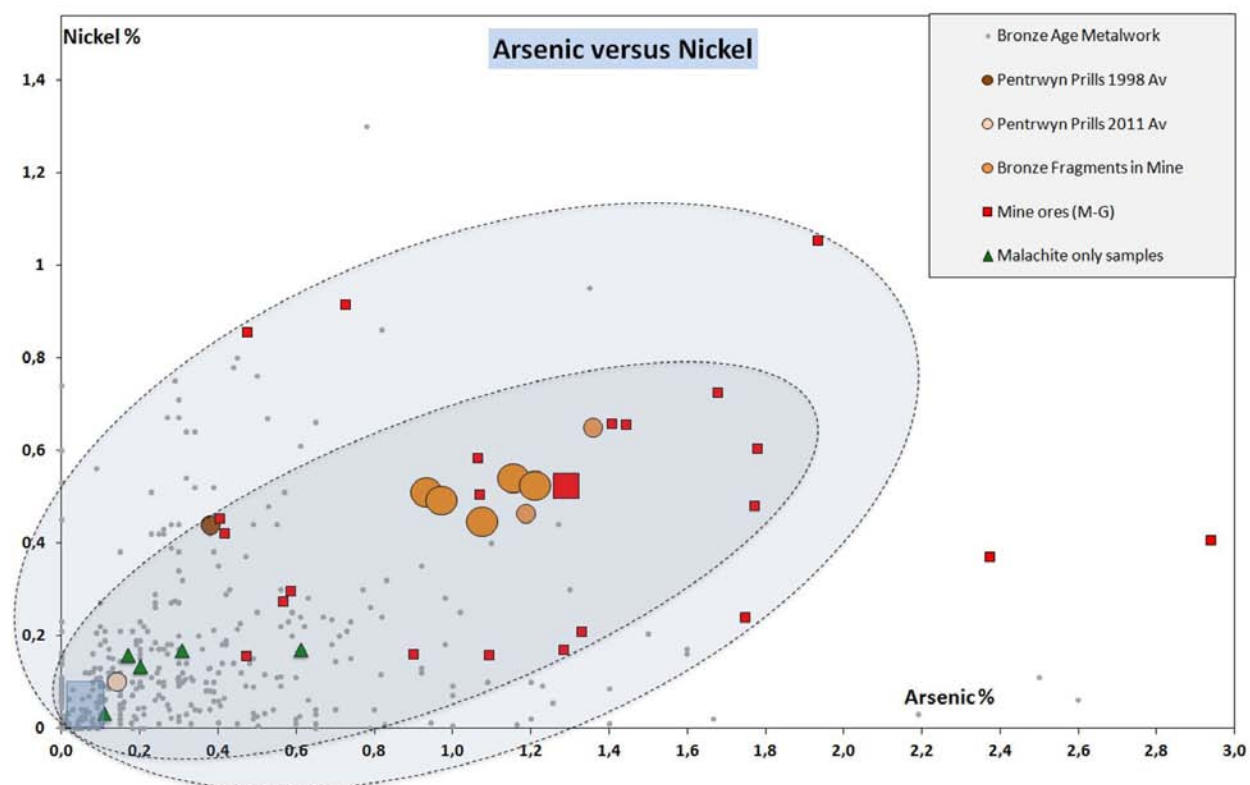
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FIGURE 5. *Arsenic and nickel plot of Great Orme ores (average is large square), bronze particles from the mine, copper prills from Pentrwyn smelting site and the typical range of British Bronze Age metalwork data. Shaded square indicates where low impurity metal would plot (less than 0.1%).(Data: Table 1, Lewis 1996, Williams 2014, and Williams forthcoming).*

Note that all these results have been normalized to 100% copper from variable ores that contain 16% to 38% copper using the convention used by Pernicka (2004,315). For simplicity, this is based on the ideal smelting situation where there would be a 100% transfer of nickel and arsenic into to the copper metal produced rather than into the slag phase. There is evidence in the literature that high levels of transfer are achieved in reducing atmospheres as these two elements preferentially move to the copper metal (Tylecote et al 1977,19, Hauptmann 2007, 27,204-207). The other key thing to consider is that smelting oxide ores (albeit with slight traces of sulphides in some ores) do not require the oxidizing roasting step that sulphide copper ores require before smelting to remove the sulphur and which would cause some arsenic loss. Therefore, going straight to a reducing smelting stage with oxide ores means a large proportion of arsenic in the ores can be retained. Hence, the level of arsenic required in an oxide ore to give a metal with a particular arsenic content in the copper metal is lower than with a sulphide ore.

To test the claims in the literature of high arsenic and nickel retention during smelting oxide ores, two smelting experiments were undertaken separately with two people experienced in experimental smelting. Firstly with David Chapman from Ancient Arts and later another experiment with Simon Timberlake, both using pre-analyzed Great Orme ores. These field experiments using simple bellows-powered pit boles and ores introduced as coarse milled powders, will be reported in detail in a future paper. However, the initial analyses of the copper prills are indicating high arsenic and nickel retentions sometimes exceeding 80% even without the probable accumulated generational skills of the ancient smelters in achieving the best reducing conditions and temperatures for optimum smelting results, probably achieved by attention to colour and smell, etc.

Returning to the arsenic–nickel graph of the ores, which is starting to define range of compositions for these two elements. We can test this range by plotting the results from the bronze particles from the mine and we see a strong coincidence with the average ore analysis. If we plot the copper from the Pentrwyn smelting prills they have lower levels of impurities but still within the range of the ores. Hence, the geochemical signature of the ores is emerging with the broad ellipse encompassing all points but with an inner
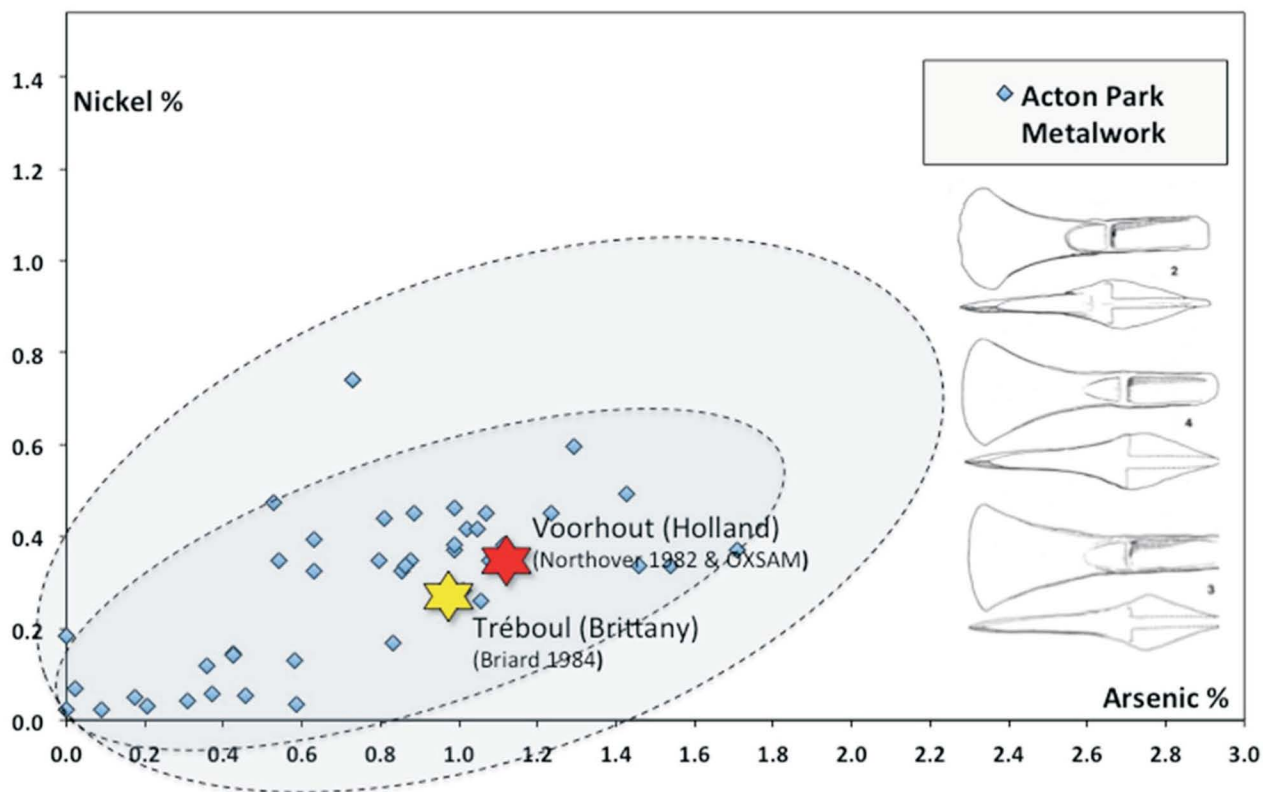
FIGURE 6. *Arsenic – Nickel plot of the Acton Park metalwork assemblage (c 1500 – 1400 BC) and similar metalwork from the Voorhout hoard in Holland and from Tréboul in Brittany (star symbols are mean values). The ellipses define the inner and outer range of ore samples. (Data: Rohl and Needham 1998, OXSAM database, Briard et al 1984, Northover 1982).*

ellipse defining a core area containing most of the metal compositions produced (Fig. 6 and 7).

This defined geochemical range can now be compared against the Acton Park assemblage from the early Middle Bronze Age whose type locality is near Wrexham in North Wales. This data (Rohl and Needham 1998 and OXSAM online database) defines an area almost identical to that of the ores (Fig. 6). In addition, the Voorhout hoard in Holland has been identified as belonging to the Acton Park assemblages (Butler 1963, Northover 1982b,54 and 1989,220), also plot close to the centre of the area defined by the average ore. A similar correlation is seen for the Tréboul hoard from Brittany.

So the geochemistry part of the mine-based group is starting to be defined, essentially ranging from low to high arsenic and nickel. Similar work on other elements shows that the Great Orme ores have characteristically both low antimony and fairly low silver levels with variable cobalt. The lead (Pb) can vary from very low levels to several percent due the lead vein that crosses the Great Orme site and so some addition could have been unintentional. However, the very high levels in a few artefacts mean deliberate lead alloying cannot be excluded as a possibility. The

mine-based metal group that emerges coincides with Northover's artefact based-metal groups M1, M2 and parts (but not all) of his groups O, N and P (Northover 1980,237).

As previously mentioned, Northover defined 14 artifact-based metal groups in the British Bronze age and Rohl and Needham defined 23 groups incorporating lead isotopes. However, for simplicity it is useful to focus discussion on the dominant artefact-based metal groups during the Early Bronze Age and the various periods in the Middle/Late Bronze Age. Seven dominant groups have been very broadly defined in Fig. 2 and those roughly equivalent Northover's artefact-based groups (A, C, P and S) are indicated. The Group 4 range encompasses Northover's M1 and M2 metal plus part of his O metal. Group 5 includes his N2 metal. Group 4 and 5 can be divided broadly on As>Ni and As<Ni. The various elements shown in the pie charts are merely symbolic indications and are not directly proportional to their concentration ranges. From the ore geochemical work described above we can eliminate dominant groups 1 and 7 because Great Orme metal does not contain significant antimony or silver unless by mixed metal recycling. However, we are then left
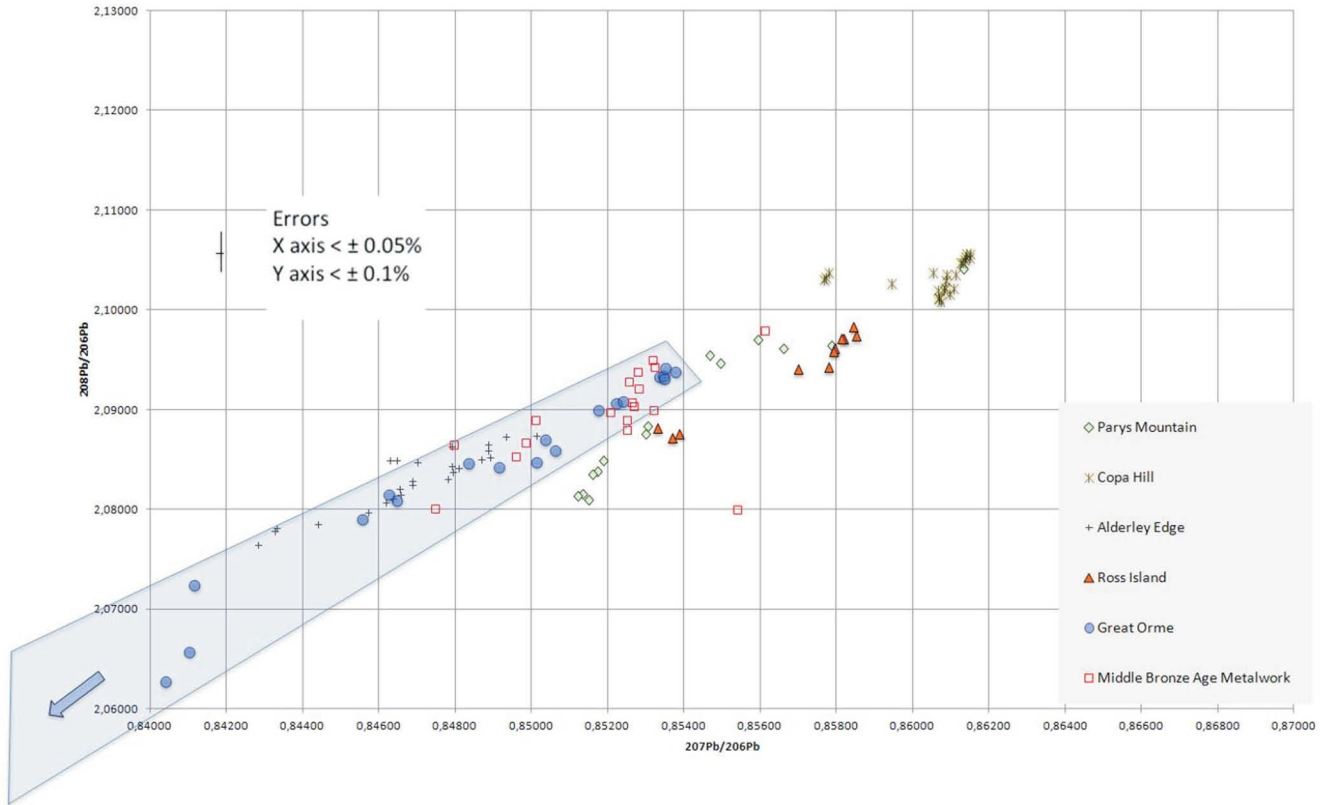
FIGURE 7. *Lead isotope data for major British and Irish Bronze Age mines including the zone of radiogenic ores of the Great Orme mine. Squares show data from British Middle Bronze Age metalwork of all assemblages. (Data from Rohl & Needham 1998, Williams 2014 and Williams, forthcoming).*

with a number of other dominant groups, particularly those containing varying levels of arsenic and nickel (groups 4,5 and 6). To decide whether these are from Great Orme metal or not we need to discriminate using lead isotopes, a technique completely independent of the geochemistry technique.

RESULTS - LEAD ISOTOPES

Fig. 8 shows a plot of the isotope ratios for the main British and Irish Bronze Age copper mines. The foundation of this technique is based on the ores from each mine having been formed by a mineralizing event, typically involving hydrothermal solutions, in which the ratios of the mixture of lead isotopes present is distinct to that particular ore deposit. Fig. 8 shows that the ores from the main mines mostly occupy separate positions on the ratio graph. The Great Orme data overlaps with the small Alderley Edge mine but the latter's radiocarbon dates suggest it was closed well before the large Great Orme mine was at its zenith. The other aspect of the Great Orme data is that rather than having a small discreet area on the graph it is spread over a wide zone

extending well beyond the bottom left-hand corner of the graph. This is examined in more detail elsewhere (Williams 2017 in prep.) but is due to the ore intermittently containing uranium (often around 200ppm) which produces significant new lead (Pb207 and Pb206) by radioactive decay and so changes the lead isotope ratios of parts the ore deposit over time. A further complication at the Great Orme is that there is an earlier lead vein(s) crossing the copper deposit, which has lead isotope ratios at the top end of the shaded Great Orme range shown in Fig. 7. Away from the lead vein, the copper ores have low lead contents and so the lead produced from uranium decay significantly affects their ratios shifting the values towards and beyond the bottom right in Fig. 8. However, for over half the samples there is apparently enough lead picked up from the zone of lead mineralization (or by being in an area of copper mineralization with lower uranium levels) to keep the values in the upper part of the shaded Great Orme range shown in Fig. 8.

So what do the lead isotope values for Bronze Age artefacts reveal about the sources of the copper used? While the dominant 'A' metal artefacts of the Copper Age/Early Bronze Age have lead
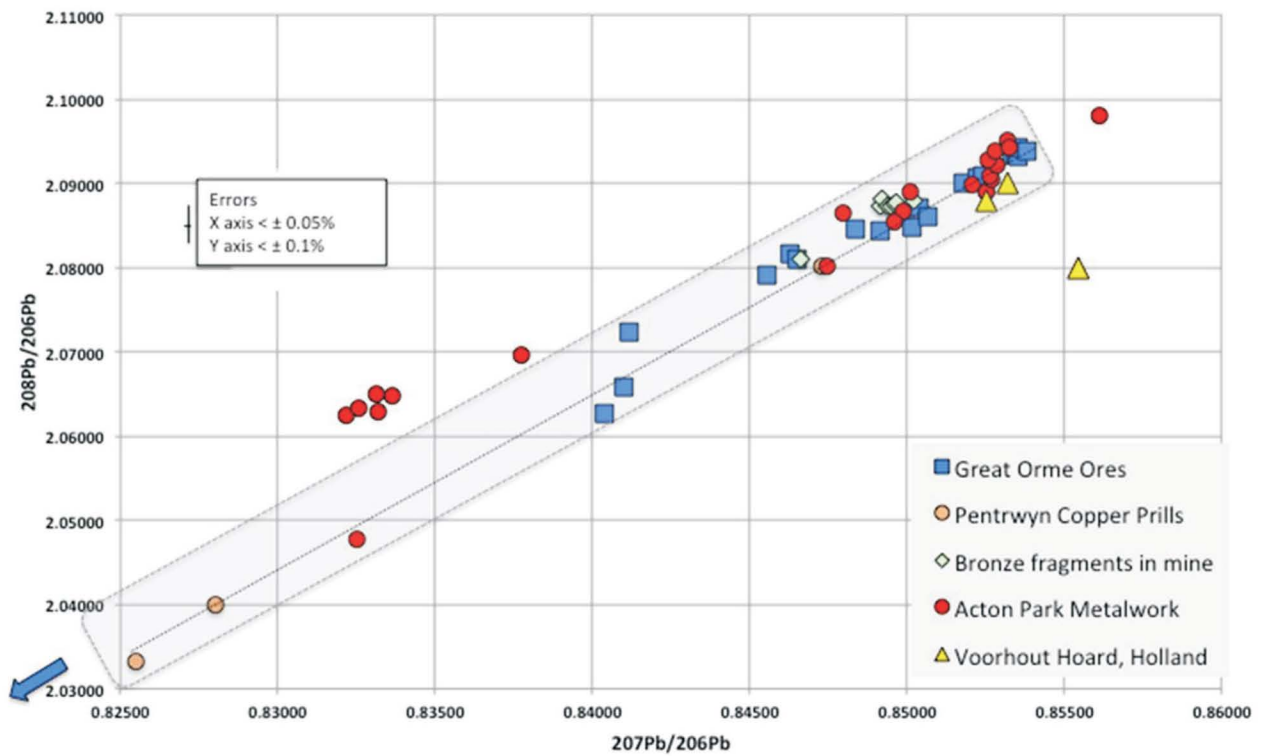
FIGURE 8. *Lead isotope data for the radiogenic Great Orme ores, bronze particles from the Mine, copper prills from the Pentrwyn smelting site and British Action Park metalwork Including the Dutch Voorhout hoard. (Data from Rohl & Needham 1998, Williams 2014 and Williams forthcoming).*
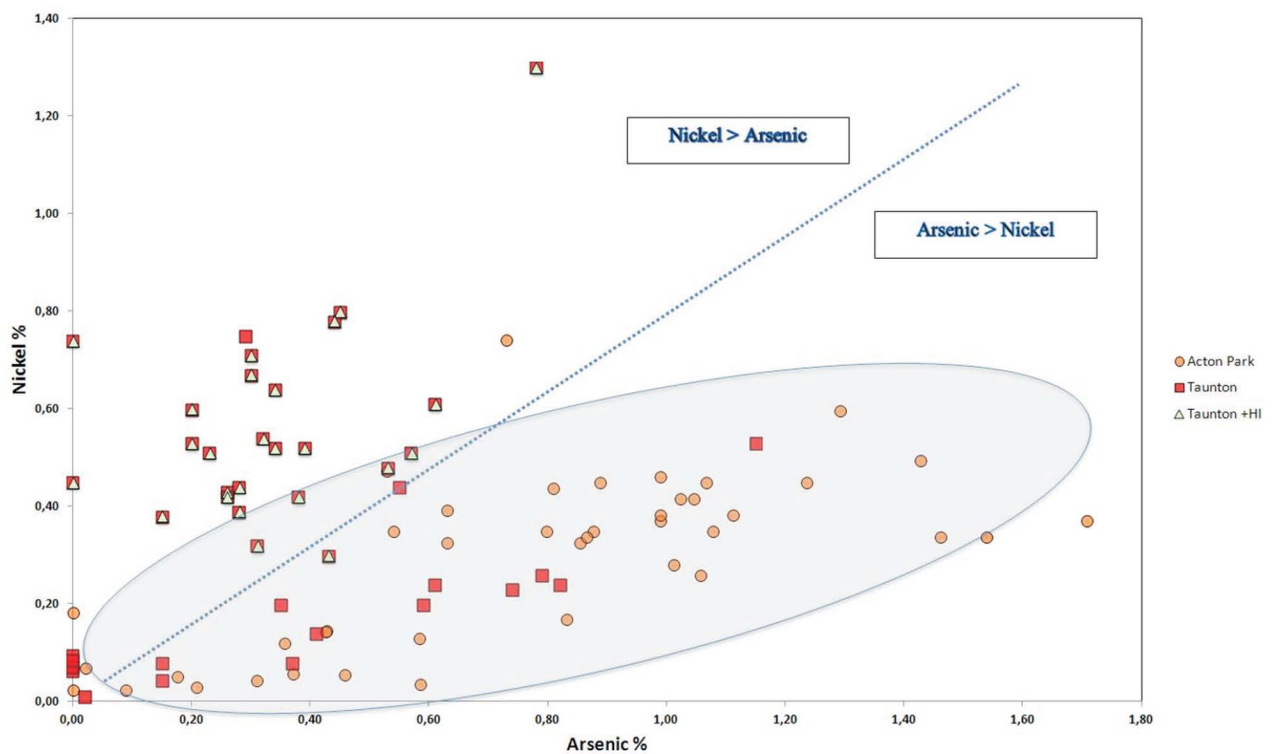

FIGURE 9. *British Middle Bronze Age Metalwork from the Acton Park assemblage (circles) and the following Taunton assemblage (squares). Taunton metalwork data points with lead isotope values outside the Great Orme range are shown by the addition of a triangle. Ellipse is the inner range of Great Orme ores (see Fig. 6). (Data: Rohl and Needham 1998 and OXSAM database).*

isotope ratios that match the Ross Island ores (O'Brien 2004,544), the Middle Bronze Age (MBA) metal artefacts shown in Fig. 7, cover a wide range, with many of the later MBA artefacts not matching any known British or Irish mine and suggesting imported sources. Zooming in on the zone defined by the Great Orme lead isotope ore data (Fig. 8), the bronze particles from the mine fall neatly within the ore range and also the copper prills from the Pentrwyn site (which also extend to match the low lead copper ores beyond the bottom left-hand corner). Hence, the lead isotope component of the mine-based metal group seems consistent with these two local metals giving confidence to look at metal artefacts more generally. In Fig. 9 the Acton Park metalwork data is also plotted and they show a very strong match with the Great Orme ores, with one or two exceptions, which are probably due to mixed metal. In addition, two of the plastaves in the Voorhout hoard from Holland, plot closely in the same area (no data is available for the Tréboul hoard from Brittany yet).

DISCUSSION

Overall, both the geochemical and lead isotope components of the Great Orme mine-based metal group are being firmly defined in the current work programme. Returning to Fig. 2, which shows the broadly dominant artefact-based metal groups of the Early and Middle/Late Bronze Age, most of these dominant groups can now be eliminated as coming from the Great Orme. While the geochemistry component allowed the elimination of dominant groups 1 and 7, the lead isotopes allow the elimination of groups 3, 5 and 6, mainly leaving group 4 (group 2 was very small in the Middle Bronze Age). Hence, the Great Orme mine strongly emerges as the dominant source of the metal during the Acton Park phase and probably also produced significant metal in the periods either side (Arreton and Taunton) along side the dominant groups of those adjacent periods.

The application of the two components of the mine-based metal group can be demonstrated in Fig. 9 where the arsenic and nickel levels of both Acton Park phase metal artefacts and those of the following Taunton period are plotted. The smaller inner ellipse defines the inner core of the arsenic-nickel field of the Great Orme mine-based metal group based on the ores (see Fig. 6). Some of the Taunton period metalwork falls outside this field, suggesting the appearance of a new metal with nickel contents greater than arsenic and probably imported. This suspicion is confirmed when we apply the lead isotope component and highlight the Taunton metalwork

that falls outside the Great Orme isotope field (triangles in squares). The small area of overlap in Fig. 9 (possibly involving some mixed metals recycling) shows the importance of applying both components.

This technique also works with Penard metalwork in the following period whose metal chemically falls in the bottom left hand corner of the arsenic-nickel graph (usually less than 0.4% on both axes) and can be distinguished by isotope values which virtually all fall outside the Great Orme range. So, to increase the level of confidence to a high level that an artifact is made from primary Great Orme metal, both the chemistry and lead isotope data are required. However, where the object is well away from overlaps with Taunton and Penard chemistries (e.g. greater than 0.5% arsenic and nickel 0.2 to 0.6%) there is a higher probability of a match based on chemistry alone. This is useful given that only a very small proportion of the thousands of chemically analyzed artefacts have also had their isotope ratios measured. In addition, particular typologies can sometimes be used as a general guide if there is evidence of a Great Orme match from chemical and isotopic data for examples of that type of artefact. This is the case with shield-pattern palstaves from the early Middle Bronze Age. Therefore, using only this typology with its chemical compositions (from the literature and OXSAM database) a distribution map across Wales and the West of England can be produced. However, this mainly reflects the study areas of researchers. The correlation between shield-palstaves and Great Orme metal was further demonstrated by analyzing three of them for this project from north Wales and Staffordshire.

Given the lack of analyses of shield-pattern palstaves outside the West of England and Wales and without a major research programme to analyze the hundreds of these artefacts outside those areas we can only use an assumed typological connection. Therefore, a more speculative distribution map can produced based on the assumption that the shield-pattern palstaves typology alone, without analyses, may well indicate Great Orme metal (Fig. 10). This plot has not only exploited the data in the literature and in OXSAM but also the large amount of new finds by metal detectorists over the last 18 years that are recorded on the Portable Antiques Scheme database. In addition, the British Museum index cards of Bronze Age finds, recently been put online, have been used. In all 470 shield-pattern palstaves have been plotted using GIS. A future project could sample some of these palstaves for chemical and isotope analysis to see if the assumptions hold up. The distribution shown (Fig. 10) bears many resemblances to the distribution
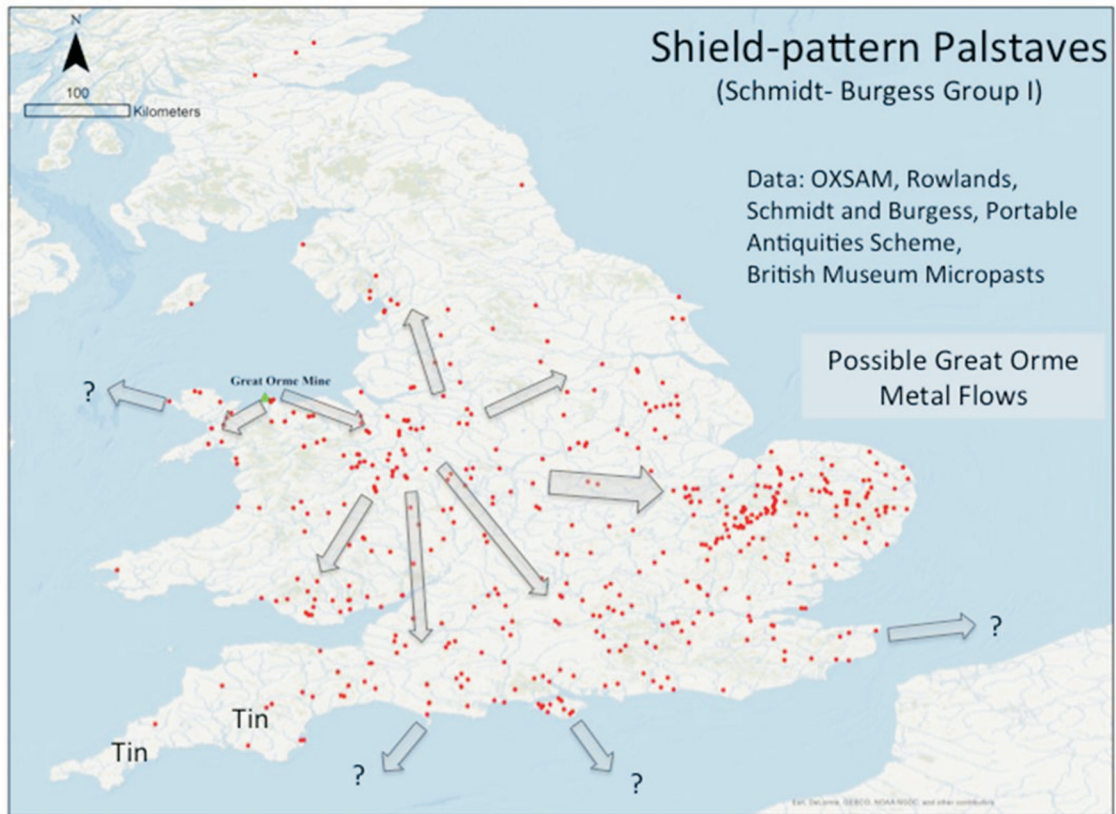
FIGURE 10. *Distribution of shield-pattern palstaves. Indications from chemical analyses and some isotopic analyses, mainly in western Britain, suggest that this type of palstave is usually made of Great Orme metal. Possible metal flows are indicated.*
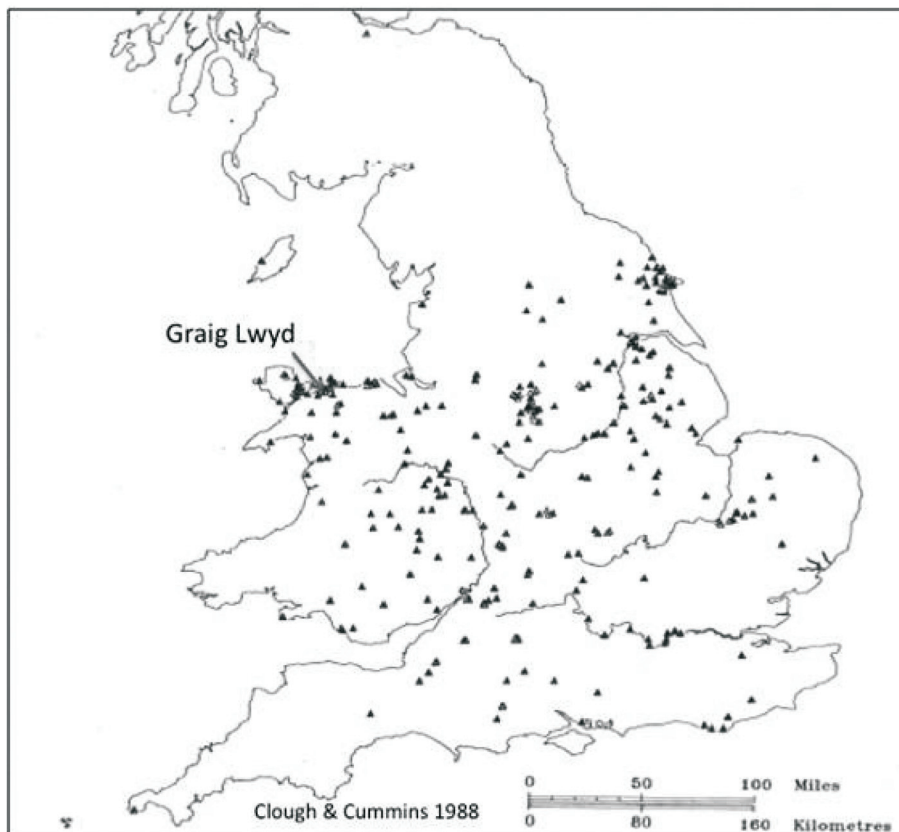

FIGURE 11. *Distribution of Neolithic stone axes from Graig Lwyd, 10 km from the Great Orme. Note the many similarities with MBA shield-pattern palstave distribution(see Fig. 11)(Clough and Cummins 1988)*
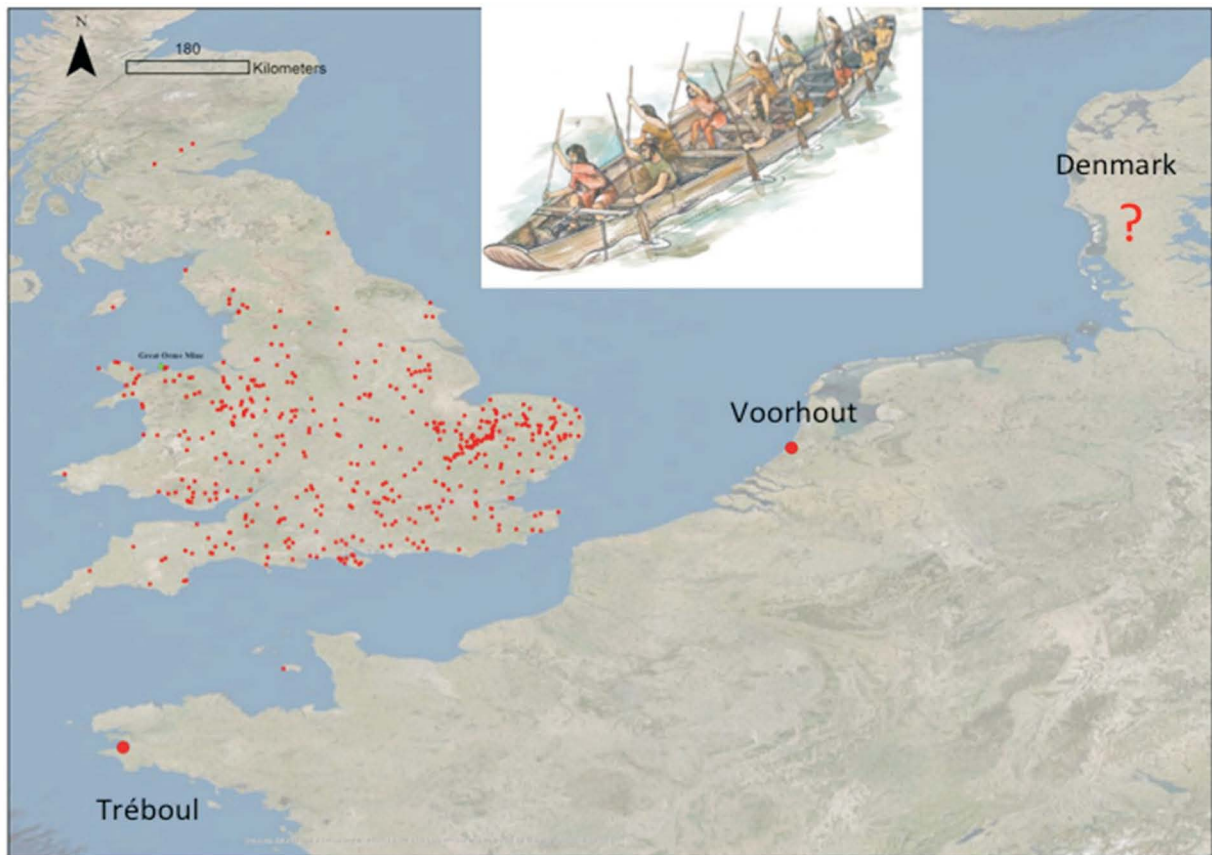
FIGURE 12. *Great Orme metal is believed to have reached Voorhout in Holland (chemical & isotopic data) and Tréboul in Brittany (chemical data). Other possible links to the near continent including Denmark are still being investigated. Cross channel links were probably via sawn plants boats (inset is Ferriby boat reconstruction by Roger Waites).*

of Neolithic axes produced at the Graig Lwyd axe factory 10km from Great Orme (Fig. 11 from Clough and Cummins 1988). This suggests some continuity in the exchange networks from the Late Neolithic. We can also speculate on the directions of flow of possible exchange networks (Fig. 11) subject to more analyses confirming this broader distribution of palstaves as being Great Orme metal. The metal flows with flow control zone and accumulation zones could be developed like those suggested by Needham for 'A' metal from Ireland (Needham 2004, Fig.19.9.). The exercise with shield-pattern palstaves is now being extended to weapons including the types of spearheads, dirks and rapiers, which are consistent with the Great Orme mine-based metal group compositional range.

Based on a wide range of mainly unpublished metalwork analyses (now within the OXSAM database) Northover (1982b,54) claimed that Acton Park metal dominated the supply to Wales and Lowland Britain and was the only time in the British Bronze Age when Britain was self sufficient in copper (and presumably tin from Cornwall/Devon). This 'golden age' of what was very probably Great Orme metal production also saw metal exchange with the continent. There is evidence of this metal reaching Holland from the Voorhout hoard (typological, compositional and isotopic, Northover 1982a, Bulter 1963) and Brittany from the Tréboul hoard (typological and compositional) (Fig. 12). These hoards are being investigated further along with new data from Scandinavia that might potentially provide a link with the amber trade. Schmidt and Burgess (1981, 120-4) made a strong case that the invention of the palstave took place in north Wales and then spread across Britain and into the Continent. The timing would fit well with the flowering of the Great Orme mine and suggests the abundant metal supply may have helped initiate a period of innovation producing the palstave concept.

SUMMARY

The Great Orme Bronze Age copper mine has been shown, using a new mine-based metal group methodology, to be a major source of an arsenic–nickel metal with low antimony, contrary to low impurity claims of past literature. Evi-

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dence suggests that the 'golden age' of production at the Great Orme was around 1500 to 1400 BC in the early Middle Bronze Age (Acton Park), when it probably dominated Wales and Lowland Britain and with some metal exchange to the near continent. This appears to be followed by a long decline probably associated with the exhaustion of the richest areas and becoming less productive as the mine got deeper. An initial examination of distribution of shield-pattern palstaves is highlighting connectivity between communities within Britain and the near continent and this analysis is being extended to other types of metal artefacts. The possibility that the invention of the palstave in north Wales may be linked to the emergence of the Great Orme mine as an abundant supply of metal is also being evaluated. The overall social implications both locally and nationally are currently being assessed.

ACKNOWLEDGEMENTS

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